UNIVERSITAT ROVIRA I VIRGILI

# INTEGRATION OF FLOTATION TECHNOLOGIES AND ADVANCED OXIDATION PROCESSES FOR OIL AND GAS AND DESALINATION INDUSTRIES EFFLUENTS REUSE

**Sílvia Jiménez Herrera**

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# Integration of Flotation Technologies and Advanced Oxidation Processes for Oil and Gas and Desalination Industries Effluents Reuse

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**Silvia Jiménez Herrera**

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**i Recerca**

**SILVIA JIMÉNEZ HERRERA**

# Integration of Flotation Technologies and Advanced Oxidation Processes for Oil and Gas and Desalination Industries Effluents Reuse

Doctoral Thesis

Supervised by:

**Dr. Sandra Contreras Iglesias**

**Dr. Mª del Mar Micó Reche**

**Dr. Francisco Medina Cabello**

Departament d'Enginyeria Química

UNIVERSITAT ROVIRA i VIRGILI

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ROVIRA i VIRGILI

ESCOLA TÈCNICA SUPERIOR D'ENGINYERIA QUÍMICA
DEPARTAMENT D'ENGINYERIA QUÍMICA
Av. dels Països Catalans, 26
43007, Tarragona (Spain)
Tel. +34 977 55 96 03 / 04
Fax +34 977 55 96 21
e-mail: secdeq@etseq.urv.es
http://www.etseq.urv.es/DEQ/

I STATE that the present study, entitled "Integration of Flotation Technologies and Advanced Oxidation Processes for Oil and Gas and Desalination Industries Effluents Reuse", presented by Silvia Jiménez Herrera for the award of the degree of Doctor, has been carried out under my supervision at the Chemical Engineering Department of this university.

Tarragona, 28th of March 2017

Doctoral Thesis Supervisors

F. MEDINA.

Dr. Sandra Contreras Iglesias Dr. Francisco Medina Cabello Dr. Mª Mar Micó Reche

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# Summary

The research of this thesis is framed in the collaboration between the R+D Department of the company Acciona Agua S.A.U. and the Catheter research group of the Chemical Engineering Department from the Rovira i Virgili University.

This thesis is based on water treatment technologies, mainly enhanced DAF and advanced oxidation processes (AOPs), applied to two types of industrial wastewater: produced water (PW), from the oil and gas industry, and cleaning waters from seawater desalination reverse osmosis (RO) membranes. Both lines of research were included within two R & D projects of Acciona Agua S.A.U. On one hand, PW was a new and novel line of research. On the other, despite the fact that the company has a great experience in desalination, the issues related to desalination wastewaters reuse were addressed for the first time. AOPs were expected to be a suitable technology for the purpose of treating these effluents.

PW is the aqueous effluent that is brought to the surface along with oil or gas in extraction operations. It includes formation water (trapped underground) and injection water that are extracted together with the fossil fuel during oil and gas production. PW has a complex composition that includes organic and inorganic substances. Salts, free and emulsified oil and grease (O&G), benzene, toluene, ethylbenzene and xylene (BTEX), polycyclic aromatic hydrocarbons (PAHs), phenols and organic acids are its main components. For the treatment and reuse of this PW, integrated processes consisting in a pretreatment related to flotation and settling, followed by an advanced oxidation process (AOP) have been proposed.

For the pretreatment, dissolved air flotation (DAF) and settling processes were studied and compared to a novel flotation technology based on the use of glass microspheres of limited buoyancy and its combination with conventional DAF (Enhanced DAF or E-DAF). They were evaluated as pretreatments for AOPs to polish PW for reuse purposes. Settling and E-DAF without air injection showed adequate turbidity and O&G removals, with eliminations higher than 87% and 90% respectively, employing 70 mg $L^{-1}$ of $FeCl_3$ and 83 min of settling time; and 57.9 mg $L^{-1}$ of $FeCl_3$, 300 mg $L^{-1}$ of microspheres and a flocculation rate of 40 rpm. A linear correlation was observed between final O&G concentration and turbidity after E-DAF. After that first stage, pretreated PW with O&G content below the requirements for discharging was obtained, which could be even further decreased through a later ultrafiltration membrane. However, the resulting effluent did not satisfy quality requirements for its reuse, since the rest of the components, mainly the dissolved organic compounds, were not eliminated in those mentioned pretreatment. Therefore, AOPs such as photocatalysis, photo-Fenton, Fenton and ozonation were studied to include one of these processes within the integrated treatment solution after the E-DAF or settling.

The best results were obtained by ozonation combined with $H_2O_2$, where most of the components added in the synthetic PW essayed in this work were eliminated, including a high percentage of acetic acid (the most recalcitrant component, not eliminated by the rest of AOPs studied). The optimum conditions for ozonation were 4 g $h^{-1}$ $O_3$ and 1500 mg $L^{-1}$ $H_2O_2$, at pH 10. After 2 h a 74% of TOC removal was achieved and the acetic acid elimination was 77.8%. Photocatalysis adding 500 mg $L^{-1}$ P25 under solar radiation achieved after 240 min a TOC and phenol removals of 18% and 100%, respectively; malonic acid remained and there was no degradation of acetic acid. With the photo-Fenton process under simulated solar radiation adding 557 mg $L^{-1}$ $H_2O_2$ and 55.7 mg $L^{-1}$ Fe at pH

3, a 16.5% of TOC removal was achieved after 90 min, phenol was completely eliminated and malonic acid was removed up to an 89%; but the acetic acid remained intact, and additional intermediates as benzaldehyde were formed. With the Fenton process at 70ºC by adding 557 mg $L^{-1}$ $H_2O_2$ and 55.7 mg $L^{-1}$ Fe, a 18% of TOC removal was achieved after 60 min. As in the case of photo-Fenton, toluene, xylene, naphthalene and phenol were rapidly eliminated but no acetic acid removal occurred and intermediates compounds were also formed.

As conclusion, the combination of E-DAF (or settling) followed by the ozonation process with 4 g $h^{-1}$ $O_3$ and 1500 mg $L^{-1}$ $H_2O_2$ at initial pH 10 could be suggested as a suitable polishing process for the reuse of PW. If salts elimination is also required, reverse osmosis final treatment should be used.

During normal operation, RO membranes found in seawater desalination plants can become fouled mainly due to the suspended or emulsified materials that may be present in the feed water. Depending on the type of fouling (if most part of the fouled material is organic or inorganic), different types of cleaning are applied. For instance, alkaline cleaning-soaking cycles with permeate water are commonly used against the organic fouling of the membranes. These operations generate a significant amount of wastewater that was treated in this thesis by different AOPs in order to be reused for irrigation or in other stages of the process and contribute to osmosis desalination plant concept of zero liquid discharge. These cleaning waters from RO membranes are expected to contain organic matter detached from the membrane together with common cleaning products: such as tetrasodium ethylenediaminetetraacetate ($Na_4$-EDTA) and sodium dodecyl sulfate (SDS).

First, Fenton process was applied for the removal of the organic load of these cleaning waters. Fenton experiments were performed at pH 3 after selecting ratios of $H_2O_2$/COD (wt) between 1.9 and 20, and $H_2O_2/Fe^{2+}$ (wt) between 0.13 and 82.80. For the studied conditions, it was observed that the optimal reaction time was 157 min and the optimal reagents doses were above 4000 mg $L^{-1}$ of $H_2O_2$ and 200 mg $L^{-1}$ of $Fe^{2+}$. This combination achieved a maximum TOC removal of 67% and a final biological oxygen demand ($BOD_5$) value of 14.8 mg $L^{-1}$ $O_2$.

Photo-Fenton and photocatalysis processes were also applied. Highest elimination was achieved with the photo-Fenton process at pH 3, where 79% of TOC removal was obtained with 1400 mg $L^{-1}$ $H_2O_2$ and 70 mg $L^{-1}$ $Fe^{2+}$ after 60 min of simulated solar radiation, and 85.6% after 157 min. After this time, also total removal of SDS was achieved, what implied obtaining suitable effluent for its reuse on irrigation. This photo-Fenton reaction could be also performed at pH 7, because at 157 min, the same elimination was reached. The addition of P25 accelerated the photo-Fenton process, although after one hour, similar elimination was reached for both conditions. 77% of TOC removal after 180 min was obtained under solar radiation at pH 3 by adding 1200 mg $L^{-1}$ of $H_2O_2$ with 250 mg $L^{-1}$ of P25 instead of Fe. Under UV-C radiation and by adding 1200 mg $L^{-1}$ of $H_2O_2$ at free pH, 61% of TOC removal was achieved at 157 min.

Life Cycle Assessment was also applied as a sustainability tool to assess the best treatment processes for both type of wastewaters from an environmental point of view. For the PW pretreatments, in general, impacts were slighter minor in the DAF process followed by settling process. Concerning the AOPs in the PW treatment, that was the next step, photo-Fenton was the process that caused less environmental impacts and the one that generated the higher impacts was Fenton with temperature. Among the AOPs applied in the treatment of RO membranes cleaning waters, Fenton process was the least polluting, although similar results were obtained by the photo-Fenton process. The one that generated the higher impacts was UV-C/$H_2O_2$ due to the energy consumption of the lamps.

# Resumen

La investigación realizada en esta tesis se ha llevado a cabo con la colaboración entre el departamento de I+D de la empresa Acciona Agua S.A.U. y el grupo Catheter del departamento de ingeniería química de la Universitat Rovira i Virgili.

Esta tesis está basada en tecnologías de tratamiento de agua, principalmente DAF mejorado y procesos de oxidación avanzada (POAs), aplicados a dos tipos de aguas residuales industriales: la produced water (PW, de las siglas en inglés, *produced water*), procedente de la industria del petróleo y el gas, y las aguas del lavado de las membranas de ósmosis inversa (OI) procedentes de las plantas desalinizadoras. Ambas líneas de investigación estaban incluidas dentro de dos proyectos de I+D de la empresa Acciona Agua S.A.U. Por una parte, la PW fue una línea de investigación nueva y novedosa. Por otro lado, a pesar de que la empresa tiene una gran experiencia en desalación, se abordó por primera vez una de las cuestiones relacionadas con la reutilización de aguas residuales de desalación. Se esperaba que los POAs fueran una tecnología adecuada para el tratamiento de estos efluentes.

La PW es el efluente acuoso que llega a la superficie junto con el petróleo o gas en las operaciones de extracción. Incluye el agua de formación (que se encontraba atrapada bajo tierra) y el agua de inyección que se extraen juntas con el combustible fósil durante la producción de petróleo y gas. La PW tiene una composición compleja que incluye sustancias orgánicas e inorgánicas. Sus principales componentes son sales, aceites y grasas libres y emulsionados (O&G), benceno, tolueno, etilbenceno y xileno (BTEX), hidrocarburos aromáticos policíclicos (HAPs), fenoles y ácidos orgánicos. Para el tratamiento y reutilización de esta PW, se han

propuesto procesos integrados, que consisten en un pretratamiento relacionado con flotación y sedimentación, seguido de un proceso de oxidación avanzada.

Para el pretratamiento, se estudiaron la flotación por aire disuelto (DAF) y los procesos de sedimentación y se compararon con una novedosa tecnología de flotación basada en el uso de microesferas de vidrio de flotabilidad limitada y su combinación con el DAF convencional (DAF mejorado o E-DAF). Se evaluaron como pretratamientos para POAs para la purificación de la PW con fines de reutilización. La sedimentación y E-DAF sin inyección de aire mostraron eliminaciones adecuadas de turbidez y de O&G, con porcentajes superiores al 87% y 90% respectivamente, empleando 70 mg $L^{-1}$ de $FeCl_3$ y 83 min de tiempo de sedimentación; y 57.9 mg $L^{-1}$ de $FeCl_3$, 300 mg $L^{-1}$ de microesferas y velocidad de floculación de 40 rpm. Se observó una correlación lineal entre la concentración final de O&G y la turbidez después del E-DAF. Después de esa primera etapa, se obtuvo PW pretratada con un contenido de O&G por debajo de los requisitos para la descarga, que podría disminuirse aún más con una posterior ultrafiltración. Sin embargo, el efluente resultante no satisfizo los requerimientos de calidad para su reutilización, ya que el resto de los componentes, principalmente los compuestos orgánicos disueltos, no fueron eliminados con los mencionados pretratamientos. Por lo tanto, se estudiaron POAs como la fotocatálisis, foto-Fenton, Fenton y ozonización, para incluir uno de estos procesos dentro de la solución de tratamientos integrados después del E-DAF o la sedimentación.

Los mejores resultados se obtuvieron con la ozonización combinada con $H_2O_2$, donde se eliminaron casi todos los componentes añadidos a la PW sintética utilizada en este trabajo, incluyendo un alto porcentaje de ácido acético, que es el componente más recalcitrante, no eliminado mediante ninguno de los otros POAs que fueron estudiados. Las condiciones óptimas para la ozonización fueron 4 g $h^{-1}$ de $O_3$ y 1500 mg $L^{-1}$ de $H_2O_2$, a pH 10. Después de 2 h se obtuvo un 74% de eliminación de TOC y la eliminación de ácido acético fue del 77.8%. La fotocatálisis con adición de 500 mg $L^{-1}$ de P25 y con radiación solar consiguió después de 240 min unas eliminaciones de TOC y de fenol del 18% y 100% respectivamente; el ácido malónico no se eliminó y no hubo tampoco degradación alguna de ácido acético. Con el proceso foto-Fenton bajo radiación solar simulada y añadiendo 557 mg $L^{-1}$ de $H_2O_2$ y 55.7 mg $L^{-1}$ de Fe a pH 3, se obtuvo un 16.5% de eliminación de TOC después de 90 min, se eliminó por completo el fenol y se eliminó hasta un 89% del ácido malónico; pero el ácido acético permaneció intacto, y se formaron intermediarios adicionales como el benzaldehído. Con el proceso Fenton a 70ºC mediante la adición de 557 mg $L^{-1}$ de $H_2O_2$ y 55.7 mg $L^{-1}$ de Fe, se obtuvo un 18% de eliminación de TOC después de 60 min. Como en el caso del proceso foto-Fenton, se eliminaron rápidamente el tolueno, xileno, naftaleno y fenol, pero no se produjo la eliminación de ácido acético y también se formaron compuestos intermedios.

Como conclusión, la combinación de E-DAF (o sedimentación) seguida de un proceso de ozonización con 4 g $h^{-1}$ de $O_3$ y 1500 mg $L^{-1}$ de $H_2O_2$, a pH inicial 10 podría ser una buena opción para el tratamiento de PW con fines de reutilización. Si también se requiere la eliminación de las sales, se debería realizar una posterior ósmosis inversa.

Durante el funcionamiento normal, las membranas de OI de las plantas de desalinización de agua de mar pueden ensuciarse debido principalmente a los materiales suspendidos o emulsionados que pueden estar presentes en el agua de alimentación. Dependiendo del tipo de ensuciamiento, si la mayor parte del ensuciamiento es orgánico o inorgánico, se aplican diferentes tipos de limpieza. Por ejemplo, los ciclos de limpieza alcalina con agua permeada se usan comúnmente contra el ensuciamiento orgánico de las membranas. Estas operaciones generan cantidades significativas de agua residual, que fue tratada en esta tesis mediante diferentes POAs, para ser reutilizada para riego o en otras etapas del proceso y contribuir así al concepto de planta de desalinización por OI de vertido cero de líquido. Se considera que estas aguas de lavado de membranas de OI contienen materia orgánica separada de la membrana junto con productos de limpieza comunes tales como etilendiaminotetraacetato tetrasódico ($Na_4$-EDTA) y dodecilsulfato sódico (SDS).

En primer lugar, se aplicó el proceso Fenton para la eliminación de la carga orgánica de estas aguas de lavado. Los experimentos Fenton se realizaron a pH 3 después de seleccionar relaciones de $H_2O_2$/DQO (peso) entre 1.9 y 20 y $H_2O_2/Fe^{2+}$ (peso) entre 0.13 y 82.80. Para las condiciones estudiadas, se observó que el tiempo de reacción óptimo fue 157 min con unas dosis óptimas de reactivos superiores a 4000 mg $L^{-1}$ de $H_2O_2$ y 200 mg $L^{-1}$ de $Fe^{2+}$. Con esta combinación se alcanzó una eliminación máxima de TOC del 67% y un valor final de demanda biológica de oxígeno ($DBO_5$) de 14.8 mg $L^{-1}$ de $O_2$.

También se aplicaron los procesos foto-Fenton y fotocatálisis. La mayor eliminación se consiguió con el proceso foto-Fenton a pH 3, donde se obtuvo un 79% de eliminación de TOC con 1400 mg $L^{-1}$ de $H_2O_2$ y 70 mg $L^{-1}$ de $Fe^{2+}$ después de 60 min bajo radiación solar simulada, y 85.6 % después de 157 min. Después de este tiempo, también se consiguió la eliminación total de SDS, lo que podría implicar la obtención de un efluente de agua adecuado para su reutilización en irrigación. Esta reacción de foto-Fenton también podría realizarse a pH 7, ya que a los 157 min se alcanzó la misma eliminación. La adición de P25 aceleró el proceso foto-Fenton, aunque después de una hora, se alcanzó una eliminación similar para ambas condiciones. Se obtuvo un 77% de eliminación de TOC después de 180 min bajo radiación solar a pH 3, añadiendo 1200 mg $L^{-1}$ de $H_2O_2$ con 250 mg $L^{-1}$ de P25 en lugar de Fe.

Bajo radiación UV-C, añadiendo 1200 mg $L^{-1}$ de $H_2O_2$ y a pH libre, se consiguió un 61% de eliminación de TOC a los 157 min.

Se aplicó también el Análisis del Ciclo de Vida como herramienta de sostenibilidad para evaluar los mejores procesos de tratamiento para ambos tipos de aguas residuales desde el punto de vista ambiental. En general, para los pretratamientos de PW, los impactos fueron menores en el proceso DAF seguido por el proceso de sedimentación. En cuanto a los POAs para el tratamiento de PW, que fue la siguiente etapa, el proceso foto-Fenton fue el que causó menos impactos ambientales, mientras que el que más impactó fue Fenton con temperatura. Entre los POAs aplicados al tratamiento de las aguas de lavado de membranas de OI, el proceso Fenton fue el de menor impacto, aunque similar al proceso foto-Fenton. El que más impactó fue el UV-C/$H_2O_2$ debido al consumo de energía de las lámparas.

# Resum

La investigació realitzada en aquesta tesi s'ha dut a terme amb la col·laboració entre el departament de R+D de l'empresa Acciona Aigua S.A.U. i el grup Catheter del Departament d'Enginyeria Química de la Universitat Rovira i Virgili.

Aquesta tesi està basada en tecnologies avançades de tractament d'aigua, principalment DAF millorat i processos d'oxidació avançada (POAs), aplicats a dos tipus d'aigües residuals industrials: l'aigua produïda (PW, de les sigles en anglès de *produced water*), procedent de la indústria del petroli i el gas, i les aigües del rentat de les membranes d'osmosi inversa (OI) procedents de les plantes dessalinitzadores. Les dues línies d'investigació estaven incloses dins de dos projectes de R+D de l'empresa Acciona Aigua S.A.U. D'una banda, la PW va ser una línia d'investigació nova i innovadora. D'altra banda, tot i que l'empresa té una gran experiència en dessalació, es va abordar per primera vegada una de les qüestions relacionades amb la reutilització d'aigües residuals de d'operacions de neteja de dessalació. S'esperava que els POAs fossin una tecnologia adequada per al tractament d'aquests efluents.

La PW és l'efluent aquós que arriba a la superfície juntament amb el petroli o gas a les operacions d'extracció. Inclou l'aigua de formació (que es trobava atrapada sota terra) i l'aigua d'injecció, que s'extreuen juntes amb el combustible fòssil durant la producció de petroli i gas. La PW té una composició complexa que inclou substàncies orgàniques i inorgàniques. Els seus principals components són sals, olis i greixos lliures i emulsionats (O&G), benzè, toluè, etilbenzè i xilè (BTEX), hidrocarburs aromàtics policíclics (HAPs), fenols i àcids orgànics. Per al tractament i reutilització d'aquesta PW, s'han proposat processos

integrats, que consisteixen en un pretractament relacionat amb flotació i sedimentació, seguit d'un procés d'oxidació avançada (POA).

Per al pretractament, la flotació per aire dissolt (DAF) i els processos de sedimentació van ser estudiats i comparats amb una innovadora tecnologia de flotació basada en l'ús de microesferes de vidre de flotabilitat limitada i la seva combinació amb el DAF convencional (DAF millorat o E-DAF). Es van avaluar com pretractaments per a la purificació de la PW amb fins de reutilització. La sedimentació i E-DAF sense injecció d'aire van mostrar eliminacions adequades de terbolesa i d'O&G, amb percentatges superiors al 87% i 90% respectivament, emprant 70 mg $L^{-1}$ de $FeCl_3$ i 83 min de temps de sedimentació; i 57.9 mg $L^{-1}$ de $FeCl_3$, 300 mg $L^{-1}$ de microesferes i velocitat de floculació de 40 rpm. Es va observar una correlació lineal entre la concentració final d'O&G i la terbolesa després de l'E-DAF. Després d'aquesta primera etapa, es va obtenir la PW pretractada amb un contingut d'O&G per sota dels requisits per a la descàrrega, que podria disminuir-se encara més amb una posterior ultrafiltració. No obstant això, l'efluent resultant no va satisfer els requeriments de qualitat per a la seva reutilització, ja que la resta dels components, principalment els compostos orgànics dissolts, no van ser eliminats amb els esmentats pretractaments. Per tant, es van estudiar POAs com la fotocatàlisi, foto-Fenton, Fenton amb temperatura i ozonització, per incloure un d'aquests processos dins de la solució de tractaments integrats després de l'E-DAF o la sedimentació.

Els millors resultats es van obtenir amb l'ozonització combinada amb $H_2O_2$, on es van eliminar gairebé tots els components afegits a la PW sintètica utilitzada en aquest treball, incloent un alt percentatge d'àcid acètic, que és el component més recalcitrant, no eliminat per cap de la resta de POAs que van ser estudiats. Les condicions òptimes per a la ozonització van ser 4 g $h^{-1}$ de $O_3$ i 1500 mg $L^{-1}$ de $H_2O_2$, a pH 10. Després de 2 h es va obtenir un 74% d'eliminació de TOC i l'eliminació d'àcid acètic va ser del 77.8% . La fotocatàlisi amb l'addició de 500 mg $L^{-1}$ de P25 i amb radiació solar va aconseguir després de 240 min unes eliminacions de TOC i de fenol del 18% i 100% respectivament; l'àcid malònic no es va eliminar i no hi va haver tampoc degradació alguna de àcid acètic. Amb el procés foto-Fenton sota radiació solar simulada i afegint 557 mg $L^{-1}$ de $H_2O_2$ i 55.7 mg $L^{-1}$ de Fe a pH 3, es va obtenir un 16.5% d'eliminació de TOC després de 90 min, es va eliminar per complet el fenol i es va eliminar fins un 89% de l'àcid malònic; l'àcid acètic va romandre però intacte, i es van formar intermediaris addicionals com el benzaldehid. Amb el procés Fenton a 70ºC mitjançant l'addició de 557 mg $L^{-1}$ de $H_2O_2$ i 55.7 mg $L^{-1}$ de Fe, es va obtenir un 18% d'eliminació de TOC després de 60 min. Com en el cas del foto-Fenton, es van eliminar ràpidament el toluè, xilè, naftalè i fenol, però no es va produir l'eliminació d'àcid acètic i també es van formar compostos intermedis.

Com a conclusió, la combinació d'E-DAF (o sedimentació) seguida d'un procés d'ozonització amb 4 g $h^{-1}$ de $O_3$ i 1500 mg $L^{-1}$ de $H_2O_2$, a pH inicial 10 podria ser una bona opció per al tractament de PW amb fins de reutilització. Si també es requereix l'eliminació de les sals, s'hauria de realitzar una posterior etapa d’osmosi inversa.

Durant el funcionament normal, les membranes d'OI de les plantes de dessalinització d'aigua de mar poden embrutar-se degut principalment als materials suspesos o emulsionats que poden estar presents en l'aigua d'alimentació. Depenent del tipus d'embrutiment, si la major part del embrutiment és orgànic o inorgànic, s'apliquen diferents tipus de neteja. Per exemple, els cicles de neteja alcalina amb aigua permeada s'usen comunament contra l'embrutiment orgànic de les membranes. Aquestes operacions generen quantitats significatives d'aigua residual, que va ser tractada en aquesta tesi mitjançant diferents POAs, per a ser reutilitzada per a reg o en altres etapes del procés i contribuir així al concepte de planta de dessalinització per OI amb abocament zero de líquid. Es considera que aquestes aigües de rentat de membranes d'OI contenen matèria orgànica separada de la membrana juntament amb productes de neteja comuns com ara etilendiaminotetraacetato tetrasòdic ($Na_4$-EDTA) i dodecilsulfat sòdic (SDS).

En primer lloc, el procés Fenton es va aplicar per a l'eliminació de la càrrega orgànica d'aquestes aigües de rentat. Els experiments Fenton es van realitzar a pH 3 després de seleccionar relacions de $H_2O_2$ / DQO (pes) entre 1.9 i 20 i $H_2O_2$ / $Fe^{2+}$ (pes) entre 0.13 i 82.80. Per a les condicions estudiades, es va observar que el temps de reacció òptim va ser 157 min amb unes dosis òptimes de reactius superiors a 4000 mg $L^{-1}$ de $H_2O_2$ i 200 mg $L^{-1}$ de $Fe^{2+}$. Amb aquesta combinació es va assolir una eliminació màxima de TOC el 67% i un valor final de demanda biològica d'oxigen ($DBO_5$) de 14.8 mg $L^{-1}$ de $O_2$.

També van ser aplicats els processos foto-Fenton i fotocatàlisi. La major eliminació es va aconseguir amb el procés foto-Fenton a pH 3, on es va obtenir un 79% d'eliminació de TOC amb 1400 mg $L^{-1}$ de $H_2O_2$ y 70 mg $L^{-1}$ de $Fe^{2+}$ després de 60 min sota radiació solar simulada, i 85.6% després de 157 min. Després d'aquest temps, també es va aconseguir l'eliminació total de SDS, el que podria implicar l'obtenció d'un efluent d'aigua adequat per a la seva reutilització en irrigació. Aquesta reacció de foto-Fenton també podria realitzar-se a pH 7, ja que als 157 min es va arribar a la mateixa eliminació. L'addició de P25 accelerà el procés foto-Fenton, encara que després d'una hora, s'arribà a una eliminació similar per a ambdues condicions. Es va obtenir un 77% d'eliminació de TOC després de 180 min sota radiació solar a pH 3, afegint 1200 mg $L^{-1}$ de $H_2O_2$ amb 250 mg $L^{-1}$ de P25 en lloc de Fe. Sota radiació UV-C, afegint 1200 mg $L^{-1}$ de $H_2O_2$ i a pH lliure, es va aconseguir un 61% d'eliminació de TOC als 157 min.

Es va aplicar també l'Anàlisi del Cicle de Vida com a eina de sostenibilitat per avaluar els millors processos de tractament per a ambdós tipus d'aigües residuals des del punto de vista ambiental. En general, per als pretractaments de PW, els impactes van ser menors en el procés DAF seguit pel procés de sedimentació. En quant als POAs per al tractament de PW, que va ser la següent etapa, el procés foto-Fenton va ser el que va causar menys impactes ambientals, i el que més va impactar va ser Fenton amb temperatura. Entre els POAs aplicats al tractament de les aigües de rentat de membranes d'OI, el procés Fenton va ser el de menor impacte, encara que similar al procés de foto-Fenton. El que més va impactar va ser l'UV-C/ $_2O_2$ a causa del consum d'energia de les làmpades.

# Chapter 1. Presentation and Description of the Thesis

**Content**

## 1.1. DESCRIPTION OF THESIS TOPIC

This thesis is divided into two parts, since the treatment of two types of wastewater is studied: the water generated in the oil and gas industry (specifically those generated in the upstream sector: the so-called produced water (PW)), and cleaning waters from seawater desalination reverse osmosis (RO) membranes.

Although the composition of both types of wastewater is different, and the focus of study in this thesis was the PW, which is composed of a high salt content, and that in fact, it was simulated with seawater, its treatment for reuse purposes was carried out through an efficient integrated solution composed of individual treatment technologies or steps whose final stage would be a reverse osmosis to eliminate the salts.

In relation to these RO membranes, they are also used in the desalination plants for the removal of salts contained in seawater. For the organic cleaning of RO membranes some chemicals are added and an effluent is generated (which was treated in this thesis for reuse purposes).

Acciona Agua company operates some seawater desalination plants such as ‘Sureste’ located in Tenerife and whose cleaning waters from the RO membranes were analyzed to simulate the wastewater used in this thesis.

Thus, these two types of water have in common the relation with seawater (PW has been simulated in a seawater matrix, and RO membranes cleaning waters, although they do not contain salts, come from cleaning membranes that have been used to desalinate seawater) and also that with both types of water, advanced oxidation processes were tested for its advanced treatment.

The main objective of the industrial doctorate project was the study and development of technologies for the treatment of PW from the oil and gas industry. Desalination and reuse of water for industrial use has presented a significant growth in the last five years. The need for water is vital in all areas of industry, and has a direct bearing on industrial growth. The value of industrial water market in the coming years will be dominated by industries such as oil and gas, refinery and petrochemical, power generation, food, pharmaceutical, microelectronics, pulp and paper industry and mining. In particular, the market value of the water from the oil and gas industry in the period 2013 to 2017 was estimated at 10000 million.

The management of the PW in the extraction of oil and gas is the most important challenge of the oil industry in the coming years. The volume of water produced in the extraction of crude oil increases as the age of wells operation increases because it is necessary to inject much water to maintain the production. The technological solutions for the treatment of PW must be robust, because a lack of efficiency or uncontrolled shutdown process can affect production. Furthermore, this market requires flexible solutions, since the characteristics of the water to be treated are highly dependent on geographic location. Due to the gradual depletion of reserves, the energy requirement is increasing and producers need to optimize their processes. This also affects the treatment processes of the water involved in the extraction, because it requires better quality water.

Thus, different integrated processes were studied in this thesis, among others, dissolved air flotation following by advanced oxidation technologies.

On the other hand, desalination is another important sector. Desalination has evolved into a viable water supply alternative allowing to tap the largest water reservoir in the world - the ocean. The scarcity of fresh water resources and the need for additional water supplies is already critical in many arid regions of the world and will be increasingly important in the future. RO membranes are used in these desalination plants and they can become fouled, so cleanings are performed. These operations generate a significant amount of wastewater which is also treated in this thesis by advanced oxidation processes, with the aim to reducing their organic load for reuse purpose and contributing to the concept of a zero-liquid discharge osmosis desalination plant.

This industrial doctorate has been possible due to the collaboration between Acciona Agua and CATHETER research group of the Rovira i Virgili University.

## 1.2. DESCRIPTION OF EACH CHAPTER OF THE THESIS

This thesis is organized in 9 chapters. Chapters 2, 3 and 4 are dedicated to PW, chapters 5 and 6 are dedicated to RO membranes cleaning waters, in chapter 7 a life cycle analysis for the PW treatments and RO membranes cleaning waters treatment has been carried out, in chapter 8 the final conclusions and future work for both types of wastewater are presented and chapter 9 shows the list of publications and communications produced during the doctorate.
The content of the different chapters is described below.

Chapter 1 (**Presentation and Description of the Thesis**) describes the theme of the thesis, the organization of the chapters and the objectives of the research work.

Chapter 2 (**State of the Art of Produced Water Treatment**) presents a compilation of the most important information about PW treatment. On the one hand, on the composition of these waters and the ranges of concentration of each parameter (as an exhaustive characterization of the PW should be done as the first step to select an optimum treatment option); and on the other hand, a deep review of all the treatments that can be carried out to eliminate the different components of these industrial wastewaters and the efficiency that can be achieved with each one of them according to the available literature. The possible treatments to be classified have been classified as physical, biological, thermal, membrane treatment, chemical and combination, modification or improvement of individual treatments has been presented. Besides, a summary of the most relevant legislation that applies to the different fates of the treated water has been made, including different possible applications for reuse.

As discussed above, the interest in the reclamation of these industrial wastewaters and their reuse is gaining interest. Up to now, the main attention has been centered in the removal of the oil and grease fraction, together with suspended solids. However, for certain applications a reclamation process involving the removal of dissolved organic matter is needed. For this purpose, a chemical treatment based on advanced oxidation technologies could be applied. For this reason, a review of the studies carried out with advanced oxidation processes for the treatment of PW has been included in this chapter.

Although there are some preview reviews that show information about PW in the literature, they are focused mainly on possible treatments for the removal of oil and grease and suspended solid fractions. The review presented in chapter 2 includes, besides this information, an updated summary on more advanced technologies necessary for the removal of other components of the PW, beside most relevant commercial processes existing for the treatment of PW, and also an overview of the most relevant requirements for different possible reuse applications for this wastewater (e.g. for irrigation, injections, etc). An extensive bibliographic search has been done and all the information shown in this chapter is updated. Finally, some critical conclusions have been defined at the light of the information available in the literature.

In Chapter 3 (**Pretreatment of Produced Water for Oil and Grease Removal: Enhanced Flotation / Sedimentation**), dissolved air flotation (DAF), enhanced DAF and settling have been studied as PW pretreatments, i.e., the first stage of the integrated solution for oil and grease removal before the PW polishing by advanced oxidation process.

For the study performed in this chapter, PW was synthesized in a seawater matrix containing the oil and grease fraction and phenol as representative of the dissolved organic compounds. And the main focus of this chapter was the removal of the oil and grease fraction, evaluating the effect of the pre-treatments tested in phenol concentration. For this purpose, different pretreatments, using the same available and cheap coagulant $FeCl_3$, have been studied: DAF, sedimentation and two types of enhanced flotation based on the use of glass microspheres, to determine the best process and conditions as a pretreatment for a later advanced oxidation process.

There are some previous studies that use DAF with simulated PW or with a single hydrocarbon, but in this chapter of the thesis PW has been synthetized in a more realistic way, using real seawater as matrix (instead of other studies in which salts or NaCl are added). To choose the best process for this type of wastewater, and taking into account the problems presented by DAF, other treatments have been studied, concluding that with a settling process or with enhanced flotation using glass microspheres instead of microbubbles (i.e. without saturated water injected), better results for oil and grease and turbidity removals are achieved (removals of 86% and 90%, respectively with both treatments), with the advantage of reducing process energy consumption since only the stirring step for the coagulation-flocculation is required. The process with microspheres has been previously applied in the treatment of algae but not in PW, so it is a novelty for this area.

In Chapter 4 (**Produced Water Treatment by Advanced Oxidation Processes**), different AOPs such as photocatalysis, photo-Fenton, Fenton and ozonation are studied to include one of these processes within the integrated treatments solution for the PW polishing after the pretreatment studied in the previous chapter.

The best results were obtained by ozonation combined with $H_2O_2$, where most of the components added in the synthetic PW essayed in this work were eliminated.

Chapter 5 and 6 are dedicated to the treatment for cleaning waters from seawater desalination RO membranes. In Chapter 5 (**Reverse Osmosis Membranes Cleaning Waters Treatment for Reutilization Purposes. Part I:**

**Application of Fenton Process**), Fenton process is studied as a plausible treatment for the organic load removal of the RO membranes cleaning waters in desalination plants. Among the Advanced Oxidation Processes (AOPs), Fenton reaction was chosen because of the low cost of iron, the ease of use of $H_2O_2$ and its harmless decomposition to the environment. These cleaning waters are composed of simulated organic matter, tetrasodium ethylenediaminetetraacetate and sodium dodecyl sulfate. The novelty of this research is that no references were found regarding the oxidation of these components coexisting in the same matrix as they are present on the cleaning waters of this thesis and the possibility of treating these effluents that are generated in large volumes in the desalination plants and that could have application e.g. for irrigation.

Due to the moderate performance of the Fenton process observed in chapter 5, Chapter 6 (**Reverse Osmosis Membranes Cleaning Waters Treatment for Reutilization Purposes. Part II: Application of Photo-Fenton and Photocatalysis Processes**) explores the application of photo-Fenton and photocatalysis processes to enhance the organic load removal of the RO membranes cleaning waters.

In Chapter 7 (**Life Cycle Assessment applied to the Produced Water and Reverse Osmosis Membranes Cleaning Water Treatments**) Life Cycle Assessment (an environmental management tool that enables quantification of environmental burdens and their potential impacts) has been used to compare the different treatments that were applied in this thesis to PW and RO membranes cleaning waters for the reuse of these wastewater to take into account, in addition to the elimination efficiency, the environmental impact of these technologies.

For the PW, the impacts of the DAF, E-DAF and settling pretreatments were studied and compared, followed by the different advanced oxidation processes.

For the RO membranes cleaning waters the advanced oxidation processes applied to this wastewater have been also studied and compared.

Chapter 8 (**Conclusions**) presents all the conclusions obtained from the different studies performed within this thesis, together with contributions and recommendations for future research in the same research line that could continue the work performed in this thesis.

Chapter 9 (**Publications and Communications**) presents the list of publications and communications made during the development of the thesis.

## 1.3. OBJECTIVES

As discussed earlier in this chapter, the main objective of this thesis is the application of advanced technologies to treat two types of industrial wastewaters generated in large volumes, that could be reused after their reclamation for industrial applications or other beneficial uses such as irrigation: the water generated in the oil and gas industry (specifically those generated in the upstream sector: the so-called produced water (PW)) and the wastewater from the reverse osmosis (RO) membranes cleaning processes.

The specific objectives are:

For the PW:

- To develop the analytic methods needed for the characterization of the target fractions of this wastewater.
- To determine the best integrated solution for PW polishing. This integrated solution includes a pretreatment and an advanced oxidation process (AOP).
- To define the optimum operating conditions for each of the selected process, as well as the efficiency of removal of the target fractions.

For the cleaning waters from seawater desalination RO membranes:

- To select a suitable AOP for the treatment of these waters.
- To define the optimum operating conditions of the selected process, as well as the efficiency of organic matter removal.

For both wastewaters:

- To evaluate the tested processes from an environmental point of view using Life Cycle Assessment as sustainability tool.

# Chapter 2. State of the Art of Produced Water Treatment

**Content**

## 2.1. INTRODUCTION

The Oil & Gas industry is characterized by the high volume water consumption and wastewater generation associated with extraction activities (the so-called produced water) -upstream sector- and by the generation of complex wastewater associated with refining activities -downstream sector-, as it is shown in Figure 2.1. In both cases, wastewater has a high pollution potential and is complex, both regarding the chemical composition and the technologies required for proper treatment. As a result, efficient treatment and reuse of treated water is one of the main technological challenges with regard to the management of the effluent.

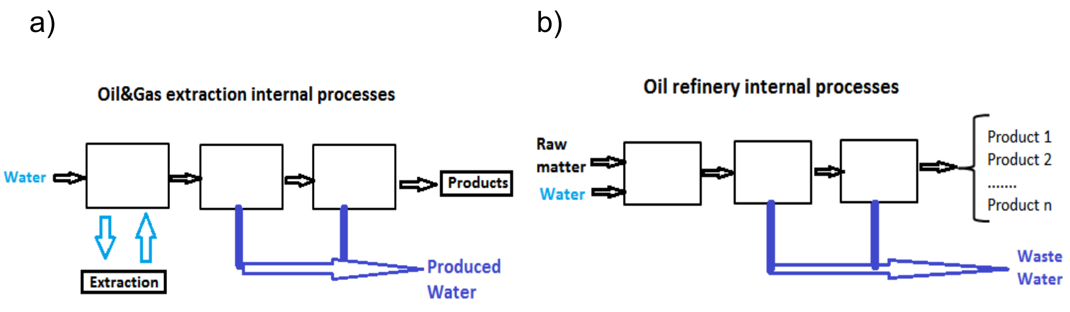


Figure 2.1. Process scheme for the upstream (a) and downstream (b) activities.

Formation or natural water is always found together with petroleum in reservoirs. It is slightly acidic and sits below the hydrocarbons in porous reservoir media. When oil and gas are extracted, the pressure in the reservoir is reduced, and additional water is usually injected into the reservoir water layer to maintain hydraulic pressure and enhance oil recovery (Igunnu and Chen, 2012). Produced water (PW) includes formation water (trapped underground) and injection water that are extracted together with the fossil fuel during oil and gas production (Arthur et al. 2011; Fakhru'l-Razi et al. 2009; Neff, 2002; Veil et al.

2004), containing also hydrocarbons and chemicals added during the production and treatment processes (Strømgren,1995). PW is generally classified as oilfield produced water, natural gas produced water and coal bed methane (CBM) produced water depending on the provenance (Igunnu and Chen, 2012).

Comparing the global production of barrels of water and oil, water to oil ratio (WOR) is approximately 3:1. Global volume of PW generated is up to 39.5 $Mm^3$ $day^{-1}$, although the WOR is increasing. By 2025, due to the ageing wells, the WOR is expected to reach an average of 12 (v/v) for onshore crude oil resources. This will reinforce the growth of the market of PW's management (Arowoshola et al. 2011).

PW quality varies significantly based on the geochemistry of the producing formation, the type of hydrocarbon produced, and the characteristics of the producing well (Guerra et al. 2011). Therefore PW properties and volume from one location can vary as well over time. Water contains various toxic organic and inorganic compounds, which are naturally occurring in the extraction wells, and others that are related to chemicals added for extraction purposes.

If PW meets appropriate water quality criteria, it may be reused again within the oil and gas production process, or even for purposes such as irrigation, livestock watering, aquifer storage, municipal and other industrial uses (Guerra et al. 2011). To this end, specific treatment of PW is needed according to the requirements of each end-user and applications.

## 2.2. SOURCES OF PRODUCED WATER

Oil and gas extraction from onshore and offshore wells entails the generation of PW, either if the fuel production comes from conventional or unconventional sources such as coal bed methane, tight sands, and gas shale:

**Conventional Oil and Gas**: When organic matter is buried under layers of sediments, geothermal forces, that exert high pressures and temperatures, during thousands of years, cause hydrocarbon pyrolysis that convert that matter into petroleum, oil and gas. If this process takes place in a confined layer of porous material, an oil and gas reservoir is formed as the pores in the rock harbor the fuel. The reservoir keeps it pressure until the well is drilled, when the high pressure is released and pushes oil and gas out to the surface (Guerra et al. 2011; Saad et al. 2016).

**Unconventional Petroleum Resources**: On the last years alternative oil and gas sources are being exploited. Only the last technological developments and the decrease on conventional source oil availability have made them profitable. Some of these unconventional sources are shale oil and gas, tight sands, and coal bed methane. In shale, oil and gas are retained within deep sedimentary formations which make necessary high amounts of water, chemicals and energy for their extraction. Tight sands are found around low permeability compacted sediments. These low permeability sands contains gas in their interstices. Coal bed methane or coal bed natural gas is formed by bacterial processes and high temperature and pressure processes during the bituminization of coal phase. The gas is allocated also within the interstices of the coal material.

The United States has the biggest deposits of shale. The formation of the Green River in Wyoming, Colorado, and Utah contains the largest of the United States oil shale deposit. United States Federal Government manages the seventy per cent of the resource commercially most important in the Green River (Guerra et al. 2011; Saad et al. 2016).

Shale gas is found trapped within shale formations. As the matrix permeability of shale is low, for providing permeability, fractures are necessary for commercial quantities of gas production. Since always, shale gas has been produced from shales with natural fractures; the recent increase of shale gas has been due to the technology development in hydraulic fracturing (fracking) to create extensive artificial fractures around the wells. It has become an increasingly important source of natural gas in the United States since the start of this century, and interest has spread to potential gas shales in the rest of the world. In 2000 shale gas provided only 1% of U.S. natural gas production; by 2010 it was over 20% and the U.S. government's Energy Information Administration predicts that by 2035, 46% of the United States' natural gas supply will come from shale gas. Gas shale has been for long periods in the United States in Illinois and Appalachian basins. Due to recent advances in technology, the Barnett Shale in Texas has also been highly economic. Tight sands gas is a resource of non-conventional natural gas produced from low permeability compacted sediments. Like shale gas, advances in technology have increased the development of compact sand in an economic resource. Gas is tightly contained in the formation of low permeability reservoir and wells must be stimulated to produce from the formation of the deposit. The basins of narrow arenas in the United States are superimposed on some gas shale basins, but there is no coincidence of compact sand in shale gas basins. Sandstone production occurs in the Great Plains, Rocky Mountains, the region's four corners, onshore gulf coast, and in Arkansas/Oklahoma.

Coal bed methane or natural gas is a non-conventional resource trapped in coal seams underground. Methane ($CH_4$) is formed in the coal seam as a result of the bacterial processes (biogenic) and the chemical reactions that occur with high temperature and pressure during the bituminization phase (thermogenic). Higher rank coals methane is formed by thermogenic production, and lower rank coals produced methane by biogenic production. In addition, the volume of gas increases with coal, the depth and the reservoir pressure. Coal has a large surface area per volume, so that the seams of coal may contain large volumes of gas in comparison with conventional gas deposits of comparable size (Taulis, 2007). It can be recovered from underground coal before, during, or after mining operations. It can also be extracted from “unminable” coal seams that are relatively deep, thin or of poor or inconsistent quality. Deeper, higher pressure causes fractures in the coal seam is close, making formations less permeable and more difficult so that the gas moves through the coal. Many of the basins of methane from the bed of coal in the region of the Rocky Mountains, including the Powder River and San Juan basins contain subbituminous coals. Subbituminous coal is soft enough to use conventional pit wells and the well is drilled to the top of the coal seam (Guerra et al. 2011).

## 2.3. CHARACTERISTICS OF PRODUCED WATER

The complex composition of PW is variable. Its physical and chemical properties depend on the geographic location of the field, the geological formation and the type of hydrocarbon product being produced. PW contains some of the chemical characteristics of the hydrocarbon with which it has been in contact for centuries. Its properties and volume can even vary throughout the lifetime of a reservoir (Veil et al. 2004).

PWs discharged from gas/condensate platforms are about 10 times more toxic than the PWs discharged from oil wells, but, the volumes from gas production are much lower; hence the total impact may be less (Duraisamy et al. 2013).

The major groups of constituents of concern in PW are:

- Salts (expressed as salinity, total dissolved solids (TDS), or electrical conductivity).
- Oil and Grease (O&G).
- BTEX (benzene, toluene, ethylbenzene, and xylenes).
- PAHs (polyaromatic hydrocarbons).
- Organic acids.
- Phenol.
- Various natural inorganic and organic compounds (e.g., chemicals that cause hardness and scaling such as calcium, magnesium, sulfates, and barium).

- Chemical additives used in drilling, fracturing, and operating the well that may have some toxic properties (e.g., biocides, corrosion inhibitors) (Arthur et al. 2011).

In the oil and gas industry, most regulatory policies and technical requirements focus their attention on O&G content, however salt content is also important in onshore operations.

There is a dispute over O&G, since O&G content in PW is defined by the method in which it is measured. The US EPA Method 1664 uses a direct measurement method in which O&G is defined as "a mixture of those components of produced water that are extractable in hexane at pH 2 or lower and remain after vaporization of the hexane". Therefore, this would include dispersed oil and water soluble organics except low molecular weight phenols, (which are highly soluble in water), low molecular weight acids, (which are soluble in water and volatile) and BTEX (which are highly volatile).

Table 2.1 summarizes the principal components in PW according to some references.

Table 2.1. Main components in produced water

| Component | Concentration, mg $L^{-1}$ | Reference | Concentration, mg $L^{-1}$ | Reference |
|---|---|---|---|---|
| **Na** | 0-150000 | (Database 2002) | 132-97000 | (Tibbetts et al. 1992) |
| **Cl** | 0-250000 | (Database 2002) | 80-200000 | (Tibbetts et al. 1992) |
| **Ba** | 0-850 | (Fillo, Koraido, | 1.3-650 | (Tibbetts et al. 1992) |

| | | | | |
|---|---|---|---|---|
| | | and Evans 1992) | | |
| **Sr** | 0-6250 | (Fillo et al. 1992) | 0.02-1000 | (Tibbetts et al. 1992) |
| **Sulfate** | 0-15000 | (Database 2002) | 2-1650 | (Tibbetts et al. 1992) |
| **Bicarbonate** | 0-15000 | (Database 2002) | 77-3990 | (Tibbetts et al. 1992) |
| **Ca** | 0-74000 | (Database 2002) | 13-25800 | (Tibbetts et al. 1992) |
| **K** | 24-4300 | (Tibbetts et al. 1992) | | |
| **Sulfite** | 10 | (Tibbetts et al. 1992) | | |
| **Mg** | 8-6000 | (Tibbetts et al. 1992) | | |
| **Iron** | 0.1-100 | (Tibbetts et al. 1992) | | |
| **Al** | 310-410 | (Tibbetts et al. 1992) | | |
| **B** | 5-95 | (Tibbetts et al. 1992) | | |
| **Cr** | 0.02-1.1 | (Tibbetts et al. 1992) | | |
| **Li** | 3-50 | (Tibbetts et al. 1992) | | |
| **Mn** | 0.004-175 | (Tibbetts et al. 1992) | | |

| | | | | |
|---|---|---|---|---|
| **Ti** | 0.01-0.7 | (Tibbetts et al. 1992) | | |
| **Zn** | 0.01-35 | (Tibbetts et al. 1992) | | |
| **Arsenic** | 0.005-0.3 | (Fakhru'l-Razi et al. 2009; Tibbetts et al. 1992) | | |
| **Lead** | 0.008-0.88 | (Fakhru'l-Razi et al. 2009; Tibbetts et al. 1992) | | |
| **Density (Kg m$^{-3}$)** | 1140 | (Fakhru'l-Razi et al. 2009; Tibbetts et al. 1992) | | |
| **TDS** | 100-400000 | (Database 2002) | 6554 | (Fakhru'l-Razi et al. 2009) |
| **COD** | 1220-2600 | (Fakhru'l-Razi et al. 2009; Tibbetts et al. 1992) | | |
| **TSS** | 1.2-1000 | (Fakhru'l-Razi et al. 2009; Tibbetts et al. 1992) | | |

| | | | | |
|---|---|---|---|---|
| **TOC** | 0-1500 | (Fakhru'l-Razi et al. 2009; Tibbetts et al. 1992) | 0,1-11000 | (Neff 2002) |
| **pH** | 4.3-10 | (Fakhru'l-Razi et al. 2009; Tibbetts et al. 1992) | | |
| **Total oil and grease** | 2-560 | (Fakhru'l-Razi et al. 2009) | | |
| **Saturated hydrocarbons** | 17-30 | (Neff 2002) | | |
| **Total BTEX** | 0.73-24.1 | (Ogp 2002) | 0.39-35 | (Tibbetts et al. 1992) |
| **Benzene** | 0.032-14.97 | (Ogp 2002) | | |
| **Toluene** | 0.058-5.86 | (Ogp 2002) | | |
| **Ethylbenzene** | 0.086-0.57 | (Ogp 2002) | | |
| **m-Xylene** | 0.258-1.29 | (Ogp 2002) | | |
| **p-Xylene** | 0.074-0.34 | (Ogp 2002) | | |
| **o-Xylene** | 0.221-1.06 | (Ogp 2002) | | |
| **Total NPD** | 0.766-10.4 | (Ogp 2002) | | |
| **Naphthalene** | 0.194-0.841 | (Ogp 2002) | | |
| **C1-naphthalenes** | 0.309-2.9 | (Ogp 2002) | | |
| **C2-naphthalenes** | 0.145-3.21 | (Ogp 2002) | | |
| **C3-naphthalenes** | 0.056-2.08 | (Ogp 2002) | | |
| **Phenanthrene** | 0.009-0.11 | (Ogp 2002) | | |
| **C1-phenanthrenes** | 0.017-0.32 | (Ogp 2002) | | |

| | | | | |
|---|---|---|---|---|
| **C2-phenanthrenes** | 0.014-0.365 | (Ogp 2002) | | |
| **C3-phenanthrenes** | 0.009-0.27 | (Ogp 2002) | | |
| **Dibenzothiophene** | 0.001-0.023 | (Ogp 2002) | | |
| **C1-dibenzothiophenes** | 0.006-0.103 | (Ogp 2002) | | |
| **C2-dibenzothiophenes** | 0.004-0.12 | (Ogp 2002) | | |
| **C3-dibenzothiophenes** | 0.003-0.089 | (Ogp 2002) | | |
| **Total 16 EPA PAH** | 0.0058-0.129 | (Ogp 2002) | | |
| **Fluorene** | 0.0041-0.067 | (Ogp 2002) | | |
| **Acenaphthene** | 0.0003-0.015 | (Ogp 2002) | | |
| **Chrysene** | 0.0006-0.015 | (Ogp 2002) | | |
| **Ammoniacal nitrogen** | 10-300 | (Tibbetts et al. 1992) | | |
| **Phenols** | 0.009-23 | (Tibbetts et al. 1992) | | |
| **Total organic acids** | 0.001-10000 | (Neff 2002) | | |
| **Formic acid** | 26-584 | (Røe Utvik 1999) | | |
| **Acetic acid** | 8-5735 | (MacGowan et al. 1988) | | |
| **Propanoic acid** | 36-98 | (Røe Utvik 1999) | | |
| **Butanoic acid** | ND-46 | (Røe Utvik 1999) | | |
| **Pentanoic acid** | ND-33 | (Røe Utvik 1999) | | |
| **Oxalic acid** | ND-495 | (MacGowan et al. 1988) | | |

| | | | | |
|---|---|---|---|---|
| **Malonic acid** | ND-1540 | (MacGowan et al. 1988) | | |
| **Aliphatic acids** | 1.8-120 | (Rabalais et al. 1991) | | |
| **Benzoic acid** | 0.13-16 | (Rabalais et al. 1991) | | |
| **C1- Benzoic acid** | 0.089-16 | (Rabalais et al. 1991) | | |
| **C2-Benzoic acid** | 0.043-3.8 | (Rabalais et al. 1991) | | |

### 2.3.1. Dissolved and dispersed oil compounds

Oil is composed of hydrocarbons as benzene, toluene, ethylbenzene, and xylenes (BTEX), naphthalene, phenantherene, dibenzothiophene (NPD), polyaromatic hydrocarbons (PAHs) and phenols. The majority of the hydrocarbons do not dissolve in the water, so most of the oil is dispersed in water (Ekins et al. 2007) in the shape of an emulsion, or clearly separated into two phases.

The amounts of dissolved and suspended oil present in PW (prior to treatment) are related to following factors:

- Oil composition
- pH, salinity, TDS (total dissolved solids), temperature,
- oil/water ratio,
- type and quantity of oilfield chemicals,
- type and quantity of various stability compounds (waxes, asphaltenes, fine solids) (Hansen and Davies 1994).

So O&G in PW can be in the form of free oil, dispersed oil and emulsified oil.

#### 2.3.1.1. Dissolved oil

It includes water soluble organic compounds: BTEX, phenols, aliphatic hydrocarbons, carboxylic acid, and low molecular weight aromatic compounds (Røe Utvik, 1999). The water-soluble organic compounds in PW are polar constituents with a low number of carbons. Organic acids such as formic and propionic are typically found in PW. pH and temperature increase soluble organics in PW. Pressure enhances dissolved organic compound concentration slightly. In addition, salinity does not significantly affect the dissolved organics in PW (Bostick et al. 2001). The amounts of soluble oil in PW depend on type of oil, volume of water production, artificial life technique, and age of production (Stephenson, 1992).

#### 2.3.1.2. Dispersed oil

It includes PAHs and some of the heavier alkyl phenols, like $C_6$–$C_9$ alkylated phenols that are less soluble in PW and are present as dispersed oil (Faksness et al. 2004). Dispersed oil consists of small droplets of oil suspended in the PW. The amount of dispersed oil in PW depends on the shear history of the droplet, the density of oil, the amount of oil precipitation and interfacial tension between the water and oil (Stephenson, 1992).

### 2.3.2. Dissolved formation minerals

This inorganic content is strongly related to the geochemical characteristics of the well. They are usually high in concentration, and classified as cations and anions, naturally occurring radioactive materials and heavy metals.

#### 2.3.2.1. Cations and anions

Cations such as $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Ba^{2+}$, $Sr^{2+}$, $Fe^{2+}$ and anions such as $Cl^-$, $SO_4^{2-}$, $CO_3^{2-}$, $HCO_3^-$ affect PW chemistry in terms of buffering capacity, salinity, and scale potential (Hansen et al. 1994). Salinity, mainly due to dissolved sodium and chloride and in a lesser extent to calcium, magnesium, and potassium, may vary from a few parts per million to about 300.000 mg $L^{-1}$ (Jacobs et al. 1992; Pitre 2013).

#### 2.3.2.2. Heavy metals and naturally occurring radioactive materials (NORM)

PW contains trace quantities of various heavy metals such as cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc (Hansen et al. 1994) mostly from natural origin. Their concentration can reach $10^2$ to $10^5$ times that in seawater (SOEP, 1996).

NORM are originated in geological formations and are brought to surface as dissolved solids in PW. NORM may precipitate into scale or sludge when the water temperature reduces as it reaches the surface. The most abundant NORM compounds are $^{226}Ra$ and $^{228}Ra$ (Veil et al. 2004) and barium. According to (Gäfvert, Færevik, and Rudjord 2006) Norwegian Petroleum Industry handles produced water effluents with $^{226}Ra$ and $^{228}Ra$ concentrations that range from detection limits, 0.3–1.3 Bq $L^{-1}$ respectively, up to 16 and 21 Bq $L^{-1}$.

### 2.3.3. Productions solids

Production solids name a wide range of solid organic and inorganic materials that accompany PW. They include formation solids, particles detached from the surrounding materials, corrosion and anti-scale products from the pipes and equipment, bacteria, waxes, and asphaltenes (Fakhru'l-Razi et al. 2009).

Some other inorganic crystalline substances such as $SiO_2$, $Fe_2O_3$, $Fe_3O_4$, and $BaSO_4$ can also be found (Deng et al. 2009).

### 2.3.4. Production chemical components

In addition to its natural components, PW may include chemical additives dosed in drilling, to treat or prevent operational problems and in the oil/water separation process (Arthur et al. 2011; Stephenson, 1992). This group of substances is selected by the manufacturers attending to the characteristics of the well of the fuel itself. They include gas hydrate inhibitors, corrosion inhibitors, oxygen scavengers, scale inhibitors, biocides to mitigate bacterial fouling, asphaltene dispersants, paraffin inhibitors, defoamers, emulsion breakers and clarifiers, coagulants, flocculants, etc. (Daigle et al. 2012).

### 2.3.5. Dissolved gases

$CO_2$, $O_2$, and $H_2S$ are common gases included in PW (Hansen et al. 1994).

## 2.4. REGULATORY REQUIREMENTS

Among all components, O&G, defined from different points of view as will be seen later, are one of the group of compounds that present more demanding restrictions for discharge and/or reuse according the legislation, constituting the main focus of the treatment.

Upstream PW contains originally of average approximately 500 mg $L^{-1}$ of O&G. Nevertheless PW to spillage can contain:

- 15 mg $L^{-1}$ of O&G with an installation working correctly and optimized,
- 35-40 mg $L^{-1}$ is the typical limit of spillage according to the international regulations,
- 100 mg $L^{-1}$ when the installation presents problems, principally for the generation of complex emulsions (water down in oil in water).

### 2.4.1. Irrigation Reuse

In Europe, although in average about 21% of the total amount of withdrawn water is used in agriculture, in Southern European Countries, the share of total water use by agricultural activities can be higher than 50% (e.g. in Spain is ca. 60% according to AQUASTAT reports).

In the United States, irrigation also represents the majority of fresh water use. Estimations made in 2000 accounted a 70% of total water consumption in the

Western US for irrigation. In this area, 64% of the water used comes from surface water sources, while nationally is 59% (Fipps, 2003). Part of this 5% difference could be supplied by PW resources discharged into streams and channels to be used downstream for beneficial uses such as irrigation.

Irrigation requires both large water volumes and high water quality. Parameters such as the sodium adsorption ratio (SAR) or the electrical conductivity (ECw, dS $m^{-1}$) are important criteria for ensuring that the water quality will not damage the crops. When the source water has a high salinity, there is a greater potential for salt damage at lower SAR levels. Given the saline nature of PW with high sodium content, the SAR and ECw are both important parameters to consider before reuse.

Boron is another important parameter to consider. The Food and Agriculture Organization publication (Fipps, 2003). includes boron concentration recommendations for various types of crops.

There are also other specifications for minor components which can affect the growth of plants when used in concentrations higher than those indicated for applications at short and long term. In addition to these components, the following constituents and parameters are also potentially harmful at high concentrations for the crops (Fipps, 2003):

- pH normal range 6.5–8.4
- Chloride < 70 mg $L^{-1}$ generally safe for all plants
- Nitrate < 10 mg $L^{-1}$ nitrate nitrogen ($NO_3$-N), 45 mg $L^{-1}$ nitrate ($NO_3$).

According to the U.S. EPA guidelines for water reuse for irrigation (2012), the water quality for irrigation for public areas and agricultural irrigation for food crops that will not be commercially processed or any crop eaten row is: pH 6-9, ≤ 10 mg $L^{-1}$ BOD, ≤ 2 NTU, no detectable fecal coliforms/100 mL and at least 1 mg $L^{-1}$ residual chlorine. The water quality for irrigation of restricted access areas and agricultural irrigation for food crops that will be commercially processed or non-food crops and pastures is: pH 6-9, ≤ 30 mg $L^{-1}$ BOD, ≤ 30 mg $L^{-1}$ TSS, ≤ 200 fecal coliforms/100 mL and at least 1 mg $L^{-1}$ residual chlorine.

In Europe there is not yet a Directive defining requirements for water reuse. However, some European countries have set limits for certain water reuse applications. E.g., in Spain the norm regulating water reuse is the Royal Decree 1620/2007. The quality required varies according to the use to which it will allocate reused water, demanding the highest quality for urban residential use, aquifer recharge by direct injection, crop irrigation that are going to be eaten raw and cooling towers. Concerning reuse for irrigation, the following maximum acceptable values have been set: irrigation of crops that are going to be eaten raw: intestinal nematodes 1egg/100 ml, Escherichia coli 100 CFU/100 ml, 20 mg $L^{-1}$ TSS, 10 NTU; irrigation of crops that are not going to be eaten raw: intestinal nematodes 1egg/100 ml, Escherichia coli 1000 CFU/100 ml, 35 mg/L TSS, no limit on turbidity; other irrigation uses: 1egg/100 ml, Escherichia coli 10000 CFU/100 ml, 35 mg $L^{-1}$ TSS, no limit on turbidity.

### 2.4.2. Reuse for Extraction

Oil and gas extraction causes a reduction of the pressure in the reservoir and water in injected to maintain hydraulic pressure and improve the recovery of oil. The reinjection of PW is one of the best economic and environmental options for the PW generated, in addition to solving simultaneously the problem of maintaining pressure in the reservoir. Thus, PW that is a waste product can be transformed into a money resource. Summarizing, the benefits of PW reinjection (PWRI) are:

- Disposal of PW
- Pressure maintenance and displacing the crude oil in the reservoir
- Environmentally friendly
- Economic advantages
- Meets new regulations

The general specifications for acceptable quality of oil-fields PW for reinjection are less than 10 mg $L^{-1}$ of TSS and less than 42 mg $L^{-1}$ of O&G (Bader, 2007).

PW generated in onshore operations, after a pretreatment, is usually reinjected into the wells. Sand removal and other solids should be removed in order to avoid plugging and damage to the injection pumps.

### 2.4.3. Ocean Discharge

The general practice for PW is its treatment through gravity-based separation and discharge into the environment, which can pollute soil, surface water and underground water (Fakhru'l-Razi et al. 2009). For a long time, only non-polar oil in water or O&G was regulated by government, while not paying much attention to dissolved organics in PW, but it is currently being taken into account the consequences of dissolved organic components, heavy metals and production chemicals on living organisms since metals and hydrocarbons from oil platforms are very toxic to the ecosystem and fish exposed to alkyl phenols (Grant and Briggs, 2002; Nature Technology Group, 2005).

PW generated in offshore operations (platforms) is usually discharged into the sea. The US offshore regulations govern the quality of the PW by the O&G concentration, toxicity limitation, and prohibition of offshore discharges of produced sand. There is no current regulation on suspended solids. However, suspended solids tend to have oil adhering onto them, so they should be also taken into account.

In Russia, for example, the limit for suspended solids in sea water is 10 mg $L^{-1}$.

Regarding toxicity, US regulations allow the toxicity criteria to be met through dilution.

A general limit set in the legislation for discharging PW into the sea was 40 mg $L^{-1}$ O&G, but an increase in environmental concerns has forced many countries to implement more stringent regulatory standards.

The Convention for the Protection of the Marine Environment of the North–East Atlantic sets that the maximum monthly discharge limit to 30 mg $L^{-1}$ O&G in the North-Est Atlantic area (OSPAR Commission, 2005).

In the United States, Environmental Protection Agency (USEPA) stipulates an average amount of oil in PW of 29 mg $L^{-1}$ per month for the outer continental shelf region and a maximum of 42 mg $L^{-1}$ for daily discharge (USEPA, 1996).

In Australia, permitted offshore discharge of O&G in PW is 30 mg $L^{-1}$ and the People's Republic of China now sets the monthly average limits of O&G and chemical oxygen demand at 10 and 100 mg $L^{-1}$, respectively (Tellez et al. 2002).

In Spain, MAH/285 / 2007 is the Catalan regulation on sea discharge, on which the limits are set for several parameters as 6-8 pH, 50 mg $L^{-1}$ O&G, 700 mg $L^{-1}$ COD, 300 mg $L^{-1}$ BOD5, 300 mg $L^{-1}$ TOC, etc.

The EU Water Framework Directive (WFD) adopted in 2000 (Directive 2000/60/EC) is committed to 'zero discharge' in response to the need for a more protective system to tackle aquatic pollution. Since 2005, oil operators in Norway agreed to implement a zero environmental harmful discharge. To achieve this, the Norwegian Oil Industries Associations developed the Environmental impact factor (EIF), which considers all the contaminants in PW (Nature Technology Group, 2005). Similarly, OSPAR commission has agreed on zero discharge of pollutants into the sea. Most oil and gas companies around the world are now working towards the implementation of 'zero-discharge' of contaminants in PW.

In addition to legislation, many water-stressed countries with oilfields are looking for ways to supplement their limited fresh water resources by focusing on efficient and economical methods to treat PW, so that it can be channeled to agricultural and industrial uses (Veil et al. 2004).

Table 2.2 (a) and (b) shows worldwide limits of discharge.

Table 2.2. Worldwide produced water effluent oil concentration limitations according to a) (Stewart, 2008), b) (Neff et al. 2011)

a)

| **Country** | **Oil concentration limitation** |
|---|---|
| Ecuador, Colombia, Brazil | 30 mg $L^{-1}$ All facilities |

| | |
|---|---|
| Argentina and Venezuela | 15 mg $L^{-1}$ New facilities |
| Indonesia | 25 mg $L^{-1}$ Grandfathered facilities |
| Malaysia, Middle East | 30 mg $L^{-1}$ All facilities |
| Nigeria, Angola, Cameroon, Ivory Coast | 50 mg $L^{-1}$ All facilities |
| North Sea, Australia | 30 mg $L^{-1}$ All facilities |
| Thailand | 50 mg $L^{-1}$ All facilities |
| USA | 29 mg $L^{-1}$ OCS water<br>Zero discharge inland water |

b)

| **Country** | **Monthly average, mg $L^{-1}$** | **Daily maximum, mg $L^{-1}$** |
|---|---|---|
| Canada | 30 | 60 |
| USA | 29 | 42 |
| OSPAR (NE Atlantic) | 30 | - |
| Mediterranean Sea | 40 | 100 |
| Western Australia | 30 | 50 |
| Nigeria | 40 | 72 |
| Brazil | - | 20 |

## 2.5. PRODUCED WATER MANAGEMENT

Among the many different technology choices available, selection of a management option for PW varies according different factors such as chemical and physical properties of the water, volumes, duration, and flow rate of water generated, desired end use of the water, regulations, technical and economic feasibility of any particular option, availability of suitable infrastructure for disposal, etc.

Water management technologies and pollution prevention strategies can be organized into this hierarchy:

(1) Minimization

(2) Recycle / Re-use

(3) Disposal (when water cannot be managed through minimization, re-use, or recycle).

Examples of technologies and practices for each group are shown in Tables 2.3, 2.4 and 2.5.

Table 2.3. Water Minimization Technologies (Arthur et al. 2011)

| **Approach** | **Technology** |
|---|---|
| **Produced Water** | |
| Reduce the volume of water entering the wells | Mechanical blocking devices (e.g., packers, plugs, cement jobs).<br>Water shut-off chemicals (e.g., polymer gels). |
| Reduce the volume of water managed at the surface by remote separation | Dual completion wells (downhole water sink).<br>Sea floor separation modules. |
| **Flowback Water** | |
| Use less water in frac fluids | Substitute other materials, like $CO_2$ or nitrogen in place of water as main ingredient in frac fluids.<br>Consider using gelled frac fluids instead of “slickwater” fluids. |

Table 2.4. Water Re-Use and Recycle Management Options (Arthur et al. 2011)

| **Management option** | **Use** |
|---|---|
| **Produced Water** | |

| | |
|---|---|
| Re-injection for enhanced recovery | Steam flood for oil sands. |
| Injection for future water use | Aquifer storage and recovery |
| Injection for hydrological purposes | Subsidence control |
| Agricultural use | Irrigation.<br>Livestock and wildlife watering.<br>Managed/ constructed wetlands. |
| Industrial use | Oil and gas industry application.<br>Power plants.<br>Other (vehicle wash, fire-fighting, dust control on gravel road). |
| Treat to drinking water quality | Use for drinking water.<br>Other domestic uses. |
| **Flowback Water** | |
| Use flowback water for future frac fluids | Use after settling, filtration, or other basic treatment step.<br>Use after more advanced treatment steps. |

Table 2.5. Water Disposal Technologies (Arthur et al. 2011)

| **Practices** |
|---|
| Discharge |
| Underground injection (other than for enhanced recovery) |
| Evaporation |
| Offsite commercial disposal |

## 2.6. CONVENTIONAL TREATMENTS OF PRODUCED WATER

According to the previous section, the final disposition of the water determines the type and extent of treatment (Arthur et al. 2011).

PW treatment technologies applied in the petroleum industry are historically limited to physical separation technologies such as the API separator, coalescers or hydrocyclones. These technologies are, in most cases, not capable of producing an effluent compatible with fresh water standards for beneficial reuse in for example irrigation or industrial processes (Dores et al. 2012) .

Currently, the majority of PW generated worldwide at onshore facilities is reinjected into the soil, either for disposal or for enhanced oil recovery processes. As a result, the treatment facilities in onshore oil and gas production operations are mostly designed to remove dispersed oil and grease (O&G) and suspended solids, to avoid formation plugging and damage to the injection pumps. In offshore operations, because the common practice is to discharge the treated PW to the sea, the main treatment objective is to reduce O&G to acceptable levels and mitigate toxicity impacts on aquatic fauna and flora. This normally means reducing the O&G concentrations in the treated PW to 30-40 mg $L^{-1}$, depending on the location (Dores et al. 2012; Veil et al. 2004).

When oil is extracted from the well, it is treated for its dewatering in a treatment train as it is shown in Figure 2.2. The first stage of the produced fluids separation system consists of two-phase separators, or in some cases of three-phase separators where there will be generated a gas stream, an oil stream (that will go to the Oil Treatment System) and a water stream that will go to the Water Treatment System (USEPA, 1996).

The water treatment system receives, therefore, PW from the oil treatment system and from the initial phases separator. This water treatment system is composed by a primary treatment (hydrocyclone, corrugated plate separator, API separator, or similar) and a secondary treatment (usually a floater). This final PW to spillage can contain:

- 15 mg $L^{-1}$ of O&G with an installation working correctly and optimized.

- 35-40 mg $L^{-1}$: typical limit of spillage according to the international regulations.
- 100 mg $L^{-1}$: when the installation presents problems, principally for the generation of complex emulsions (water down in oil in water).

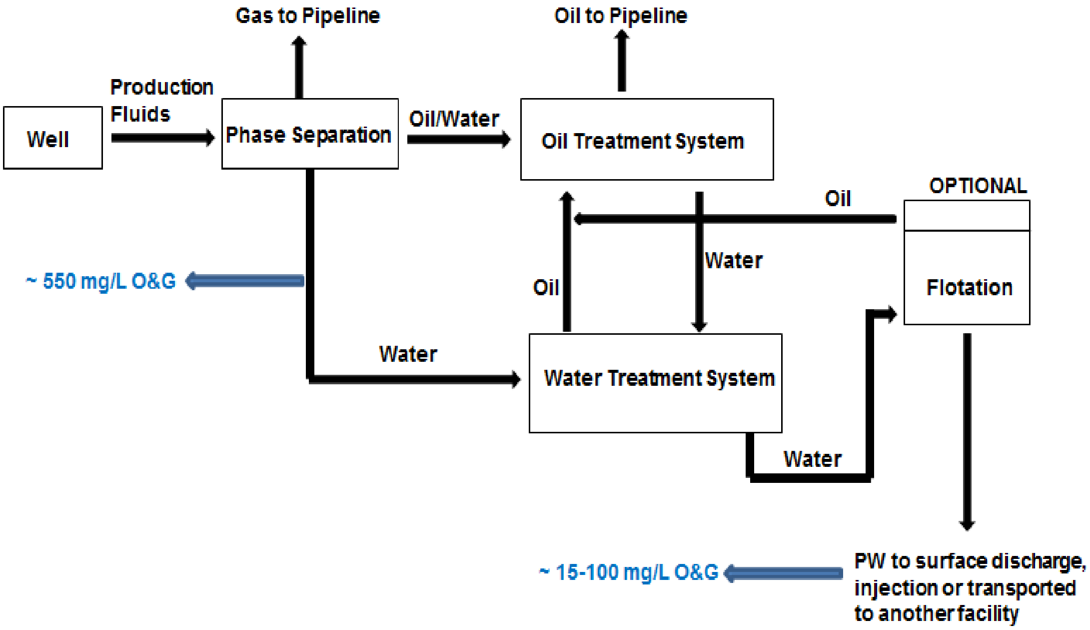


Figure 2.2. Produced water treatment system, (modified from USEPA, 1996)

## 2.7. POLISHING TREATMENTS OF PRODUCED WATER

Treatment processes depend on the characteristics of PW and therefore, experimental studies for determination of characteristics of PW are required for designing a treatment process, relying solely on the literature is not recommended (Çakmakce et al. 2008).

Considering the limit of 30 mg $L^{-1}$ of O&G according to discharge legislation, and especially if the PW is to be destined to reuse (irrigation, livestock watering, aquifer storage, municipal and other industrial uses) the train of treatment shown in the previous section is not sufficient and it will be necessary a tertiary water treatment or a polishing treatment for the reduction of O&G content, and other concerning substances. Some of those will be described in this section.

In 1995 the American Petroleum Institute, (API), made its recommendation on the Best Available Technology for Produced Water Management on Offshore Gas and Oil Installations. According to that report, the factors that contribute to the toxicity of PW are: very small particles, salinity (9% or greater), volatile compounds, extractable organics (acidic, basic, neutral), ammonia and hydrogen sulfide.

The treatment methods assessed by the group to reduce the pollutants in PW to almost undetectable levels are based on combinations of different technologies: Carbon Adsorption (modular granular activated carbon systems), Air stripping (packed tower with air bubbling through the PW stream), Membrane Filtration (nanofiltration and reverse osmosis polymeric membranes), Ultra-violet light (irradiation by UV lamps), Chemical Oxidation (ozone and/or hydrogen peroxide oxidation) and Biological Treatment (aerobic system with fixed film biotower or suspended growth) (Igwe et al. 2013).

Since then there have been advances in treatments. In this section many separate and combined physical, chemical, and biological methods are proposed for PW treatment.

### 2.7.1. Physical Treatment

#### 2.7.1.1. Physical adsorption

Adsorption produces a very high quality treated water, with concentrations down to a few ppb and lower. However, most of these systems are expensive to install and operate, and their application is generally limited to situations that require polishing to such high quality. Walnut shell filters would be an exception, due the lower cost and the quality of the treated water obtained (Daigle et al. 2012).

Adsorbent materials can retain both organic and inorganic compounds. They have been used to remove manganese, iron, total organic carbon (TOC), BTEX, oil and more than 80% of heavy metals present in PW (Drewes et al. 2009), by means of different materials.

The main inconvenient of these methods are that suspended particles in PW plug adsorbent media, reducing removal efficiency, and the costs related to the regeneration of the adsorbents and chemical wastes generated (McGhee, 1991). Another important drawback is that pollution does not disappear and would have to be removed from the solid phase by another treatment as wet oxidation or incineration.

Activated carbon has been proven as capable of removing soluble content, including BTEX. Organoclays can also remove insoluble free hydrocarbons that contribute to total petroleum hydrocarbons (TPH) and O&G content (Younker and Walsh, 2014). Combination of both adsorbents proved to be efficient in removing total petroleum hydrocarbons (TPH) (Doyle and Brown, 2000). Copolymers can reduce oil content of PW to around 85% (Carvalho et al. 2013). Zeolites are often used as ion-exchange resins. Use of hydrophobic zeolite pellets in a fixed bed to adsorb dissolved organic compounds in PW was proposed by Hansen and colleagues (1994); on the other hand, Mitchell and colleagues (Mitchell et al. 1992) proposed a resin-filled column to remove soluble organic compounds. In both methods, acid backwash and solvents can regenerate the adsorbents. Janks and Cadena (1992) used “tailored” zeolites, made by adsorbing neutralized amines onto natural zeolites, to remove BTEX from saline PW. The projected process removal efficiency was 70–85%.

In the process addressed to treat waters containing substances with –COOH, NH, and –OH groups, surfaces of PET fibers were modified from oleophilic to hydrophilic to treat oilfield-PW. Treated effluent characteristics were as follows: O&G< 2.4 mg $L^{-1}$, Suspended solids< 2 mg $L^{-1}$. The effluent can be used for water injection in enhanced oil recovery processes (Yang et al. 2002).

In a combined adsorption process consisting of the patented Crudersorb technology and polymeric resins, offshore-PW was treated to reduce O&G concentration levels to less than 29 mg $L^{-1}$. Crudersorb removed suspended and dispersed oil droplets while resin removed dissolved hydrocarbons, aliphatic carboxylic acids, aromatic carboxylic acids, and phenolic compounds (Ali et al. 1998).

A hydrophilic fiber ball that was developed through surface modification methods, could remove O&G of PW from alkaline/surfactant/polymer flooding efficiently (Liu et al. 2007).

In a proposed system consisting of two beds of strong acid ion exchange resin in series, oil-free PW could be treated to remove calcium and magnesium. The chemical structure of strong acid- cation-exchange resin is sulfonated copolymer of styrene and divinylbenzene. The system worked well with TDS of less than 50000 mg $L^{-1}$. When the TDS of PW is higher, sodium competes with calcium and magnesium for sites on the resin (Jan et al. 2013).

Doyle and colleagues (Doyle et al. 1997) tested the combination of a modified polymer or bentonite, or an organoclay and granular activated carbon, in packed bed adsorption column, removing hydrocarbons consistently and effectively. Results showed that the system reduced total petroleum hydrocarbon and O&G to non-detectable levels, and reduced BTEX.

Li and colleagues (Li et al. 2008) studied oil removal from PW by using modified porous ceramics filtration media (MPCFM) in a fixed bed column. Porous filtration media was modified with containing hydrogen silicone oil (CHSO).

#### 2.7.1.2. Cyclones

A hydrocyclone o cyclon is a mechanical device designed to reduce or increase the concentration of a dispersed phase, solid, liquid or gas of different density, by means of centrifugal forces within a vortex. Depending on the model of hydrocyclone being used, they can remove particles in the range of 5 to 15 µm. The liquid/liquid type of hydrocyclone is used for PW treatment. The company ProSep designs and engineers liquid/liquid hydrocyclone separation systems for primary free oil separation, secondary PW treatment, or in conjunction with its patented CTour™ Process.

The Epcon compact floatation unit (CFU) (from Cameron company) is a vertical separator vessel that is capable of separating three-phases, namely water/oil/gas by centrifugal force and gas-flotation. The Epcon unit removal efficiency for dispersed oil was only 50–70% (Knudsen et al. 2013).

Seureau et al. (2013) designed a three-phase cyclonic separator to remove solids and oil from offshore-PW. The system combines the functional characteristics of both desanding and de-oiling hydrocyclones.

A double cone air sparged hydrocyclone (DCASH) was designed for PW treatment. This system used air bubbles and centrifugal force to enhance removal efficiency of oil droplets (Liu et al. 2013).

Deng and colleagues (Deng et al. 2002) proposed crossflow oil–water separator for polymer flooding. The system consisted of different coalescence and separator sections. Sludge was removed from the bottom and oil and gas was separated from the top. Oil concentration in treated PW fell to less than 100 mg $L^{-1}$.

Van den Broek et al. (2013), compared oil removal efficiencies of different de-oiling systems. Their rankings with respect to performance of three physical separators were: centrifuges, hydrocyclones, and plate separators. These systems have a low removal efficiency and dissolved and hazardous components could not be removed.

#### 2.7.1.3. Flotation

Flotation process is used on conventional treatment trains. However microbubbles-enhanced flotation processes can be considered also suitable for PW polishing depending on its characteristics, as being able to remove small size droplets of oil, even as emulsion (Benyahia et al. 2006). Gas flotation can remove particles as small as 25 mm and can even remove contaminants up to 3 mm in size if coagulation is added as pre-treatment, but it cannot remove soluble oil constituents from water (Drewes et al. 2009).

Conventional Dissolved Air Flotation (DAF) process aims to remove suspended particles from water by bringing them to the surface, and subsequently separate them from the liquid phase. Air is dissolved at high pressure in a saturator, and microbubbles are formed by cavitation when water is released into the flotation tank at atmospheric pressure. The microbubbles become attached to the particles, increasing their buoyancy and allowing them to rise to the surface (Al-Shamrani et al. 2002). In many cases, to increase the efficiency of the DAF process, a previous coagulation–flocculation step is carried out (e.g. with ferric chloride) (Zouboulis and Avranas, 2000).

However PW usually contains natural and added surfactants, thus oils become emulsified and tend to stay in the aqueous phase, which complicates the treatment by flotation processes of this type of water. Another characteristic of PW is its high salinity that can negatively affect flotation since density, dynamic viscosity and surface tension are all higher in seawater than in freshwater and also due to the lower solubility of air in this kind of matrix (Haarhoff and Edzwald, 2013).

These technologies consists of four basic steps: (1) air bubble generation, (2) contact between gas bubble and oil droplets, (3) attachment of gas bubbles to oil droplets, and (4) rising up of air-oil combination (Goududey, 2013), given that this aggregate is significantly less dense than water itself. This results into the formation of foam on the surface of the water which is skimmed off as froth (Casaday, 2013), while the clarified water is collected at the bottom of the flotation zone.

Depending on the origin of the microbubbles, the technologies are labeled as dissolved air (or gas) flotation (DAF or DGF) and induced gas flotation (IGF). In dissolved gas flotation units, gas is introduced into the flotation chamber solubilized inside a recirculation stream, which is injected through diffusers. The pressure difference between the solubilized stream and the flotation chamber generates the quick desolubilization of the gas in the shape of tiny microbubbles (size ranges from 50 down to 1 μm or less). In the case of gas induced flotation, the bubbles are generated by the direct injection of the gas inside the flotation chamber and the sizes tend to be bigger than in DAF, which could slightly decrease the efficiency of the process, given that flotation is more effective as smaller the gas bubbles are compared to particle or droplet size.

Both flotation technologies can be used to remove O&G, natural organic matter, volatile organics and small particles from PW. They do not require the use of chemicals rather than coagulants, which may be added to enhance the removal of target contaminants. Disposal of the sludge generated in this process has to be also considered.

Younker and Walsh investigated, at bench scale, the chemical coagulation with ferric chloride and adsorption with organoclay as pretreatment for DAF for the removal of naphthalene and dispersed oil from PW (Younker and Walsh, 2014). A new process by using glass microspheres of low density instead of air microbubbles has also been studied in simulated PW (with the added advantage of saving energy required for operating a conventional DAF unit) (Jiménez et al. 2017). Microspheres were added into the system during the rapid mix stage (coagulation phase), and then incorporated into the floc matrix to drive the flotation process, replacing the use of microbubbles. With this process, high O&G removal percentages were achieved (up to 90% of elimination). The use of microspheres in the flotation without the injection of microbubbles was revealed as more effective for the removals of turbidity and O&G than with the combination of microspheres and microbubbles. Microspheres have been also used in other studies for the removal of algae (Ometto et al. 2014).

### 2.7.2. Biological treatment

Microbial biodegradation is effective in treating various types of dissolved molecules, including petroleum hydrocarbons. On activated sludge PW dissolved contaminants are consumed by the microorganisms within the bioreactor.

In biological oxidation, dissolved organics and ammonia are converted into water and $CO_2$ and nitrates/nitrites, respectively, by harmless bacteria, algae, fungi, and protozoa, but have no effect on TDS (Jackson and Myers, 2013).

Biodegradation and properties similar to bioflocculation by microorganisms similar to bio-flocculation is the dominant mechanism of hydrocarbon removal in biological treatment. Activated sludge adsorbs and occludes soluble and insoluble materials. Bacteria produce surface-active compounds such as surfactants (biosurfactants) and emulsifiers (bioemulsifiers) that enhance the local pseudo-solubility of hydrocarbons, improving mass transfer to biodegrading bacteria (Hommel, 1990). Biodegradation of simple oil components, e.g., normal alkanes is easier than of complex and large molecules.

According to Tellez and colleagues, the total petroleum hydrocarbon (TPH) removal efficiency could be maintained in a 98–99% at a solids retention time (SRT) of 20 days by activated sludge treatment unit (Tellez et al. 2002). Freire's group studied the treatment of different mixtures of PW and sewage in an SBR reactor with acclimated sewage sludge. In 45% and 35% (v/v) mixtures of PW and sewage, COD removal efficiencies varied from 30% to 50% (Freire et al. 2001).

Total organic carbon (TOC) removal efficiency in PW was studied with acclimated microorganisms in 180 mg $L^{-1}$ NaCl through three biological systems including SBR, trickling filters and chemostat reactors (Baldoni-Andrey et al. 2013). PW containing high concentration of salt (200 g $L^{-1}$ TDS) was biodegradable. It also was obtained that continuous operation with SBR could lead to a loss of biomass and TOC removal in the SBR is higher than in trickling filter or chemostat reactor.

Freire and colleagues found that salinity did not have significant effect on COD removal of mixed wastewater, and only the recalcitrant character of the organic compounds affected the biological treatment (Freire et al. 2001). Dfaz et al. (2000), showed that some bacterial consortia degrade crude oil of 80000 mg $L^{-}$

$^{1}$ but according to Tellez and colleagues when salinity increased to 100000 mg L$^{-1}$, the biodegradation rate fell dramatically (Tellez et al. 2002). Another study focused on the identification of the type of microorganisms, found out that slow growth rod-shaped microorganisms dominate the microbial community in the aeration tank of salty wastewater treatment plants (Ng et al. 2005). In addition to cell lysing, filamentous bacteria are reduced affecting the integrity of the flocs and raise the turbidity of effluents in biological treatment of salty wastewaters (Lefebvre and Moletta 2006). Biological treatment of effluent can be improved with membranes coupling (Kang et al. 2003).

Immobilization of microorganisms can increase treatment efficiency. Li et al. (2005) studied Bacillus sp. (M-12) immobilized on polyvinyl alcohol (PVA) to remove COD of oilfield PW. More than 90% efficiency of COD removal was achieved with initial COD of 2600 mg L$^{-1}$.

In another study, Zhao and colleagues investigated the use commercial microorganisms (B350M and B350 group) immobilized on poly-ammonium carriers in BAF (Biological Aerated Filter) reactors (Zhao et al. 2006). Results showed that with a hydraulic retention time of 4 hours and a volumetric load of 1.07 kg COD/(m$^{3}$ day$^{-1}$), they could remove TOC and oil content of PW up to 78% and 94%, respectively. Palmer and colleagues (Beyer et al. 1979) used rotating biological disks to treat oilfield-PW, removing BOD and O&G up to 94% and 74%, respectively.

BAF reactors can remove oil, suspended solids, ammonia, and nitrogen, chemical oxygen demand (COD), biological oxygen demand (BOD), iron, manganese, heavy metals, soluble organics, trace organics, and hydrogen sulfide. Since BAFs do not remove dissolved solids, high concentrations of salts can decrease the effectiveness of this technology due to salt toxicity effects.

Beyer and colleagues studied a two-stage pilot lagoon (Beyer et al. 1979). The objective of the primary tank was oxidizing the suspended oil and dissolved organic compounds, and the second one oxidizing dissolved ammonia compounds. In another study, a single-stage biological oxidation was used for removing ammonia and phenols from PW. Different types of wetland-like free water surface (FWS) and subsurface flow (SSF) pilot plants were designed, constructed, and tested to treat oilfield PW. SSF wetland removed more COD than FWS wetland (Jackson and Myers, 2013). Although the wetland is a cost-effective method, the temperature dependence of the system is detrimental. In addition, if these wetlands are not lined, groundwater contamination is not prevented.

When raw wastewater is concentrated, anaerobic degradation of pollutants would be a cost-effective alternative (Tchobanoglous et al. 2003). Gallagher studied biodegradation of organic acids in simulated PW under anaerobic conditions in the presence of naphthenic acids in a fixed-film bioreactor; however, naphthenic acids were not reduced under anaerobic conditions (Gallagher, 2001).

Reed beds can remove hydrocarbons and heavy metals. In a study, an 800-m$^2$-reed bed with *Phragmites australis* plant was used to treat 20 m$^3$ day$^{-1}$ of PW and it was obtained that more than 98% of hydrocarbons were eliminated (Gurden and Cramwinckel, 2013). In a similar pilot plant, 3000 m$^3$ day$^{-1}$ of PW was treated to reduce total hydrocarbon concentration by an average of 96%. Metal concentration decreased by 78% for Al, Ba, Cr, Cu, and Zn, up to 40% for Fe, Li, Mn, Pb, As, Cd, Co, Mo, Ni, Se, Tl, and V (Al Mahruki et al. 2013). Although this system is a cost-effective method, the effluent has to be refined and requires a lot of land.

### 2.7.3. Membrane treatment

Membrane processes are separation technologies that can be applied in the treatment of PW, and include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). They are able to treat PW and generate water with high standards to meet regulations. The driving force of these membrane processes is the pressure gradient (Li and Lee, 2009).

Membrane technologies have some advantages that make them popular for PW treatment processes, such as the high quality of permeate, smaller space needed, ease of operation, sludge reduction, little chemicals required, possibility for recycling of waste streams, possibility for having an automated plant, moderate capital costs, the ability to be combined easily with other separation processes, low energy consumption and continuous separation (Ashaghi et al. 2007). According to the above mentioned advantages, those membrane separation processes can, in some circumstances, be viable for the treatment of PW (Mondal and Wickramasinghe, 2008). But there are also some disadvantages for using membrane processes, which include concentration polarization, membrane fouling, low selectivity or low flux and low membrane lifetime.

Membranes can be classified based on the type of materials in polymeric and inorganic membranes. Depending on the pore size, from largest to smallest size, can be classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes respectively, to obtain from a lower to a higher water quality (RO>NF>UF>MF, in quality) respectively but requiring both a higher energy consumption (RO>NF>UF, MF), so if we want to find a commitment of quality and energetic saving we would remain with NF depending on what you need to remove.

**Polymeric membranes**

Some advantages of polymeric membranes, mainly made of polyacrylonitrile (PAN) and Polyvinylidenediflouride (PVDF), are their high ability for the removal of particles, emulsified and dispersed oil, the small size, low energy requirements and they are cheaper than ceramic membranes. But as disadvantages, they cannot separate volatile and low molecular weight compounds, the fouling problems due to oil, sulfide or bacteria, which may be required to be cleaned daily, inability to be used at temperatures above 50 ºC, and the possibility of having radioactive byproduct in the effluent, so it would be necessary some pre-treatment processes (Ashaghi et al. 2007).

These membranes are relatively cheap.

Their life cycle is approximately 7 years. Their efficiency for dead-end and cross-flow operations are 85% and 100%, respectively (Drewes et al. 2009).

**Inorganic membranes**

Inorganic membranes have better chemical and thermal stability than polymeric membranes.

Ceramic membranes have been investigated for PW treatment and have been found to be successful in reducing total suspended solids and suspended oil, with higher yields than polymeric devices. However, while operators can accept the relative high capital cost of ceramic membranes, the high cross flow recycle rates that has been shown to be required to manage fouling, contribute substantially to operating costs, which is one of the most important challenges for the adoption of ceramic membranes for PW treatment (Duraisamy et al. 2013).

**Microfiltration/ultrafiltration**

Microfiltration membranes (MF) have the largest pore size (0.1–3 mm) and they are typically used for the removal of suspended solids and turbidity reduction. In ultrafiltration membranes (UF) pore sizes are between 0.01 and 0.1 mm. They are employed in the removal of color, odor, viruses and colloidal organic matter (Drewes et al. 2009; Han et al. 2010).

UF is the most effective method for oil removal from PW in comparison with traditional separation methods (He and Jiang 2008), and it is more efficient than MF for the removal of hydrocarbons, suspended solids and dissolved constituents from oilfield PW (Bilstad and Espedal 1996). Both MF and UF operate at low transmembrane pressure (1–30 psi).

Zhong and colleagues developed a generation of ceramic MF membrane composed of zirconia ($ZrO_2$) to treat PW containing maximum oil concentrations of 200 mg $L^{-1}$, that was first treated by flocculation and then passed through an MF membrane at an applied pressure of 1 bar (Zhong et al. 2010). The concentration of oil was reduced to 8.7 mg $L^{-1}$ from 200 mg $L^{-1}$, and the treated PW satisfied the Chinese national discharge standards.

Using flocculation as a pre-treatment step for a MF membrane, less fouling occurs and the removal efficiency for O&G is increased to 95.6%. Also, by integrating UF with MF membranes removal of suspended foulants is achieved and the flux recovery increases to 61% (Ebrahimi et al. 2010).

Asatekin and Mayes modified UF membranes by incorporating an amphiphilic copolymer additive, polyacrylonitrile-graft-poly (ethylene oxide) (PAN-g-PEO), for PW treatment (Asatekin and Mayes, 2009). During their experiments, 96% of the dispersed and free oils were successfully removed, which is a higher efficiency compared to PAN-UF commercial membranes, for which the removal rate of COD is only 41-44%.

**Reverse osmosis and nanofiltration**

Reverse Osmosis membranes can remove contaminants as small as 0.0001 mm, but its major disadvantage is membrane fouling and scaling (Drewes et al. 2009; Wilf et al. 2007).

Early studies on using RO to treat PW failed due to insufficient process integration and poor treatment (Doran and Leong, 2000). Nicolaisen and Lien however reported a successful RO treatment of oilfield PW in Bakersfield, California (Nicolaisen and Lien 2003). The pilot system, which was operated for over 1700 hour during 6 months, produced 20 gpm of clean water. Bench-scale studies indicated that successful RO membrane processes for oilfield PW would require an appropriate pre-treatment in order to reduce fouling and not compromise the integrity of the membrane (Mondal and Wickramasinghe 2008; Xu and Drewes 2006).

Capital costs of RO membrane systems vary depending on the size of rejection required, materials of construction and site location, but it is also a main drawback of this technology. RO membrane systems generally have a life expectancy of 3–7 years (Drewes et al. 2009).

NF is a robust technology for water softening and metals removal and is designed to remove contaminants as small as 0.001 mm (Drewes et al. 2009). It is applicable for treating water containing TDS in the range of 500–25000 ppm. NF membranes have been employed for PW treatment on both bench and pilot scales (Nicolaisen and Lien, 2003; Xu and Drewes, 2006). Mondal and Wickramasinghe (Mondal and Wickramasinghe, 2008) studied the effectiveness of NF membranes for the treatment of oilfield PW. Results showed a minimal improvement with RO when compared with the effectiveness of brackish water NF treatment of the same feed water, indicating that these membranes, which require lower operating pressures, could be a cheaper and a suitable alternative for PW treatment.

Ebrahimi et al. tested $TiO_2/TiO_2$ (1000 Da) and $TiO_2/Al_2O_3$ (750 Da) ceramic NF membranes to treat PW containing a TOC content of 292 mg $L^{-1}$ and 2.6 mg $L^{-1}$ of oil as a post-treatment in a combined system of membranes (Ebrahimi et al. 2010). These tubular NF membranes completely removed the oil and reduced the TOC content by 49.8% at a low applied pressure (1 bar). During these experiments, the permeate flux average for the NF membranes was 123 L $m^{-2}$ $h^{-1}$ bar for 10 mg $L^{-1}$ of oil at 60 ºC.

It has to be taken into account, though, that in the membrane processes, dissolved organic matter is concentrated in the rejection stream.

### 2.7.4. Thermal Technologies

Thermal treatment technologies of water are employed specially in regions where the cost of energy is relatively cheap, most of the time related to oil extracting countries.

Multistage flash (MSF) distillation, vapour compression distillation (VCD) and multieffect distillation (MED) are the major thermal desalination technologies that could be applied for the treatment of PW, since it has a high salts concentration. Hybrid thermal desalination plants, such as MED–VCD, have been used to achieve higher efficiency (Hamed, 2004).

#### 2.7.4.1. Evaporation

Evaporation is generally used for treatment of water with higher concentrations of solids, particularly salts. It was proposed for treating saline wastewater containing oil components (Bertness and Lipoma, 1986). Vertical tube, falling film, and vapor compression evaporation have advantages for PW treatment because they eliminate physical and chemical treatments, costs of waste and life cycle are lowered, require less maintenance materials and maintenance labor, and reduce the amount of PW de-oiling equipment required.

GE Water & Process Technologies (GE) is the pioneer and an industry leader in PW evaporation and crystallization systems, having developed its patented high pH evaporation technology.

#### 2.7.4.2. Freeze-thaw/evaporation

This technology uses the principle of solubility dependence of temperature. When the solution cools below the freezing point of the solvent but not below the depressed freezing point of the solution, there are obtained relatively pure crystals of solvent and not frozen concentrated solutions. If this process is coupled with conventional evaporation, larger volumes of clean water could be obtained. The process is capable of removing 90% of total recoverable petroleum hydrocarbons, total suspended solids, total dissolved solids, volatile organic compounds, semi-volatile organic compounds and heavy metals present in PW. But it has several limitations like the requirements of sub-zero ambient temperatures and large land surface (Boysen and Boysen, 2008).

#### 2.7.4.3. Multistage flash

Multistage flash (MSF) distillation process is a mature and robust technology for brackish and sea water desalination. The evaporation of water is produced by a decrease in the pressure instead of heating (Watson et al. 2003). The percentage of recovery of water is ca. 20%. The remaining concentration of TDS (2-10 mg $L^{-1}$) often makes necessary to include a post-treatment (Drewes et al. 2009). A drawback that has also to be taken into account is the formation of scale on surfaces, making necessary the use of acid solutions or scale inhibitors. Energy requirements ranges from 3.35 to 4.70 kWh $bbl^{-1}$ (Darwish et al. 2003), what makes it a relatively cost-effective process. Nevertheless, the market has been limited due to the availability of membrane technologies.

#### 2.7.4.4. Multieffect distillation

Multieffect distillation (MED) process can also be used for seawater desalination and PW treatment. It is based on the application of multiple stages or effects to evaporate water, minimizing the energy consumption by increasing the efficiency of evaporation.

Depending on the design of the evaporator, the recovery of water that can be achieved ranges from 20 to 67% (Watson et al. 2003). Nevertheless, and as in the previous case, the scale formation in old designs has prevented a more widespread use. This problem has tried to be overcome by the use of falling film evaporators (Hamed 2004).

MED is good for PW treatment with high TDS content (Drewes et al. 2009; Hamed, 2004). To avoid scaling, scale inhibitors and acids may be required and pH control is essential to prevent corrosion. Energy consumption in MED processes ranges from 1.3 to 1.9 kWh $bbl^{-1}$ (Darwish et al. 2003).

#### 2.7.4.5. Vapour compression distillation (VCD)

Vapour generated in the evaporation chamber is compressed thermally or mechanically, which raises the temperature and pressure of the vapour.

The heat of condensation is returned to the evaporator and utilized as a heat source. VCD is a reliable and efficient desalination process and can operate at temperatures below 70 ºC, which reduces scale formation problems (Khawaji et al. 2008). Energy consumption of a VCD plant is significantly lower than that of MED and MSF. The overall cost of operation depends on various factors, including water origin, zero liquid discharge target, size of the plant, materials and site location. Cogeneration of low-pressure steam can significantly reduce the overall cost (Drewes et al. 2009). The VCD process is used to treat PW and RO concentrate (i.e., brine concentrator application) in a near-zero liquid discharge (ZLD) application. To achieve this ZLD, the VCD system can work as a crystallizer (Arowoshola et al. 2011).

#### 2.7.4.6. Hybrid Multieffect distillation–vapour compression

Hybrid MED–VCD has been recently used to treat PW. This system increases the production and energy efficiency. This new technology would replace the older MSF plants (Drewes et al. 2009).

GE has developed PW evaporators that use mechanical vapour compression. These evaporators have more advantages than other conventional PW treatment methods, such as the reduction in chemical doses, overall cost, storage, fouling severity, handling, softer sludge and other waste stream.

More than 16 PW evaporators have been installed in Canada, and more are expected to be installed in other regions of the world (Heins and McNeill, 2007). The life expectancy of PW evaporators is 30 years (Drewes et al. 2009).

Sidem / Entropie is the world leader in sea water desalination through low temperature distillation processes such as MED and MED–VCD. The high purity of treated PW (<2 mg $L^{-1}$ TDS) allows for direct use in industrial applications, with or without minor polishing. These industrial applications include the production of boiler feed water, process water and water for closed loop cooling systems for many industries.

### 2.7.5. Chemical Treatment

#### 2.7.5.1. Chemical precipitation

Different coagulants like modified hot lime, FMA (a mixed metal polymer), Spillsorb, calcite and ferric ions have been used as coagulant to treat PW (Zouboulis and Avranas, 2000).

In the modified hot lime process, PW containing 2000 mg $L^{-1}$ hardness, 500 mg $L^{-1}$ sulfides, 10000 mg $L^{-1}$ TDS, and 200 mg $L^{-1}$ oil could be successfully converted to feed-water quality for a steam generator. In this process, alkali consumption and sludge production could be reduced by 50% in comparison with conventional hot lime (Garbutt, 2013).

FMA is an inorganic mixed metal (Fe, Mg, and Al) polynuclear polymer. This chemical had good de-oiling, coagulation, and scale inhibition properties, particularly in PW with high SS levels. SS and oil were removed to levels between 92% and 97%, respectively (Zhou et al. 2000). Houcine used spillsorb, calcite, and lime to remove heavy metals from PW. Results showed that lime removal efficiency is greater (>95%) than with others and that it was an economical chemical (Houcine, 2013).

In a study on treatment of oil and gas fields PW, an oxidant, ferric ions, and flocculants were used to remove hydrocarbons, arsenic, and mercury (Frankiewicz and Gerlach, 2000).

Despite these results, coagulation and flocculation can be used to remove suspended and colloidal particles, but seemed not to be effective for removing dissolved constituents. Furthermore, the increased concentration of metals, potentially toxic, in the formed sludge can also be another drawback.

#### 2.7.5.2. Electrochemical process

An electrochemical process is a chemical reaction that either causes or is caused by the movement of electrical current. These processes are a type of oxidation-reduction reaction in which one atom or molecule loses an electron to another atom or molecule. Electrochemistry is a relatively cheap green technology, compared with other current treatments applied to PW. It does not generate secondary waste nor involve the use of additional chemicals, and offers improved beneficial uses of PW.

Li et al. (2006) showed that the COD removal efficiencies by photoelectrocatalysis of synthetic PW are much higher than removal by photocatalysis and electrochemical oxidation. Li et al. (2007) reported that photoelectrocatalysis exhibited a superior capability to reduce genotoxicity than photocatalysis.

Photoelectrolysis of PW generates hydrogen, which can be utilized in a fuel cell to produce clean water, which upon further treatment can be converted into drinking water.

The application of fuel cell technology to treat PW in the future will be possible if there are cost reductions, efficiency improvement and increased life span (Kirubakaran et al. 2009).

An electrochemical catalytic plant was applied at pilot scale by Ma and Wang to eliminate organic substances in oil field PW, using double anodes with active metal and graphite, iron as the cathode and a noble metal catalyst with a large surface. They achieved a reduction of 90% in COD and BOC in 6 min, suspended solids by 99%, $Ca^{2+}$ content by 22%, corrosion rate by 98% and bacteria (sulfate reducing bacteria and iron bacteria) by 99% in 3 min under 15V/120A (Ma and Wang 2006).

Electrodeposition is a consolidated technology that is extensively used in various fields of electrochemistry, where positively charged metal ions are deposited on the surface of the object connected to the negatively charged electrode (cathode) by the passage of electric current to become metal. This process can be used for recovery of metals from PW. For example, it has been used for Cu recovery from PW (Gooch, 1997; Myung et al. 2000; Wicks, 2007).

An option for PW treatment could be an electrochemical process unit integrating some of these chemical processes to achieve production of clean water, storage of energy and recovery of valuable metals from oilfield PW (Igunnu and Chen, 2012).

**Electrodialysis (ED):**

Most salts contained in PW that are dissolved in water are ionic. These ions are attracted to electrodes with an opposite electric charge. In ED, arranged alternately membranes that allow either cations or anions (but not both) to pass are placed between a pair of electrodes. A spacer sheet that permits feed water to flow along the face of the membrane is placed between each pair of membranes. Positively charged ions ($Na^+$ etc) migrate to cathode and negatively charged ions ($Cl^-$ etc) migrate to anode. During migration the charged ions are rejected by similarly charged ion exchange membranes. The basic electrodialysis unit is formed by several hundred cell pairs bound together with electrodes on the outside. The raw feed water must be pre-treated to remove materials that could harm the membranes or clog the narrow channels in the cells. Feed water passes in parallel paths through all of the cells, providing a continuous flow of desalted water and brine to emerge from the membrane stack. The feed water is circulated through the stack with a low-pressure pump that allows to overcome the resistance of the water as it passes through the narrow passages.

ED was applied to the PW from a conventional well in Wind River Basin of Wyoming that contained $H_2S$, oil, acid, BTEX, dissolved solids etc. About 93% of total TDS (8300 to 10000 mg $L^{-1}$) is accounted for as sodium, chloride, calcium and bicarbonates. O&G content was about 65 mg $L^{-1}$ and BOD value was more than 330 mg $L^{-1}$ (contributed by acetates and volatile acids). The treatment trailer consists of the following units:

1. Flotation unit to remove oil.
2. Two fluidized bed biological reactors to remove dissolved organics. The first one is anaerobic and removes nitrates and large amount of organics. The second one is aerobic reactor to ensure the oxidation of dissolved organics.

3. ED unit for desalting/demineralization. ED provided a cost-effective demineralization in this case. The feed water had approximately 9000 mg $L^{-1}$ TDS and the ED removed approximately 89% of TDS from the PW (Hayes and Arthur 2004).

### 2.7.5.3. Room temperature ionic liquids

McFarlane and colleagues studied nine different hydrophobic ionic liquids (liquids that contains only ions) in PW remediation by separating organics from PW (McFarlane et al. 2005). Results showed that certain hydrophobic ionic liquids are effective in the selective removal of particular contaminants in PW, and yet may be almost ineffective to other contaminants such as paraffinic organic compounds. However, practical application of the ionic liquids tested for removal of selected water soluble organics from the aqueous waste streams seems to be limited by the small, though significant, solubility of the ionic liquids in the aqueous phase and by difficulty in solvent regeneration.

### 2.7.5.4. Demulsifiers

Some surfactants used as production chemicals are responsible for the stabilization of oil-water emulsions. They reduce the oil-water interfacial tension, and zeta potential on the surfaces of the oil droplets (Deng et al. 2005). The ‘skin’ surrounding the tiny droplets in the oil–water emulsion prevents the water droplets from uniting and the emulsion remains stable. Demulsifiers are surface-active agents that would disrupt the effects of surfactants. They can be used to separate emulsions present in PW. Almarouf and colleagues developed an effective oil–water separator for the treatment of stable emulsions in PW combining effects of chemical demulsification and oil droplet coalescence (Almarouf et al. 2015).

Solids such as iron sulfides, silts, clay, drilling mud, paraffin, etc. complicate the demulsification process (Holloway, 2013).

#### 2.7.5.5. Ion Exchange

The ion exchange process can remove arsenic, heavy metals, nitrates, radium, salts, uranium, and other elements from the PW. The resins immersed in the water are either naturally occurring inorganic zeolites or synthetically produced organic resins. Ion exchange is a reversible chemical reaction where cations or anions present in the water are replaced by similarly charged ions present within the resin (All Consulting, 2003). Ion exchange has been applied in several industrial applications, including the treatment of Coal Bed Methane PW. Resins are especially useful in the elimination of monovalent and divalent ions and metals present in PW (Clifford, 1999). According to Nadav, ion exchange has the capacity to remove boron from RO permeate of PW (Nadav, 1999). Ion exchange technology has a lifetime of approximately 8 years and requires pretreatment for solid removal, as well as the use of chemicals for resin regeneration and disinfection. The cost of operation represents more than 70% of the total costs of this technology (Drewes et al. 2009).

#### 2.7.5.6. Macro-porous polymer extraction technology

Macro-porous polymer extraction (MPPE) is deemed as one of the best available technologies and best environmental practices for PW management (Akzo Nobel MPP, 2004). It consists on a liquid–liquid that uses macro-porous polymer particles to immobilize the extraction phase. Polymers were initially designed for absorbing oil from water but later applied to PW treatment in 1991 (Meijer and Madin, 2010).

Dispersed and dissolved hydrocarbons are removed by the immobilized extraction liquid. The processes work generally with two columns working alternating extraction and regeneration (Akzo Nobel MPP 2004).

The first commercial MPPE unit offshore was installed in the North Sea. MPPE achieved 99% removal of BTEX, and a removal efficiency of 95–99% for aliphatic compounds below C20 and total aliphatic removal efficiency of 91–95% (Pars and Meijer 2013).

This technology can reduce the toxic content of PW. Pretreatment through flotation processes such hydrocyclones, is required before the PW from oilfields passes through the MPPE unit. Nevertheless in gas/condensate PW streams pre-treatment is not necessary and MPPE can eliminate aliphatics, as well as BTEX and PAHs (Meijer et al. 2004).

Statoil carried out a comparison between different treatments technologies and found that the MPPE technology had the highest Environmental Impact Factor reduction of approximately 84% (Grini et al. 2013). The main drawback of this technology it is relatively high cost per unit.

### 2.7.5.7. Advanced Oxidation Processes (AOPs)

They include a number of different processes such as $O_3$+ $H_2O_2$, UV+$H_2O_2$, UV+$O_3$, $O_3$+UV+$TiO_2$, UV+$O_3$+$H_2O$, Fenton’s reagent and Photo-Fenton’s. In addition, there are non-conventional AOPs such as wet air oxidation and humid oxidation with peroxide. All AOPs share a common objective: to generate a powerful oxidizing hydroxyl radical that has a tremendous oxidation power, greater than ozone, hydrogen peroxide, chlorine or oxygen, reacting rapidly and non-selectively with nearly all electron-rich organic compounds, completely mineralizing dissolved organic pollutants. In the contact time provided is not sufficient to achieve complete mineralization, the process will still crack down large molecular weight organic molecules to smaller organic molecules which can be easily further removed by, for instance, a biological process or other processes such as activated carbon. Moreover, AOPs have been successfully used to reduce the concentrations of toxic organic compounds that inhibit biological treatment processes (Dores et al. 2012).

Chemical oxidation is an established and reliable technology for the removal of color, odor, COD, BOD, organics and some inorganic compounds from PW.

Shokrollahzadeh and colleagues carried out chemical oxidation of hydrocarbons in PW using ozone, hydrogen peroxide, and calcium hypochlorite to decrease the COD of PW but low eliminations were obtained. Maximum COD removal efficiency was achieved for calcium hypochlorite oxidant (Shokrollahzadeh et al. 2012).

In next section, 2.7.6, AOPs are explained in more detail.

### 2.7.6. Advanced Oxidation Processes applied to oil and gas water

As it has been shown in the previous section, these technologies are characterized by the generation of hydroxyl radicals, which are highly reactive and non-selective substances used to degrade toxic or recalcitrant organic compounds (Pera-Titus et al. 2004).

The hydroxyl radical has a high oxidation potential ($E^0 = 2.8$ V) and is able to react with practically all classes of organic compounds, resulting in complete mineralization of these compounds, that is, the formation of carbon dioxide, water and inorganic salts, or their conversion into less aggressive products (Andreozzi et al. 1999; Bolton et al. 1996; Pignatello 1992).

AOPs show the following advantages: On one hand they can achieve complete mineralization of recalcitrant compounds, in opposition to conventional water treatment methods such as flotation, filtration and adsorption with active coal, which are non-destructive physical separation processes that transfer pollutants to other phases, thereby generating concentrated deposits, as reported by Crittenden and coworkers (Crittenden et al. 1997). Other advantage is that time required for treatment can be very short depending on water characteristics (i.e. minutes). Specifically, Catalytic Wet Air Oxidation, presents significant advantages over other technologies to remove organic compounds. It can treat high loaded inlet (>50000 mg $L^{-1}$ COD) with different organic compounds obtaining few mg $L^{-1}$ outlet (conversions >99%), only air is required as a reactant and no by-products are obtained, it operates at moderate pressure and temperature conditions, and the catalyst lifetime is >2 years.

The AOPs can be classified as homogeneous and heterogeneous according to Huang and coworkers (Huang et al. 1993), while Domènech and coworkers

(Domènech et al. 2001) classified it according if light is used in the process or not. Table 2.6 shows a classification of AOP according to these authors.

Table 2.6. Classification of AOPs

| **Non-photochemical** | **Photochemical** |
|---|---|
| **Homogeneous processes** | |
| • Ozonation in alkaline media ($O_3/HO^-$)<br>• Ozonation with hydrogen peroxide ($O_3/H_2O_2$)<br>• Fenton ($Fe^{2+}$ or $Fe^{3+}$/ $H_2O_2$)<br>• Electro-oxidation<br>• Electrohydraulic discharge - ultrasound<br>• Wet air oxidation (WAO)<br>• Supercritical water oxidation (SCWO) | • Photolysis of water in vacuum ultraviolet<br>(VUV)<br>• UV/<br>• UV/ $O_3$<br>• UV/ $O_3$/ $H_2O_2$<br>• Photo-Fenton ($Fe^{2+}$ or $Fe^{3+}$/ $H_2O_2$/UV) |
| **Heterogeneous processes** | |
| • Catalytic wet air oxidation (CWAO) | Heterogeneous photocatalysis: ZnO/UV, $SnO_2$/UV, $TiO_2$/UV, $TiO_2$/$H_2O_2$/ UV |

Generally, the application of these processes is recommended only to wastewaters with a content of COD below 5 g $L^{-1}$, as a higher COD will need a high consumption of reagents (Andreozzi et al. 1999).

For the treatment of PW with high organic load, pretreatment operations, like dilution, coagulation and flocculation, to achieve a reduction of the initial load (Rivas et al. 2004), optimize reagents and energy consumption and minimize reaction time. When a later biologic treatment is not applied, AOPs can be an alternative for PW.

### 2.7.6.1. $H_2O_2$ and $H_2O_2$/UV

Hydrogen peroxide ($H_2O_2$) is a strong oxidant. The use of $H_2O_2$ becomes more effective if used in combination with other reagents or energy capable of dissociating it for generating hydroxyl radicals, which will act as oxidizing agents. With UV irradiation with wavelengths shorter than 300 nm, $H_2O_2$ can decompose and generate radicals.

Higher concentrations of $H_2O_2$ increase the degradation rate of contaminants up to a maximum value, after which it begins to decline when they reach very high $H_2O_2$ levels. López and coworkers attribute this decrease in the $H_2O_2$/UV process yield to hydroxyl radicals reacting with excess $H_2O_2$, instead of reacting with the organic substrates (Lopez et al. 2000).

The advantages of using the $H_2O_2$/UV process are the solubility in water of the reagent ($H_2O_2$), there is no mass transfer limitation, it is an effective source of $HO^•$, and there is no need for a separation process after treatment (Litter 2005).

Stepnowski and coworkers (2002) carried out the degradation of oil refinery wastewater after a pretreatment of flotation and coagulation, using $H_2O_2$ in the presence and in the absence of UV radiation, and was compared to PW (Stepnowski et al. 2002). They analyzed TPH, dichloromethane (DCM), 1,2-dichloroethane (DCE) and methyl tert-butyl ether (MTBE). In total 83% DCM was removed with 11.76 nM of $H_2O_2$ using UV radiation and the degradation of the TPH was slow, since it was removed a 69% of the total initial concentration in 8 days of the experiment. The MTBE degradation was similar to that of DCE and after 24 h there was total removal.

Philippopoulos and Poulopoulos (2003) studied the application of the $H_2O_2$/UV process for the polishing of oily wastewater from a lubricant-producing unit. Using a high concentration of $H_2O_2$, most of the compounds identified in the wastewater were eliminated. Nevertheless, the initial COD of the wastewater was reduced a 40% (resulting in 9000 mg $L^{-1}$). The cause of this could be the formation of organic acids, generated from the decomposition of organic compounds present in the wastewater, which are more recalcitrant to photo-degradation with $H_2O_2$.

#### 2.7.6.2. Fenton and Photo-Fenton processes

The classic Fenton reaction interpreted by Haber and Weiss (1934) consists of an aqueous combination of hydrogen peroxide ($H_2O_2$) and ferrous ions ($Fe^{2+}$), in acid medium, leading to the decomposition of $H_2O_2$ into a hydroxyl ion and a hydroxyl radical, and the oxidation of $Fe^{2+}$ to $Fe^{3+}$, as represented by Equation 2.1 (Bossmann et al. 1998).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + HO^{-}$$

(2.1)

As shown by Walling and Weill (1974) (Walling and Weilt 1974), the $Fe^{3+}$ formed in Equation 2.1 can react with the $H_2O_2$ present in the medium and be reduced to $Fe^{2+}$ again, forming the hydroperoxyl radical, according to Equation 2.2. This reaction, known as Fenton-like (Neyens and Baeyens 2003), occurs more slowly than reaction 2.1 (Pignatello 1992). The $Fe^{3+}$ ions also react with the $HO_2^{\bullet}$ and are reduced to $Fe^{+2}$, as shown by Equation 2.3

$$Fe^{3+} + H_2O_2 \rightarrow [Fe \ldots OOH]^{2+} + H^{+} \rightarrow Fe^{2+} + HO_2^{\cdot}$$

(2.2)

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^{+}$$

(2.3)

It is important the relation between ferrous and hydrogen peroxide ions. When higher concentration of $Fe^{2+}$ ions in relation to $H_2O_2$ are used, the hydroxyl radicals generated in Equation 2.1 would react with excess $Fe^{2+}$, according to

Equation 2.4, decreasing the attack of hydroxyl radicals on organic substrates (Neyens and Baeyens, 2003).

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^{-}$$

(2.4)

When all the $Fe^{2+}$ present in the medium is oxidized to $Fe^{3+}$, the generation of hydroxyl radicals will be interrupted and, consequently, the degradation of organic compounds, due to $Fe^{3+}$ ions can form stable organic compounds with the degradation products (mainly the organic acids) present in the medium, impairing the regeneration of $Fe^{2+}$ (Balanosky 2000; Maciel et al. 2004).

The ideal pH in Fenton’s reaction is ca. 3.

According to Pignatello (1992) (Pignatello 1992), UV irradiation strongly accelerates the degradation rate of organic pollutants from Fenton’s. Under these conditions, the photolysis of $Fe^{3+}$ complexes enables regeneration of $Fe^{2+}$ and the occurrence of Fenton’s reaction, if $H_2O_2$ is available, as it is shown by Equation 2.5.

$$Fe(OH)^{2+} + \mathrm{h\upsilon} \rightarrow Fe^{2+} + HO^{\cdot}$$

(2.5)

The ferrous ions regenerated can react again with the $H_2O_2$ in solution to generate more hydroxyl radicals, creating a photocatalytic cycle in the $Fe^{2+}/Fe^{3+}$ system.

According to this, the use of radiation reduces significantly the concentration of ferrous ions required, compared with the dark Fenton reaction (Bhatkhande et al. 2004).

As disadvantages of photo-Fenton process could be the requirement of a low pH (normally below 4) and having to remove the iron sludge after the reaction. Furthermore, some substances $Cl^{-}$, $SO_4^{2-}$, $H_2PO_4^{-}$ /$HPO_4^{2-}$ which can be present in PW may interfere in the reaction mechanism inhibiting the degradation process (De Laat et al. 2004; Nadtochenko and Kiwi, 1998).

Safarzadeh-Amiri and coworkers (1997) investigated the UV-visible photolysis of ferrioxalate in the presence of $H_2O_2$ to degrade BTEX, 1,4-dioxane, methyl tert-butyl ether, formaldehyde and formic acid, some of them present in PW (Safarzadeh-Amiri et al. 1997). The results indicated that the UV-visible/ferrioxalate/$H_2O_2$ process has a much energy efficiency than the UV-visible/Fe(II)/$H_2O_2$ process or the UV/$H_2O_2$ process, resulting in lower treatment costs.

The photo-Fenton process was also used by Moraes and coworkers (2004) for the degradation of the hydrocarbons containing in synthetic PW simulated with gasoline in saline wastewater (Moraes et al. 2004). It was obtained that, in the presence of salt (NaCl), total pollutant degradation did not occur, probably due to $Fe^{3+}$ ions that reacted with $Cl^-$ ions, forming $FeCl^{2+}$ complexes, which, in the presence of UV radiation, may give rise to $Cl_2^{\bullet-}$ radicals (with lower oxidation potential than the $HO^\bullet$ radicals), thus reducing the efficacy of the process.

Mota and coworkers (2005) studied the photo-Fenton process in degrading phenol, present in PW, using black light fluorescent lamps as an UV-A radiation source (Mota et al. 2008). Comparing Fenton and photo-Fenton processes, degradation was twice as high with the photo-Fenton reaction. The elimination of phenol increased with the intensity of the radiation source, thus increasing the regeneration of $Fe^{2+}$ ion with the consequent generation of hydroxyl radicals.

Tiburtius and coworkers (2005) investigated the degradation of a solution containing benzene, toluene and xylenes (BTX) and water contaminated with gasoline (containing 25% ethanol) applying Fenton and photo-Fenton processes (Tiburtius et al. 2005). Total hydrocarbons present in gasoline-contaminated water were degraded in a 75%, the BTX were rapidly degraded, and intermediate phenolic compounds formed in the initial phase of the reaction were completely degraded after 30 min.

Galvão and coworkers (2006) studied the photo-Fenton process in water containing diesel oil to optimize the dose of reagents. With $Fe^{2+}$ ion concentrations of 0.1 mM (an amount below the maximum discharge limit permitted by the Brazilian law, 0.27 mM), there was 99% degradation of the total organic carbon (TOC) (Galvão et al. 2006).

Coelho and coworkers (2006) investigated the performance of different AOPS for the degradation of acid water effluents from oil refineries composed by emulsified oil and slowly biodegradable compounds and toxic substances (such as phenols, sulphides, mercaptanes, ammonias, cyanides) (Coelho et al., 2006). All processes, except Fenton and photo-Fenton, did not lead to satisfactory results. With Fenton process only 27% of initial dissolved organic carbon – DOC) was removed, followed by the photo-Fenton process by using UV radiation. The combination of these two techniques, applied continuously, reduced the initial DOC by 94%. The BTEX pollutants present were removed too to non- detectable levels. The disadvantages were the high concentrations of reagents used, therefore optimization is necessary.

Mater and coworkers (2007) evaluated the efficiency of Fenton's reagent in the mineralization of organic compounds present in water contaminated by crude petroleum. Up to 75% TOC removal efficiency was achieved when high $H_2O_2$ (20%) and low $Fe^{2+}$ (1mM) concentrations were used. The simple measurement of $H_2O_2$ concentration was effective to evaluate the Fenton's reaction efficiency (Mater et al. 2007).

#### 2.7.6.3. Ozone ($O_3$)

A disadvantage of the use of $O_3$ in the wastewater treatment is the cost; $O_3$ is an expensive oxidant since requires energy to generate it (Pera-Titus et al. 2004; Renou et al. 2008). Also, the efficiency of $O_3$ depends on the gas-liquid mass transfer, which is hindered by the low solubility of $O_3$ in aqueous solution (Gogate and Pandit, 2004). Another drawback in the case of PW could be the foams generated by the bubbling of the gas inside the effluent, which contains natural and artificial surfactants.

Both direct and indirect oxidation reactions will take place; $O_3$ can react slowly and directly with an organic substrate due its high reduction potential (2.07 V) (Augugliaro et al. 2006), but it is characterized as an AOP when it decomposes to generate hydroxyl radicals (indirect reactions) (Equation 2.6).

$$2O_3 + 2H_2O \rightarrow 2HO^{\cdot} + O_2 + 2HO_2^{\cdot}$$

(2.6)

The combination of ozone with $H_2O_2$, UV radiation or ultrasound improves the efficacy in degrading organic compounds.

Morrow et al. proposed ozonolysis to degrade water soluble organic in PW, introducing into the PW a sufficient amount of gaseous ozone by use of a means for maximizing the collision frequency of ozone gas and the PW (Morrow et al. 1999). The temperature of the PW is between from about 80º to about 180ºF. The process renders a water effluent with markedly reduced O&G content. The water effluent could be used on land as a drinking or irrigation water supply source and may be safely discharged into navigable waters. Klasson et al. (2002) studied several types of methodologies for treatment of soluble organics in synthetic and actual PW using sonochemical oxidation and ozone. Sonochemical oxidation could destroy some compounds such as BTEX, the combination of ozone and hydrogen peroxide over a pH range of 3-11 did not improve the oxidation of organics to $CO_2$ but UV light, when used in combination with ozone improved the destruction of BTEX.

### 2.7.6.4. Heterogeneous Photocatalysis

Heterogeneous photocatalysis is a process in which two active phases solid and liquid are present. The solid phase is a catalyst, usually a semiconductor (CdS, $TiO_2$, ZnO, $WO_3$, etc.). When the semiconductor is illuminated with light (hʋ) of greater energy than that of the band gap, an electron is promoted from the valence band (VB) to the conduction band (CB) leaving a positive hole in the VB and an electron in the CB. The hole itself has great potential to oxidize organic species directly when absorbed to the surface of the catalyst, or indirectly via the generation of hydroxyl and superoxide radicals, promoted by the interaction of holes with water and oxygen in aqueous solution (Serpone, 1997). $TiO_2$ absorbs radiation in the near UV light ($\lambda<387$ nm), (which enables the use of sunlight), capable of forming $e^- - h^+$ pairs that can recombine (Goslich et al. 1997).

The dissolved oxygen or the hydrogen peroxide present or added to the medium, can act as an electron acceptors, generating the superoxide radical and triggering a series of reactions that may lead to the formation of hydroxyl radicals.

Bessa and coworkers (2001), studied the treatment of oilfield PW via a photocatalytic process using $TiO_2$/UV, with the addition of $H_2O_2$. It was found a considerable reduction in the concentration of targeted components. The use of $H_2O_2$ in the photocatalytic process was dispensable, undesirable indeed, due to the corrosive effects of this substance to the catalysts ($TiO_2$) (Bessa et al. 2001).

Hu and coworkers (2008) studied the degradation of MTBE (a gasoline additive) and they achieve higher degradation rate with Ag/$TiO_2$/UV than that obtained with $TiO_2$/UV. The MTBE removal obtained was around 80% (Hu et al. 2008).

Saien and Nejati degraded aliphatic and aromatic organic pollutants in refinery wastewater using the $TiO_2$/UV process (Saien and Nejati, 2007). The $TiO_2$ added wastewater samples, while saturating with air, were irradiated with an immersed mercury UV lamp (400 W, 200-550 nm). Optimal catalyst concentration, fluid pH and temperature were obtained at amounts of near 100 mg $L^{-1}$, 3 and 318K, respectively. A maximum reduction in chemical oxygen demand of more than 90% was achieved after about 4 h irradiation and hence, 73% after about only 90 min. Increasing the $TiO_2$ concentration decreases the rate of degradation, probably due to the increase in the turbidity of the solution, with the consequent reduction of light transmission.

### 2.7.6.5. Electrochemical Oxidation

In these processes, the hydroxyl radicals can be produced by two pathways: anodic oxidation (direct form) and mediated electrooxidation (indirect form). The direct electrooxidation takes place directly at the anode (e.g. Pt, $PbO_2$, doped with $SnO_2$ etc.). In indirect electrochemical oxidation, strong oxidants are produced on the anode and then chemical oxidation takes place, such as the generation of hydroxyl radicals via Fenton reagent. Chemical species, such as $H_2O_2$, are continuously formed in the cathode by the reduction of two electrons of dissolved oxygen. (Brillas and Casado, 2002).

The $H_2O_2$ generated can act as a reagent for Fenton's system by adding iron, generating hydroxyl radicals. This Fenton process, by which the $H_2O_2$ is electrochemically generated, is called the electro-Fenton process (Brillas and Casado, 2002).

The introduction of ultraviolet radiation help reducing $Fe^{3+}$ to $Fe^{2+}$ increasing the oxidation power of the system (Wang 2008).

Yavuz and Koparal investigated the degradation of 192.2 mg $L^{-1}$ of phenol with 590 mg $L^{-1}$ of COD, present in a refinery wastewater via electrochemical oxidation, using a titanium electrode coated with titanium oxide and ruthenium oxide. They obtained a 94.5% removal of phenol and 70.1% of COD (Yavuz and Koparal, 2006).

Santos and coworkers employed dimensionally stable anodes in the electroremediation of PW and refining wastewater. The removal of COD was influenced by temperature, increases in which mainly favored the electrochemical process. At a current density of 100 mA $cm^{-2}$, the most efficient COD reduction was achieved at 50ºC reaching 40% after 12 h, and 57% after 70 h, removing up to 57% of initial COD from the wastewater. This reduction could be attributed to electrooxidation/electrodegradation and also to electroflotation of oil droplets in suspension that aggregate on the surface owing to the gas formed in the cathode ($H_2$) and in the anode ($O_2$ and $Cl_2$) (Santos et al. 2006).

#### 2.7.6.6. Wet Air Oxidation and Supercritical Water Oxidation

Wet air oxidation permits the oxidation of pollutants under high pressure conditions (10-220 bar) and high temperatures (150-370°C), leading to the formation of hydroxyl radicals through dissolved oxygen reactions (Rivas et al., 1998). The efficiency of this technique can be improved with the presence of homogeneous catalysts (such as $Cu^{2+}$ salts) and heterogeneous catalysts ($MnO_2$, CuO, $Fe_2O_3$ etc.) (Domènech et al. 2001), which is known as catalytic wet air oxidation (CWAO).

Supercritical water oxidation (SCWO) consists of the homogeneous oxidation above the critical point of water (374ºC and 22.12 MPa). Supercritical water is a very good solvent for organic substances and is completely miscible with gases including oxygen and carbon dioxide. Thus, oxidation of the organics in supercritical water occurs in a homogeneous single phase and proceeds rapidly without interfacial mass transfer limitations. This technique obtains rapid results, but has high operational costs due to its high energy demand.

Sun and coworkers studied a microwave (MW)-assisted catalytic wet air oxidation (CWAO) process under low temperature (150ºC) and oxygen was supplied into reactive system with 0.8MPa pressure to treat heavily contaminated petroleum wastewater from oil refining industry. The MW-CWAO experiments were carried out in a reconstructive MW autoclave, using GAC (5 wt.%) as catalyst. The results demonstrated that more than 90% of COD removal was obtained and the biodegradability (measured as $BOD_5$/COD ratio) was increased from 0.04 to 0.47 within 30 min, indicating a significant enhancement of the biodegradability of the solution, helping in a further biotreatment of petroleum wastewater (Sun et al. 2008).

### 2.7.7. Combined Systems

The majority of the treatments described above are well for certain groups of components but they cannot act or even turn harmed by others, needing therefore different types of treatments, being the most effective the combination of several processes for a major efficiency in the treatment of the PW. For example, if only membranes are used as treatment of PW, severe fouling will be place because this wastewater contains oils, solids and bacteria. Thus, some pretreatments are required before the use of membranes (Qiao et al. 2008). For example, an acidification pretreatment will serve to remove low molecular weight organic and inorganic ones such as boron before the use of RO process. Also, some post treatment processes may also be required after the RO process to meet the requirements (Murray-Gulde et al. 2003).

Lee and Frankiewicz suggested using cyclones as pretreatment processes for reducing the content of oil and solids to less than 50 mg $L^{-1}$ and 15 mg $L^{-1}$ respectively, before using a hydrophilic UF membrane, in order to reduce the fouling problem; in this way the membrane permeability can be extended for longer time. To reduce the potential for fouling, a 12 mm desanding hydrocyclone and a deoiling cyclone were used to remove fine oil-coated solids and to reduce O&G concentrations in the PW ahead of the UF membranes (Lee and Frankiewicz, 2013). The purpose of the desanding cyclone is to remove solids greater than 6 to 10 µm from the PW. The deoiling cyclone underflow passes through the pre-filter membrane and then to UF membrane modules. For maintaining the required cross-flow fluid velocity over the membrane, a membrane concentrate re-circulation pump is utilized. The permeate stream is introduced to a 0.45 µm cartridge filter to monitor the permeate stream purity.

Some experiments were carried out to treat PW for irrigation quality standards. Taking into account the oil and salt content, microfiltration, employing sorption pellets made of a modified clay material (organoclay PS12385) and RO units for separation of salts were proposed for that. It was obtained that packed bed can separate more than 90% of the oil and the loading capacity of clay pellets was better than the activated carbon (more than 60%). TDS is separated in a 95% by the RO membrane, which could be utilized for recovering up to 90% of water from PW. If two membranes are used in series, the second with a smaller surface than the first one, results would be obtained similar to putting the membranes in parallel, but with capital cost (Barrufet et al. 2013).

A method of treating oilfield PW containing boron and solubilized hydrocarbon compounds was patented to reduce boron concentration, which comprises water softening to remove substantially all divalent cations, raising the pH of the liquid above about 9.5, and driving the liquid through a RO membrane. This method can reduce boron concentration to less than 2 mg L$^{-1}$ (Tao et al. 1993).

A pilot plant as shown in Figure 2.3, including aeration tank, air flotation, sand filter and UF membrane was utilized to treat PW for discharge or injection into an oil-well purposes. The content of suspended solid and oil was reduced to less than 1.0 mg L$^{-1}$ and 0.5 mg L$^{-1}$, respectively. Fe and bacteria concentrations also achieved the required standard for injection and discharging purposes (Qiao et al. 2008).

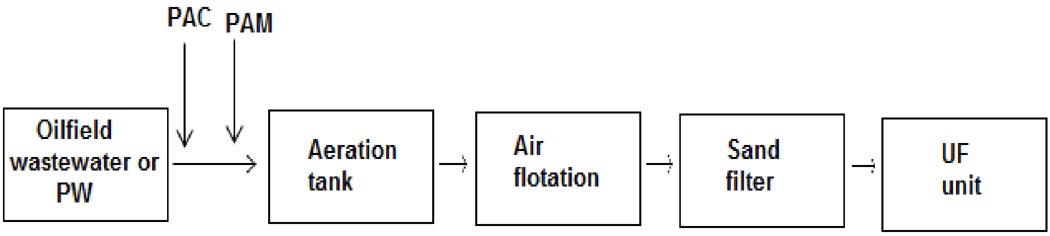


Figure 2.3. Process proposed for the treatment of the oilfield wastewater (Qiao et al. 2008)

Çakmakci and colleagues (Çakmakce et al. 2008) utilized dissolved air flotation, acid cracking, coagulation and precipitation, cartridge filters, microfiltration and ultrafiltration as pre-treatment processes, and nanofiltration and RO to salt content

In a pilot study to reuse oilfield PW for irrigation and potable water, a series of processes were proposed as shown in Figure 2.4. The proposed unit included warm softening, coconut shell filtration, cooling (fin-fan), trickling filter, ions exchange and reverse osmosis. Silica level was reduced to 3 mg $L^{-1}$ by adding 400 mg $L^{-1}$ $MgCl_2$. Hardness, TDS, boron and ammonia were removed up to 96%, 95%, 90% and 80%, respectively (Funston et al. 2002).

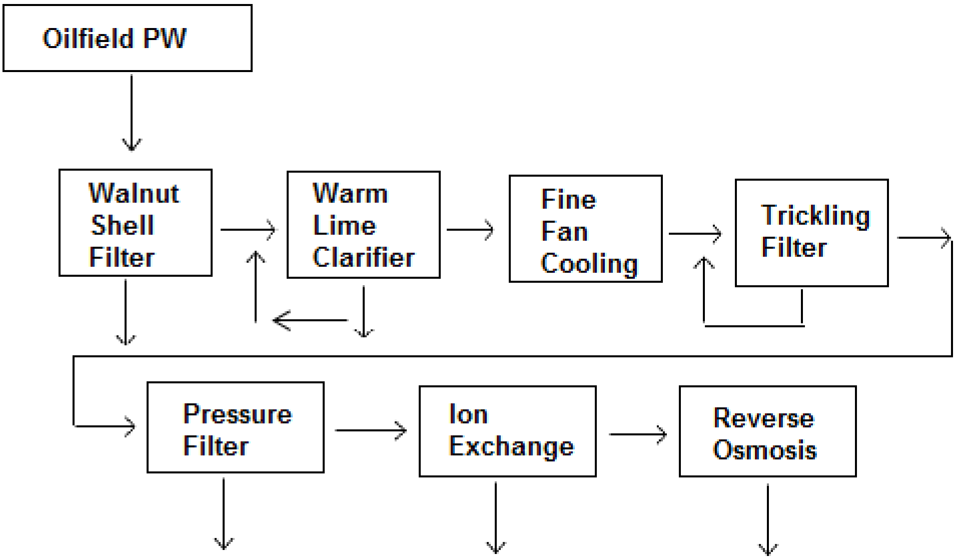


Figure 2.4. Pilot plant schematic (Funston et al., 2002)

Another configuration was included wash tanks, dissolved gas flotation, walnut shell filtration, warm lime softening, membrane bioreactor and RO to reach potable and irrigation water standards (Tsang and Martin 2004).

Doran et al. (2013) combined warm precipitate softening at pH 9.7, cooling, fixed-film biological organics oxidation, pressure filtration, ion-exchange softening and RO to treat PW (Doran et al. 2013).

A pilot-scale hybrid RO process was intended to treat PW for irrigation or discharge to surface waters. After the treatment, the conductivity was reduced by 98% and TDS by 96%, complying with the criteria for irrigation or discharge to surface waters (Murray-Gulde et al. 2003).

### 2.7.8. Commercial Treatment Processes for Produced Water

#### 2.7.8.1. CDM Technology

CDM Smith produces a technology to treat high TDS coal bed methane PW through a combination of the ion exchange process, RO and evaporation. UV disinfection is also included to reduce the bacterial activity. The total cost of treatment per barrel of PW was found to be $ 0.30 per barrel. If pretreatment processes are included before, membrane fouling is reduced and water recovery ranged from 50% to 90% (Drewes et al. 2009).

#### 2.7.8.2. Veolia: OPUS™ – Optimized pre-treatment and separation technology

This treatment is designed to remove soluble solutes (e.g., $SiO_2$, $CaSO_4$, and $Mg(OH)_2$), organics, and boron. The OPUS technology consists of the application of multiple treatment processes, involving degasification, chemical softening, media filtration, ion exchange softening, cartridge filtration and reverse osmosis (RO) technologies. The pretreatment processes ahead of the RO are designed to reduce the hardness, metals and suspended solids in the feed water.

The raw PW is acidified and degasified. It is followed by Multiflo™ chemical softening, which is a series of coagulation, flocculation and sedimentation. The water from the Multiflo™ process is then further treated with media filtration, ion exchange softening, and cartridge filtration to reduce the hardness, metals and suspended solids to lower concentrations, without pH correction. Removal of total hardness and metals in the feed water eliminates the potential for scaling of the RO membranes due to calcium carbonate, calcium sulfate, calcium fluoride, barium sulfate, strontium sulfate, iron and manganese precipitates. The pretreated water is then pressurized through an RO system, operated at an elevated pH in either single pass or double pass mode, to reduce the total dissolved solids, silica, boron, and organics present in the feed water (Veolia Water Technologies, 2016)

### 2.7.8.3. Eco-sphere: Ozonix$^{TM}$

Ozonix$^{TM}$ is a patented AOP, which saturates contaminated water with ozone using hydrodynamic cavitation, acoustic cavitation, and electrochemical oxidation to oxidize and destroy micro-organisms, without generation of harmful disinfection byproducts. As water flows through the Ozonix$^{TM}$ Reactor, bacteria cell walls are destroyed and pollutants are oxidized, producing clean water that is ready for re-use and future operations (Ecosphere Technologies, 2016). Ozonix$^{TM}$ is primarily used for the treatment of fracking flow-back water, but it could also be used for PW treatment. The feed water is mixed with supersaturated ozonized water in a reaction vessel. The hydroxyl radicals, formed from ozone, readily oxidize metals, and attack soluble and insoluble organic compounds and microorganisms. The reaction vessel had two electrodes to induce precipitation of hard salts. Water is then treated with activated carbon cartridge filter and a RO membrane. Water recovery approaches 75% (Drewes et al. 2009). With Ozonix$^{TM}$ there is no need for chemical biocides (Ecosphere Technologies, 2016).

### 2.7.8.4. GeoPure water technologies

GeoPure has the ability to treat 7500 barrels of PW per day per unit, and with operating permits from the Texas Railroad Commission, GeoPure Hydrosystems is ready to provide cost-effective PW treatment in the Permian Basin (Midland Reporter-Telegram, 2012).

The GeoPure desalination process is a combination of pre-treatment, ultrafiltration and reverse osmosis. Depending on the initial composition of water, this process uses various pretreatment technologies to remove suspended solids, dispersed oil or dissolved hydrocarbons. The effluent from the pre-treatment is then purified through polymeric UF and RO membranes. UF removes the suspended solids (such as colloids) before entering the RO. GeoPure Water Technologies, LLC performed a field test of its commercial desalination unit in the Barnett Shale Play of central Texas in 2006. In this test, the feed water contained 4200 mg $L^{-1}$ TSS, 170 mg $L^{-1}$ Fe and 940 mg $L^{-1}$ Ba, and its frac flowback water feed rate was 210000 gpd (5000 bpd). After a coagulation/flocculation process, the water was treated with GeoPure's UF and RO units. TDS concentrations of the influent and RO permeate were 15000 and 190 mg $L^{-1}$, respectively, corresponding to 98.7% TDS rejection. Total treatment costs were approximately $0.94 per barrel (coagulation/flocculation pretreatment cost included). A second test was conducted at a CBM well field in Western Wyoming. The GeoPure treatment process was tested with CBM PW containing corrosion inhibitor, alcohols, and surfactants, with a feed TDS of 9700 mg $L^{-1}$ (mostly NaCl) and 41 mg $L^{-1}$ of dissolved hydrocarbons. 99% rejection of TDS was achieved (Drewes et al. 2009).

#### 2.7.8.5. EMIT: Higgins Loop

EMIT Higgins Loop technology is widely used for Coal Bed Natural Gas (CBNG) PW treatment.

During the production of CBNG, water pumped with methane gas contains high levels of sodium (Na) and bicarbonate ($HCO_3$) and, in some cases, chlorides (Cl) and sulfates ($SO_4$). With Severn Trent Services' Higgins Loop CCIX technology, EMIT can economically and efficiently treat water used during the production of CBNG for environmental reintroduction and reuse. The Higgins Loop system utilizes I-X resins in a highly efficient resin-contacting system to remove sodium from the water and concentrate it into a dense brine solution byproduct that may even be useful within the oil and gas industry. Removing sodium from the water lowers its pH balance and reduces bicarbonate levels by extracting carbon dioxide gas from the water. Product water recovery typically exceeds 99% (Severn Trent Services, 2004).

#### 2.7.8.6. Drake: Continuous selective IX process

The Drake system is a three-phase, continuous fluidized bed system to remove monovalent cations. A strong acid cation exchange resin is used. Energy requirements are slightly less than that required for the EMIT Higgins Loop system. The maximum product water recovery is reported to be 97% (Drewes et al. 2009).

#### 2.7.8.7. Eco-Tech: Recoflo® compressed-bed IX process

The Eco-Tech compressed bed systems are an extension of conventional packed bed IX processes. One system has two separate compressed-bed columns for anion and cation removal. Another system has three separate compressed-bed columns that contain a primary cation bed and anion bed followed by a polishing cation bed. Recoflo® systems are primarily used for recovering metals from effluent electrolytes (Drewes et al. 2009). Recoflo® ion exchange technology utilizes fine mesh resin beads, a fully packed resin bed, and counter-current regeneration. These unique features help to improve exchange kinetics, reduce regenerate consumption, and increase the concentration of strip solutions. Provide significant benefits in softener performance such as: 40-80% reduction in salt and waste for regeneration compared with conventional softeners treating an equivalent quality and quantity of water, eliminate the use of acid and caustic for regeneration of WAC softeners, compact, skid-mounted, factory assembled systems and fully automated, easy to operate and maintain with easy adjustment to variable feed water conditions and effective in-situ resin cleaning (Eco-Tech, 2016).

#### 2.7.8.8. Dewvaporation: AltelaRainSM process

Dewvaporation is a desalination technology whose operation principle is based on counter current heat exchange to produce distilled water (AltelaRainSM, 2007). Feed water is evaporated in one chamber and condensed on the opposite chamber of a heat transfer wall as distilled water.

Approximately 100 bbl/day of PW with salt concentration in excess of 60000 mg $L^{-1}$ TDS can be processed by this system.

High removal rates of heavy metals, organics and radionuclides from PW have also been reported for this technology. In one plant, chloride concentration was reduced from 25300 to 59 mg $L^{-1}$, TDS from 41700 to 106 mg $L^{-1}$ and benzene concentration from 450 mg $L^{-1}$ to non-detectable after treatment with AlterRainSM.

According to Altela Inc., energy requirements of this system are low because it operates at ambient pressures and low temperatures. This makes it a viable alternative water treatment at remote oil wells where there is no high power grid, but there is no information on the overall cost of the system which is likely to be its major disadvantage.

### 2.7.8.9. Rapid Spray Evaporation (RSE)

AquaSonics International has developed a Rapid Spray Evaporation (RSE) system ejecting contaminated water at high velocities through a specialized injector-nozzle a (generated from gas-fired electrical generating plants, wastewater treatment plants, landfills, marine engines, and other sources, for desalination or for the recovery of dissolved substances).

RSD, is a recently patented process, whereby water under pressure is nebulized into a moving hot air stream. Because of the extremely high surface area of the water droplets, the water vaporizes instantly and efficiently. By careful control of the system, salt that remains behind is concentrated into a brine for material handling purposes.

As the water vaporizes within milliseconds of ejection, the solids in the solution flash or separate out. The water vapor is condensed and collected while the precipitated solids form isolated crystalline particles, which are collected through a vacuum process and sold as a byproduct. RSE ejects the salt water through a nozzle into a stream of heated air, forming a mist of droplets which vaporize almost instantly. The minute flakes of solid salt left behind fall to the bottom of the evaporation chamber where they can be collected. The best success comes from developing nozzles that allow the process to work with hydraulic pressure. AquaSonics claims to attain nearly 100% salt conversion of salt water into fresh water (Arthur et al. 2005).

#### 2.7.8.10. EARTH Canada Corporation: TORR™

The EARTH Canada Corporation has developed a technology called Total Oil Remediation and Recovery (TORR™) to remove and recover dispersed oil in water 2 µm and larger. The technology is a multi-stage adsorption and separation system. An adsorbent media, the Reusable Petroleum Adsorbent (RPA®) removes large and small oil droplets. This material is a polyurethane-based, oleophilic, hydrophobic, nontoxic, media coalescing agent. In the process of adsorption, the media continuously adsorbs the oil emulsions, coalesces, and desorbs them into larger oil droplets. In the recovery chamber, oil droplets desorbed by the media float to the top of the chamber in accordance with Stoke's Law (Plebon et al. 2005).

#### 2.7.8.11. Frac Water Inc: High Efficiency Electrodialysis (HEED™)

Frac Water Inc developed mobile ED treatment units for treating CBM PW and reusing it in fracturing treatment. Several case studies suggest that the mobile treatment units treat the PW with TDS ranges from 11400 to 27000 mg $L^{-1}$ and sulphates from 4000 to 14000 mg $L^{-1}$ (Spitz 2003).

First, for removal of particulate matter, there are cartridge filtration, carbon filters for removal of organic matter, and weak acid cation exchange resins to remove hardness and iron. Recovery of the brackish water with this ED treatment was 80-90%. The HEED™ stack configuration required up to 40% less membrane area, resulting in more than 70% increase in energy efficiency. The product water quality met the requirements for the basic gel fracturing fluids.

As disadvantages of this system are the high treatment cost and membrane fouling. The membranes should be regularly washed or cleaned in place with dilute acid and alkali solutions for restoring performance when needed (Drewes et al. 2009).

### 2.7.8.12. Crystal Solutions, LLC: Freeze-thaw/evaporation (FTE®)

Crystal Solutions, LLC, a joint venture of Gas Technology and BC Technologies, utilized FTE for PW treatment at its first best commercial treatment facility near Wamsutter, Wyoming. The FTE is based in naturally ambient temperature swings to alternately freeze and thaw PW, thus the dissolved solids become concentrated and producing fresh water suitable for various beneficial uses.

PW with 14000 mg $L^{-1}$ of TDS was concentrated to a brine of approximately 64300 mg $L^{-1}$ TDS and the fresh water (melt from ice) with 924 mg $L^{-1}$ TDS. Approximately 55 % of the feed turned into melt water melt; roughly 30% gets lost for evaporation and/or sublimation; and only about 15% of the original feed remains as concentrated brine. In this case, it was a usable product for drilling applications because the concentrated brine having a potassium chloride concentration in excess of 2% (Boysen and Boysen, 2008).

### 2.7.8.13. BioPetroClean: Automated Chemostat Treatment ACT™

Automated Chemostat Treatment™ (ACT) is a biological wastewater treatment solution. It is based on maintaining a pre-selected bacterial “cocktail” for a specified type of polluted water coupled with chemostat process. The process is maintained in a homeostatic state of bacterial growth and organic compound degradation.

Due to the low concentration of bacterial cells used in this biological wastewater treatment, no aggregates are formed and each bacterium acts as a single cell. This increases the surface area available for biodegradation, increasing the efficiency of the process.

ACT operates as a continuous flow reactor without using activated sludge. The bioreactor can be applied on-site (using the available infrastructure) due to its high flexibility in process modulation. This dramatically decreases operational and maintenance costs (BioPetroClean, 2016).

#### 2.7.8.14. Prosep: C-TOUR

C-TOUR utilizes the principles of solvent extraction and removes both dispersed oil and water soluble organics through condensate injection into PW streams.

During condensate injection and in-line mixing, hydrocarbon contaminants are extracted from the PW stream, where the contaminants and injected condensate coalesce to form larger and lighter oil droplets. These oil droplets are hydraulically or mechanically separated from the PW stream by downstream treatment equipment and redirected to applicable oil process streams.

In three sets of field trials conducted with the C-TOUR process, removal efficiency of dispersed oil, 2–3 ring PAHs, and NPD was 70%, for $C_6$, and for $C_6$ phenols approximately 60%, and for $C_4$–$C_5$ phenols 20% (Knudsen et al. 2013).

## 2.8. CONCLUSIONS

The Oil & Gas industry is considered one of the eight most water intensive industries due to the high volumes of water that are required for oil extraction and refining, and the subsequent amount of wastewater that is generated. Water present in a reservoir with a hydrocarbon resource that is produced to the surface with the crude oil or natural gas is the so-called produced water (PW). The volume generated of PW is quantified up to 39.5 $Mm^3$ $day^{-1}$ and is one of the major concerns for the extraction of Oil & Gas, the upstream activity of the sector.

Solutions to avoid the environmental impact of this type of wastewater are firstly its minimization, secondly, its reutilization and finally as a last option, its disposal after a treatment to remove the large variety of toxic compounds that PW possess, though unfortunately, the legislation only pay more attention to O&G,

being this content dependent not only on the chemical composition of the water, but also on the extraction procedure.

Characterization of the PW to determine major constituents should be the first step in an attempt to select optimum treatment options. The result of such characterization will determine if physical pre-treatment is required, if thermal treatment is necessary, if chemical dosing could be avoided, etc. Therefore, characteristics of the PW coupled with environmental factors, economic considerations, and local regulatory framework are used to select the optimal option for treatment of PW. It is also important to consider the concept of zero discharge, which in practice means not generate any additional pollutants and the minimization of waste.

Current thermal PW treatment technologies are mature but may not be relevant in the future from the point of view of energy efficiency, unless reductions are made in energy costs. Membrane technology is another polishing treatment destined fundamentally for the elimination of salts; however, for future application, progress must be made in order to reduce membrane fouling, the waste generated and to optimize backwashing. MPPE technology may well compete also in the future management of PW. Its potential to achieve a zero pollutant discharge and a significant reduction in energy consumption compared with thermal technologies are very promising, but further research is needed to reduce its relatively high cost. Another cost-effective technology can be electrochemistry or the combination of two or more technologies.

AOPs are also an efficient alternative to treat wastewater polluted with toxic organic components due to the fact that the hydroxyl radicals can totally or partially degrade mostly of organic compounds found in aqueous medium or in soils, producing the complete mineralization of these compounds or in their conversion to more biodegradable products for a possible subsequent application of a biological treatment. Several studies have been made of the application of AOPs to the treatment of oil and gas wastewater. However, in order to optimize costs, an optimization of the operating conditions with real wastewaters need to be done.

But the most effective approach is the combination of several processes for a major efficiency in the treatment of the PW since the majority of the treatments are well for certain groups of components but they cannot act or even turn harmed by others, needing therefore different types of treatments.

## 2.9. REFERENCES

Akzo Nobel MPP, S. (2004). Macro-porous polymer extraction for offshore produced water removes dissolved and dispersed hydrocarbons. Business Briefing: Exploration & Production: The Oil & Gas Review, 1–4.

Al Mahruki, A. M., Alloway, B., Patzelt, H. (2013). The Use of Reedbed Technology for Treating Oil Production Waters. In SPE International Health, Safety & Environment Conference. Society of Petroleum Engineers. http://doi.org/10.2118/98548-MS.

Ali, S. A., Henry, L. R., Darlington, J. W., Occapinti, J. (1998). New filtration process cuts contaminants from offshore produced water. Oil Gas, 96, 73–78.

All Consulting. (2003). Handbook on coal bed methane produced water: Management and beneficial use alternatives. Report available at http://www.all-llc.com/CBM/pdf/CBMBU/CBM%20BU%20Screen.pdf.

Al-Shamrani, A.A., James, A., Xiao, H. (2002). Separation of oil from water by dissolved air flotation. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 209(1), 15–26.

Almarouf, H.S., M.S. Nasser, M.J. Al-Marri, M. Khraisheh, Sagheer A. Onaizi. (2015). Demulsification of stable emulsions from produced water using a phase separator with inclined parallel arc coalescing plates. Journal of Petroleum

Science and Engineering, 135, 16-21.

AltelaRainSM. (2007). AltelaRainTM System ARS-4000: New Patented Technology for Cleaning Produced Water On-Site.

Andreozzi, R., Caprio, V., Insola, A., Marotta, R. (1999). Advanced oxidation processes (AOP) for water purification and recovery. Catal. Today, 53, 51–59.

AQUASTAT reports (visited on December 14th 2016), http://www.fao.org/nr/water/aquastat/main/index.stm.

Arowoshola, L., Cope, G., David, V., Gasson, C., González-Manchón, C., Kelleher, M., Lang H., Uzelac, J. (2011). Produced water market. Opportunities in the oil, shale and gas sectors in North America. A Global Water Intelligence publication. ISBN: 978-1-907467-14-1.

Arthur, D., Langhus, B. G., Patel, C. (2005). Technical Summary of Oil & Gas Produced Water Treatment Technologies. ALL CONSULTING, LLC.

Arthur, J. D., Dillon, L. W., Drazan, D. J. (2011). Management of Produced Water From Oil and Gas Wells. Working Document of the NPC North American Resource Development Study, 32 pp.

Asatekin, A., Mayes, A.M. (2009). Oil industry wastewater treatment with foulingresistant membranes containing amphiphilic comb copolymers, Environ. Sci.Technol. 43, 4487–4492.

Ashaghi, K. S., Ebrahimi, M., Czermak, P. (2007). Ceramic Ultra- and Nanofiltration Membranes for Oilfield Produced Water Treatment: A Mini Review. The Open Environmental Journal, 1(1), 1–8. http://doi.org/10.2174/1874233507010011053.

Augugliaro, V., Litter, M., Palmisano , L., Soria, J. (2006). The combination of heterogeneous photocatalysis with chemical and physical operations: A tool for improving the photoprocess performance. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, v. 7, p. 127–144, 2006.

Bader M. (2007) Seawater versus producedwater in oil-fields water injection operations. Desalination. 208: 159–168.

Balanosky, E. (2000). Oxidative degradation of textile waste water. Modeling reactor performance. Water Research, 34(2), 582–596. http://doi.org/10.1016/S0043-1354(99)00150-5.

Baldoni-Andrey, P., Pedenaud, P., Dehaene, P.-L., Segues, B. (2006). Impact Of High Salinity Of Produced Water On The Technical Feasibility Of Biotreatment For E & P On Shore Applications. In SPE International Health, Safety & Environment Conference. Society of Petroleum Engineers. http://doi.org/10.2118/98751-MS.

Benyahia, F., Abdulkarim, M., Embaby A., and Rao, M. (2006). Refinery Wastewater Treatment: A True Technological Challenge, The Seventh Annual U.A.E. University Research Conference. U.A.E. University.

Bertness, T.A. and Lipoma S.P. (1986). US Patent No. 4,877,536. Method of treating saline water.

Bessa, E., Sant’Anna, G. L., Dezotti, M. (2001). Photocatalytic/H2O2 treatment of oil field produced waters. Applied Catalysis B: Environmental, 29(2), 125–134. http://doi.org/10.1016/S0926-3373(00)00199-5.

Beyer, A. H., Chevron, O., Palmer, L. L., Stock, J. (1979). Biological oxidation of dissolved compounds in oilfield-produced water by a pilot aerated lagoon. J. Pet. Technol.; (United States), 31:2.

Bhatkhande, D. S., Kamble, S. P., Sawant, S. B., Pangarkar, V. G. (2004). Photocatalytic and photochemical degradation of nitrobenzene using artificial ultraviolet light. Chemical Engineering Journal, 102(3), 283–290. http://doi.org/10.1016/j.cej.2004.05.009.

Bilstad, T., Espedal, E. (1996). Membrane separation of produced water. Water Science and Technology, 34(9), 239–246. http://doi.org/10.1016/S0273-1223(96)00810-4.

BioPetroClean, visited on September 2016. http://biopetroclean.com/our-technology/act/.

Bolton, J. R., Bircher, K. G., Tumas, W., Tolman, C. A. (1996). Figures-of Merit for the Technical Development and Application of Advanced Oxidation Processes. Journal of Advanced Oxidation Technologies, 1.

Bossmann, S. H., Oliveros, E., Göb, S., Siegwart, S., Dahlen, E. P., Payawan, L., Braun, A. M. (1998). New Evidence against Hydroxyl Radicals as Reactive Intermediates in the Thermal and Photochemically Enhanced Fenton Reactions. The Journal of Physical Chemistry A, 102(28), 5542–5550. http://doi.org/10.1021/jp980129j.

Bostick D.T., Luo H. (2001). Characterization of Soluble Organics in Produced Water. Department of Energy Petroleum Energy Research Forum Project 98-04, to be published at Oak Ridge National Laboratory.

Boysen, J., Boysen, D. (2008). The Freeze-Thaw/Evaporation (FTE) process for produced water treatment, disposal and beneficial uses. Available at: http://ipec.utulsa.edu/Conf2008/Manuscripts%20&%20presentations%20received/Boysen_37_FreezeThaw.pdf.

Brillas, E., Casado, J. (2002). Aniline degradation by Electro-Fenton and peroxicoagulation processes using a flow reactor for wastewater treatment. Chemosphere, 47, 241–248.

Garbutt, C.F. (1999). Water treatment process for reducing the hardness of an oilfield produced water. Patent US5879562 A.

Çakmakce, M., Kayaalp, N., Koyuncu, I. (2008). Desalination of produced water from oil production fields by membrane processes. Desalination, 222(1-3), 176–186. http://doi.org/10.1016/j.desal.2007.01.147.

Carvalho, M. S., Clarisse, M. D., Lucas, E. F., Barbosa, C. C. R., Barbosa, L. C. F. (2013). Evaluation Of The Polymeric Materials (DVB Copolymers) For Produced Water Treatment. In Abu Dhabi International Petroleum Exhibition and Conference. Society of Petroleum Engineers. http://doi.org/10.2118/78585-MS.

Casaday, A. L. (2013). Advances in Flotation Unit Design for Produced Water Treatment. In SPE Production Operations Symposium. Society of Petroleum Engineers. http://doi.org/10.2118/25472-MS.

Clifford, D. A. (1999). Ion exchange and inorganic adsorption. In Water quality and treatment (p. 9.1). http://doi.org/10.1002/047147844X.pc1506.

Crittenden, J. C., Suri, R. P. S., Perram, D. L., Hand, D. W. (1997). Decontamination of water using adsorption and photocatalysis. Water Research, 31(3), 411–418. http://doi.org/10.1016/S0043-1354(96)00258-8.

Daigle, T.P. (2012). Ultra Deep Water Discharge of Produced Water and/or Solids at the Seabed. Report prepared by Fluor Offshore Solutions. Report prepared by Fluor Offshore Solutions.

Darwish, M. A., Al Asfour, F., Al-Najem, N. (2003). Energy consumption in equivalent work by different desalting methods: case study for Kuwait. Desalination, 152(1-3), 83–92. http://doi.org/10.1016/S0011-9164(02)01051-2.

Database, U. P. W. (2002). USGS Produced Waters Database. U.S. Department of the Interior.

De Laat, J., Truong Le, G., Legube, B. (2004). A comparative study of the effects of chloride, sulfate and nitrate ions on the rates of decomposition of H2O2 and organic compounds by Fe(II)/H2O2 and Fe(III)/H2O2. Chemosphere, 55(5), 715–723. http://doi.org/10.1016/j.chemosphere.2003.11.021.

Deng, S., Bai, R., Chen, J. P., Jiang, Z., Yu, G., Zhou, F., Chen, Z. (2002). Produced water from polymer flooding process in crude oil extraction: characterization and treatment by a novel crossflow oil–water separator. Separation and Purification Technology, 29(3), 207–216. http://doi.org/10.1016/S1383-5866(02)00082-5.

Deng, S., Yu, G., Chen, Z., Wu, D., Xia, F., Jiang, N. (2009). Characterization of suspended solids in produced water in Daqing oilfield. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 332(1), 63–69. http://doi.org/10.1016/j.colsurfa.2008.09.004.

Deng, S., Yu, G., Jiang, Z., Zhang, R., Ting, Y. P. (2005). Destabilization of oil droplets in produced water from ASP flooding.

Domènech, X., Jardim, W. F., & Litter, M. I. (2004). Procesos avanzados de oxidación para la eliminación de contaminantes. Eliminación de contaminantes por fotocatálisis heterogénea. Red CYTED VIII-G, Blesa M.A. y Sánchez Cabrero B., Editores, Ediciones CIEMAT, Madrid, 7-34, 2004.

Doran, G. F., Carini, F. H., Fruth, D. A., Drago, J. A., Leong, L. Y. C. (2013). Evaluation of Technologies to Treat Oil Field Produced Water to Drinking Water or Reuse Quality. In SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers. http://doi.org/10.2118/38830-MS.

Doran, G., Leong, L. Y. C. (2000). Developing a cost effective solution for produced water and creating a “new” water resource. In DOE/MT/95008-4. United Sates Department of Energy.

Dores, R., Hussain, A., Katebah, M., Adham, S., Global, C., Sustainability, W. (2012). Using Advanced Water Treatment Technologies To Treat Produced Water From The Petroleum Industry. SPE International, (Md).

Doyle, D. H., Brown, A. B. (2000). Produced water treatment and hydrocarbon removal with organoclay. Paper SPE 63100 presented at the 2000 SPE Annual Technical Conference, Dallas, Texas, 1-4 October.

Doyle, D. H., Daniel, F., Brown, A., Ventures, E. T. (1997). Field Test of Produced Water Treatment With Polymer Modified Bentonite. SPE 38353.

Drewes, J., Cath, T., Xu, P., Graydon, J. (2009). An Integrated Framework for Treatment and Management of Produced Water. In Technical Assessment of produced water treatment technologies (8–128).

Duraisamy, R. T., Beni, A. H., Henni, A. (2013). State of the Art Treatment of Produced Water. In Water Treatment, 199-222. Rijeka, Croatia: InTech.

Ebrahimi, M., Willershausen, D., Ashaghi, K.S., Engel, L., Placido, L., Mund, P., Bolduan, P., Czermak, P. (2010). Investigations on the use of different ceramic mem-branes for efficient oil-field produced water treatment, Desalination 250, 991–996.

Ecosphere Technologies, (visited in 2016). http://www.ecospheretech.com/environmental-engineeringtechnologies/ozonix.

Eco-Tech, visited in 2016. http://global-treatmentsolutions.com/wp-content/uploads/Recoflo-Ion-Exchanger-Softener.pdf.

Ekins, P., Vanner, R., Firebrace, J. (2007). Zero emissions of oil in water from offshore oil and gas installations: economic and environmental implications, J. Clean. Prod. 15, 1302–1315.

Fakhru'l-Razi, A., Pendashteh, A., Abdullah, L. C., Biak, D. R. A., Madaeni, S.

S., Abidin, Z. Z. (2009). Review of technologies for oil and gas produced water treatment. Journal of Hazardous Materials, 170(2-3), 530–51. http://doi.org/10.1016/j.jhazmat.2009.05.044.

Fakhru'l-Razi, A. Pendashteh, Z.Z. Abidin, L.C. Abdullah, D.R.A. Biak, Madaeni, S.S. (2010). Application of membrane-coupled sequencing batch reactor for oil-field produced water recycle and beneficial re-use, Bioresour. Technol. 101, 6942–6949.

Faksness, L.-G., Grini, P. G., Daling, P. S. (2004). Partitioning of semi-soluble organic compounds between the water phase and oil droplets in produced water. Marine Pollution Bulletin, 48(7-8), 731–42. http://doi.org/10.1016/j.marpolbul.2003.10.018.

Fillo, J. P., Koraido, S. M., Evans, J. M. (1992). Sources, Characteristics, and Management of Produced Waters from Natural Gas Production and Storage Operations. In Produced Water (151–161). Springer US.

Fipps, G. (2003). Irrigation Water Quality Standards and Salinity Management Strategies. Texas Agricultural Extension Service, Texas A&M University System. 18 pp.

Frankiewicz, T. C., Gerlach, J. (2000). Removal of hydrocarbons, mercury and arsenic from oil-field produced water. Patent US6117333 A.

Freire, D. D., Cammarota, M. C., Santanna, G. L. (2001). Biological treatment of oil field wastewater in a sequencing batch reactor. Environmental Technology, 22(10), 1125–35. http://doi.org/10.1080/09593332208618203.

Funston, R., Ganesh, R., Leong, L. Y. C., Consultants, K. J., Road, N. S. (2002). Evaluation of Technical and Economic Feasibility of Treating Oilfield Produced Water to Create a " New " Water Resource. Produced Water, Colorado Spring, Colorado.

Gäfvert, T., Færevik, I., Rudjord, A. L. (2006). Assessment of the discharge of NORM to the North Sea from produced water by the Norwegian oil and gas industry. Radioactivity in the Environment, 8, 193–205. http://doi.org/10.1016/S1569-4860(05)08013-7.

Gallagher, J. R. (2001). Anaerobic Biological Treatment of Produced Water. Pittsburgh, PA, and Morgantown, WV. Available at: http://www.energystorm.us/Anaerobic Biological Treatment of Produced Water-r 54822.html.

Galvão, S. A. O., Mota, A. L. N., Silva, D. N., Moraes, J. E. F., Nascimento, C. A. O., Chiavone-Filho, O. (2006). Application of the photo-Fenton process to the treatment of wastewaters contaminated with diesel. Science of The Total Environment, 367, 1, 42-49.

Garbutt, C. F. (2013). Innovative Treating Processes Allow Steamflooding With Poor Quality Oilfield Water. In SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers. http://doi.org/10.2118/38799-MS.

Gogate, P. R., Pandit, A. B. (2004). A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. Advances in Environmental Research, 8, 3-4, 501-551.

Gooch, J. (1997). Analysis and Deformulation of Polymeric Materials: Paints, Plastics, Adhesives, and Inks. Springer.

Goslich, R., Dillert, R., Bahnemann, D. (1997). Solar water treatment: principles and reactors. Wat. Sci. Tech, 4, 137-148.

Goududey, S. and Kaushal, R.K. (2013). Fine Particle Separation by Floatation: A Review. VSRD International journal of technical & Non-Technical Research, 4.

Grant A., Briggs A.D. (2002) Toxicity of sediments from around a North Sea oil platform: are metals or hydrocarbons responsible for ecological impacts? Mar Environ Res. 53:95–116.

Grini, P. G., Hjelsvold, M., Johnsen, S. (2013). Choosing Produced Water Treatment Technologies Based on Environmental Impact Reduction. In SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production. Society of Petroleum Engineers. http://doi.org/10.2118/74002-MS.

Guedes, A. M., Madeira, L. M., Boaventura, R. A., & Costa, C. A. (2003). Fenton oxidation of cork cooking wastewater--overall kinetic analysis. Water Research, 37(13), 3061–9. http://doi.org/10.1016/S0043-1354(03)00178-7.

Guerra, K., Dahm, K., Dundorf, S. (2011). Oil and Gas Produced Water Management and Beneficial Use in the Western United States. Science and Technology Program Report, 157.

Gurden, C., Cramwinckel, J. (2013). Application of Reedbed Technology in Production Water Management. In SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production. Society of Petroleum Engineers. http://doi.org/10.2118/61180-MS.

Haarhoff, J., Edzwald, J.K., (2013). Adapting dissolved air flotation for the clarification of seawater. Desalination, 311, 90–94.

Hamed, O. (2004). Evolutionary developments of thermal desalination plants in the Arab Gulf region. 2004 Beirut Conference.

Han, R., Zhang, S., Xing, D., Jian, X. (2010). Desalination of dye utilizing copoly(phthalazinone biphenyl ether sulfone) ultrafiltration membrane with low molecular weight cut-off. Journal of Membrane Science, 358(1-2), 1–6. http://doi.org/10.1016/j.memsci.2010.03.036.

Hansen B.R., Davies S.R. (1994). Review of Potential Technologies for the Removal of Dissolved Components from Produced Water. Chemical Engineering Research & Design, 72(2), 176–188.

Hayes, T., Arthur, D. (2004). Overview of Emerging Produced Water Treatment Technologies. 11th Annual International Petroleum Environmental Conference.

He, Y., Jiang, Z.W. (2008). Technology review: Treating oilfield wastewater. Filtration & Separation, 45(5), 14–16. http://doi.org/10.1016/S0015-1882(08)70174-5.

Heins WF, McNeill R. (2007) Vertical-tube evaporator system provides SAGD-quality feed water. World Oil Magazine; 228.

Holloway, F. H. (2013). The chemical treatment of offshore oil and gas production. In Offshore Europe Conference. Society of Petroleum Engineers. http://doi.org/10.2118/6678-MS.

Hommel, R. K. (1990). Formation and physiological role of biosurfactants produced by hydrocarbon-utilizing microorganisms. Biodegradation, 1(2-3), 107–119. http://doi.org/10.1007/BF00058830.

Houcine, M. (2013). Solution For Heavy Metals Decontamination in Produced Water / Case Study in Southern Tunisia. In SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production. Society of Petroleum Engineers. http://doi.org/10.2118/74003-MS.

Hu, Q., Zhang, C., Wang, Z., Chen, Y., Mao, K., Zhang, X., Zhu, M. (2008). Photodegradation of methyl tert-butyl ether (MTBE) by UV/H2O2 and UV/TiO2. Journal of Hazardous Materials, 154(1-3), 795–803. http://doi.org/10.1016/j.jhazmat.2007.10.118.

Huang, C. P., Dong, C., Tang, Z. (1993). Advanced chemical oxidation: Its present role and potential future in hazardous waste treatment. Waste Management, 13(5-7), 361–377. http://doi.org/10.1016/0956-053X(93)90070-D.

Igunnu, E.T., Chen, G. Z. (2012). Produced water treatment technologies. International Journal of Low-Carbon Technologies, 1-23.

Igwe, C. O., Saadi, A. A. L., Ngene, S. E. (2013). Optimal Options for Treatment of Produced Water in Offshore Petroleum Platforms. Journal of Pollution Effects & Control.

Jackson, L. M., & Myers, J. E. (2013). Design and Construction of Pilot Wetlands for Produced-Water Treatment. In SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers. http://doi.org/10.2118/84587-MS.

Jacobs, R. P. W. M., R. O. H. Grant, Kwant, J., Marquenie, J. M., Mentzer, E. (1992). The Composition of Produced Water from Shell Operated Oil and Gas Production in the North Sea. In Produced Water (13–21).

Jan, R. J., Reed, T. G. (2013). New Caustic Process for Softening Produced Water for Steam Generation. SPE Production Engineering, 7(02), 199–202. http://doi.org/10.2118/19759-PA.

Janks, J. S., Cadena, F. (1992). Investigations into the Use of Modified Zeolites for Removing Benzene, Toluene, and Xylene from Saline Produced Water. In Produced Water (473–487). Springer US.

Jiménez, S., Micó, M.M., Arnaldos, M., Ferrero, E., Malfeito, J.J., Medina, F., Contreras, S. (2017). Integrated processes for produced water polishing: Enhanced flotation/sedimentation combined with advanced oxidation processes. Chemosphere, 168, 309-317.

Kang, I. J., Lee, C. H., Kim, K. J. (2003). Characteristics of microfiltration membranes in a membrane coupled sequencing batch reactor system. Water

Research, 37, 1192–1197. http://doi.org/10.1016/S0043-1354(02)00534-1.

Khawaji, A. D., Kutubkhanah, I. K., & Wie, J.-M. (2008). Advances in seawater desalination technologies. Desalination, 221(1-3), 47–69. http://doi.org/10.1016/j.desal.2007.01.067.

Kirubakaran, A., Jain, S., Nema, R. K. (2009). A review on fuel cell technologies and power electronic interface. *Renewable and Sustainable Energy Reviews*, *13*(9), 2430–2440. http://doi.org/10.1016/j.rser.2009.04.004.

Klasson, K. T., Tsouris, C., Jones, S. A., Dinsmore, M. D., A.B.Walker, Paoli, D. W., Robinson, S. M. (2002). Ozone Treatment of Soluble Organics in Produced Water. Petroleum Environmental Research Forum Project 98-04. ORNL/TM-2002/5.

Knudsen, B. L., Hjelsvold, M., Frost, T. K., Svarstad, M. B. E., Grini, P. G., Willumsen, C. F., Torvik, H. (2013). Meeting the Zero Discharge Challenge for Produced Water. In SPE International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production. Society of Petroleum Engineers. http://doi.org/10.2118/86671-MS.

Li, L.B., Yan, S., Zeng, X.D., D. Q. L. (2002). Analysis of Organic Compounds in Oilfield Produced Water. Petrochemical Technology, 31, 472–475.

Lee, J. M., Frankiewicz, T. C. (2013). Treatment of Produced Water with an Ultrafiltration (UF) Membrane-A Field Trial. In SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers. http://doi.org/10.2118/95735-MS.

Lefebvre, O., Moletta, R. (2006). Treatment of organic pollution in industrial saline wastewater: a literature review. Water Research, 40(20), 3671–82. http://doi.org/10.1016/j.watres.2006.08.027.

Li, F., Wu, X., Wu, J., Xu, X., Ma, S. (2008). Kinetic Study of Adsorption of Oil from Oilfield Produced Water Using Modified Porous Ceramics Filtration Media in Column Mode. In 2008 2nd International Conference on Bioinformatics and Biomedical Engineering (pp. 2745–2748). IEEE. http://doi.org/10.1109/ICBBE.2008.1018.

Li, G., An, T., Chen, J., Sheng, G., Fu, J., Chen, F., Zhao, H. (2006). Photoelectrocatalytic decontamination of oilfield produced wastewater containing refractory organic pollutants in the presence of high concentration of chloride ions. Journal of Hazardous Materials, 138, 392–400. http://doi.org/10.1016/j.jhazmat.2006.05.083.

Li, G., An, T., Nie, X., Sheng, G., Zeng, X., Fu, J., Zeng, E. Y. (2007). Mutagenicity assessment of produced water during photoelectrocatalytic degradation. Environmental Toxicology and Chemistry / SETAC, 26(3), 416–423. http://doi.org/10.1897/06-264R.1.

Li, L., Lee, R. (2009). Purification of Produced Water by Ceramic Membranes: Material Screening, Process Design and Economics. Separation Science and Technology, 44(15), 3455–3484. http://doi.org/10.1080/01496390903253395.

Li, Q., Kang, C., Zhang, C. (2005). Waste water produced from an oilfield and continuous treatment with an oil-degrading bacterium. Process Biochemistry, 40(2), 873–877. http://doi.org/10.1016/j.procbio.2004.02.011.

Lin, S. H., Lo, C. C. (1997). Fenton process for treatment of desizing wastewater. Water Research, 31(8), 2050–2056. http://doi.org/10.1016/S0043-1354(97)00024-9.

Lindquist, S., C. Fell. (2009). Fuels-Hydrogen Production. In Encyclopedia of Electrochemical Power Sources (369–83).

Litter, M. I. (2005). Introduction to Photochemical Advanced Oxidation

Processes for Water Treatment. The Handbook of Environmental Chemistry, 2(September), 325–366. http://doi.org/10.1007/b138188.

Liu, S. M., Zhang, Z. J., Jiang, M. H. (2007). Treatment of ASP produced water with hydrophilic fibre ball filtration. J. Harbin Inst. Technol., 6, 837–841.

Liu, S., Zhao, X., Dong, X., Du, W., Miao, B. (2013). Treatment of Produced Water from Polymer Flooding Process Using a New Type of Air Sparged Hydrocyclone. In SPE Asia Pacific Health, Safety and Environment Conference and Exhibition. Society of Petroleum Engineers. http://doi.org/10.2118/95343-MS.

Lopez, J. L., Garc, F. S., Capparelli, A. L., Oliveros, E., Hashem, T. M., Braun, A. M. (2000). Hydroxyl radical initiated photodegradation of 4-chloro-3 , 5-dinitrobenzoic acid in aqueous solution. Journal of Photochemistry and Photobiology A: Chemistry, 137, 177–184.

Ma, H., Wang, B. (2006). Electrochemical pilot-scale plant for oil field produced wastewater by M/C/Fe electrodes for injection. Journal of Hazardous Materials, 132(2-3), 237–43. http://doi.org/10.1016/j.jhazmat.2005.09.043.

MacGowan, D. B., Surdam, R. C. (1988). Difunctional carboxylic acid anions in oilfield waters. Organic Geochemistry, 12(3), 245–259. http://doi.org/10.1016/0146-6380(88)90262-8.

Machulek, A., Moraes, J. E. F., Vautier-Giongo, C., Silverio, C. A., Friedrich, L. C., Nascimento, C. A. O., Quina, F. H. (2007). Abatement of the Inhibitory Effect of Chloride Anions on the Photo-Fenton Process. Environmental Science & Technology, 41(24), 8459–8463. http://doi.org/10.1021/es071884q.

Maciel, R., Sant'Anna Jr., G. L., & Dezotti, M. (2004). Phenol removal from high salinity effluents using Fenton's reagent and photo-Fenton reactions. Chemosphere, 57(7), 711–719. http://doi.org/10.1016/ j.chemosphere. 2004.07.

032.

McGhee, T.J. (1991). Treatment of Brackish and SalineWaters. In Water Supply and Sewerage (6th ed.). McGraw-Hill Inc., New York.

Malato, S., Blanco, J., Richter, C., Braun, B., Maldonado, M. I. (1998). Enhancement of the rate of solar photocatalytic mineralization of organic pollutants by inorganic oxidizing species. Applied Catalysis B: Environmental, 17(4), 347–356. http://doi.org/10.1016/S0926-3373(98)00019-8.

Malato, S., Blanco, J., Vidal, A., Richter, C. (2002). Photocatalysis with solar energy at a pilot-plant scale: an overview. Applied Catalysis B: Environmental, 37(1), 1–15. http://doi.org/10.1016/S0926-3373(01)00315-0.

Mater, L., Rosa, E. V. C., Berto, J., Correa, A. X. R., Schwingel, P. R., Radetski, C. M. (2007). A simple methodology to evaluate influence of H2O2 and Fe2+ concentrations on the mineralization and biodegradability of organic compounds in water and soil contaminated with crude petroleum. Journal of Hazardous Materials, 149, 379–386.

McFarlane, J., Ridenour, W. B., Luo, H., Hunt, R. D., DePaoli, D. W., Ren, R. X. (2005). Room Temperature Ionic Liquids for Separating Organics from Produced Water. Separation Science and Technology, 40(6), 1245–1265. http://doi.org/10.1081/SS-200052807.

Meijer, D. T., Kuijvenhoven Cor, A. T., Karup, H. (2004). Results from the latest MPPE field trials at NAM and total installations. In NEL Produced Water Workshop, Aberdeen, UK (21–22).

Meijer, D. T., Madin, C. (2010). Removal of Dissolved and Dispersed Hydrocarbons From Oil and Gas Produced Water With Mppe Technology To Reduce Toxicity and Allow Water Reuse. Appea Journal, 1–11.

Midland Reporter-Telegram. Posted: Sunday, November 11, (2012). http://www.mrt.com/oilreport/article_71bcf3f4-fa2e-11e1-9ea3-0019bb2963f4.html.

Mondal, S., Wickramasinghe, S. R. (2008). Produced water treatment by nanofiltration and reverse osmosis membranes. Journal of Membrane Science, 322(1), 162–170. http://doi.org/10.1016/j.memsci.2008.05.039.

Moraes, J. E. F., Quina, F., Nascimento, C. A. O., Silva D. N., Chiavone-Filho, O. (2004). Treatment of Saline Wastewater Contaminated with Hydrocarbons by the Photo-Fenton Process. Environ. Sci. Technol., v. 38, p. 1183-1187.

Morrow, L. R., Martir, W. K., Aghazeynali, H., Wright, D. E. (1999). Process of treating produced water with ozone, US Patent No. 5,868,945.

Mota, L. N., Albuquerque, L. F., Beltrame, L. T. C., Chiavone-Filho, O., Machulek Jr., A., Nascimento, C. A. O. (2008). Advanced Oxidation Processes and their application in the petroleum industry: A review. Brazilian Journal of Petroleum and Gas , 2(3), 122–142.

Murray-Gulde, C., Heatley, J. E., Karanfil, T., Rodgers, J. H., Myers, J. E. (2003). Performance of a hybrid reverse osmosis-constructed wetland treatment system for brackish oil field produced water. Water Research, 37(3), 705–13. http://doi.org/10.1016/S0043-1354(02)00353-6.

Myung, N. V, Schwartz, M., Nobe, K. (2000). Electrodeposition of GMR Ni / Cu Multilayers and Rare Earth- Iron Group Alloy Thin Film in a Recirculating Electrochemical Flow Reactor. Fundamental Aspects of Electrochemical Deposition and Dissolution. Proceedings of the International Symposium. The Electrochemical Society, INC.

Nadav, N. (1999). Boron removal from seawater reverse osmosis permeate utilizing selective ion exchange resin. Desalination, 124(1-3), 131–135.

http://doi.org/10.1016/S0011-9164(99)00097-1.

Nadtochenko, V., Kiwi, J. (1998). Photoinduced Mineralization of Xylidine by the Fenton Reagent. 2. Implications of the Precursors Formed in the Dark. Environmental Science & Technology, 32(21), 3282–3285. http://doi.org/10.1021/es9709637.

Nature Technology Group. (2005). Introduction to Produced Water Treatment. Nature Technology Solutions, 2–18. Retrieved 13 March 2010.

Neff, J. M. (2002). Bioaccumulation in Marine Organisms: Effect of Contaminants from Oil Well Produced Water. Elsevier Science Publisher, 472 pp.

Neff, J., Sauer, T. C., Hart, A. D. (2011). Bioaccumulation of Hydrocarbons from Produced Water Discharged to Offshore Waters of the US Gulf of Mexico. In Produced Water (441–477). Springer New York.

Neyens, E., Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. Journal of Hazardous Materials, 98, 33–50. http://doi.org/10.1016/S0304-3894(02)00282-0.

Ng, H. Y., Ong, S. L., Ng, W. J. (2005). Effects of Sodium Chloride on the Performance of a Sequencing Batch Reactor. Journal of Environmental Engineering, 131(11), 1557–1564. http://doi.org/10.1061/(ASCE)0733-9372(2005)131:11(1557).

Nicolaisen, B., Lien, L. (2003). Treating Oil and Gas Produced Water Using Membrane Filtration Technology. Presented at the Produced Water Workshop, Aberdeen, Scotland, March 26-27.

Ogp Report (2002). Aromatics in produced water: occurrence, fate & effects, and treatment. Available at http://www.ogp.org.uk/pubs/324.pdf.

Ometto, F., Pozza C., Whitton R., Smyth B., Gonzalez Torres A., Henderson RK., Jarvis P., Jefferson B., Villa R. (2014). The impacts of replacing air bubbles with microspheres for the clarification of algae from low cell-density culture. Water Research, 53, 168-179.

OSPAR Commission. (2005). Report on Discharges Spills and Emissions from Offshore Oil and Gas Installations.

Palmer, L. L., Beyer, A. H., Stock, J. (2013). Biological Oxidation of Dissolved Compounds in Oilfield Produced Water by a Field Pilot Biodisk. Journal of Petroleum Technology, 33(06), 1136–1140. http://doi.org/10.2118/8308-PA.

Pars, H. M., Meijer, D. T. (2013). Removal of dissolved hydrocarbons from production water by Macro Porous Polymer Extraction (MPPE). In SPE International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production. Society of Petroleum Engineers. http://doi.org/10.2118/46577-MS.

Pera-Titus, M., García-Molina, V., Baños, M. A., Giménez, J., Esplugas, S. (2004). Degradation of chlorophenols by means of advanced oxidation processes: a general review. Applied Catalysis B: Environmental, 47(4), 219–256. http://doi.org/10.1016/j.apcatb.2003.09.010.

Philippopoulos, C. J., Poulopoulos, S. G. (2003). Photo-assisted oxidation of an oily wastewater using hydrogen peroxide. Journal of Hazardous Materials, 98(1-3), 201–210. http://doi.org/10.1016/S0304-3894(02)00357-6.

Pignatello, J. J. (1992). Dark and photoassisted iron(3+)-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. Environmental Science & Technology, 26(5), 944–951. http://doi.org/10.1021/es00029a012.

Pitre, R. L. (2013). Produced Water Discharges into Marine Ecosystems. In Offshore Technology Conference. Offshore Technology Conference.

http://doi.org/10.4043/4662-MS.

Plebon, M. J., Saad, M., Fraser, S. (2005). Further Advances in Produced Water De-oiling Utilizing a Technology that Removes and Recovers Dispersed Oil in Produced Water 2 micron and Larger. EARTH Canada Corporation, Montreal, Quebec, Canada.

Qiao, X., Zhang, Z., Yu, J., Ye, X. (2008). Performance characteristics of a hybrid membrane pilot-scale plant for oilfield-produced wastewater. Desalination, 225(1-3), 113–122. http://doi.org/10.1016/j.desal.2007.04.092.

Rabalais, N. N., Mckee, B. a, Reed, D. J., Means, J. C. (1991). Fate and Effects of Nearshore Discharges of OCS Produced Waters. Volume I. Executive Summary. OCS Study/MMS 91-0004. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Regional Office, New Orleans, Louisiana, 48 pp.

Renou, S., Givaudan, J. G., Poulain, S., Dirassouyan, F., Moulin, P. (2008). Landfill leachate treatment: Review and opportunity. Journal of Hazardous Materials, 150, 468–493. http://doi.org/10.1016/j.jhazmat.2007.09.077.

Rivas, F. J., Beltrán, F., Carvalho, F., Acedo, B., Gimeno, O. (2004). Stabilized leachates: Sequential coagulation-flocculation + chemical oxidation process. Journal of Hazardous Materials, 116, 95–102. http://doi.org/10.1016/j.jhazmat.2004.07.022.

Rivas, F. J., Kolaczkowski, S. T., Beltrán, F. J.,. Mclurgh, D. B. (1998). Development of a model for the wet air oxidation of phenol based on a free radical mechanism. Chemical Engineering Science, 53, 14, 2575-2586.

Røe Utvik, T. I. (1999). Chemical characterization of produced water from four offshore oil production platforms in the North Sea. Chemosphere, 39(15), 2593–2606. http://doi.org/10.1016/S0045-6535(99)00171-X.

Saad, M.A., El-Sukkary, M.M.A., El Rayes, S.M., Pactor, J.M. (2016). Plant modification to re-use the produced water from the de-hydration unit at NGL plant for irrigation. Physical Sciences Research International, 4(1), 1-6.

Safarzadeh-Amiri, A., Bolton, J. R., & Cater, S. R. (1997). Ferrioxalate-mediated photodegradation of organic pollutants in contaminated water. Water Research, 31(4), 787–798. http://doi.org/10.1016/S0043-1354(96)00373-9.

Saien, J., Nejati, H. (2007). Enhanced photocatalytic degradation of pollutants in petroleum refinery wastewater under mild conditions. Journal of Hazardous Materials, 148, 491–495.

Santos, M. R. G., Goulart, M. O. F., Tonholo, J., Zanta, C. L. P. S. (2006). The application of electrochemical technology to the remediation of oily wastewater. Chemosphere, 64, 393–399.

Serpone, N. (1997). Relative photonic efficiencies and quantum yields in heterogeneous photocatalysis. Journal of Photochemistry and Photobiology A: Chemistry, 104, 1-12.

Seureau, J. J., Aurelle, Y., Hoyack, M. E. (2013). A Three-Phase Separator for the Removal of Oil and Solids From Produced Water. In SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers. http://doi.org/10.2118/28535-MS.

Severn Trent Services, Fort Washington, Pa. – February 5, 2004. Visited in September, 2016: http://www.severntrentservices.com/files/news/pdf/EMIT-Uses-Higgins-Loop-CCIX-System.pdf.

Shokrollahzadeh, S., Golmohammad, F., Naseri, N., Shokouhi, H., Arman-mehr, M. (2012). Chemical oxidation for removal of hydrocarbons from gas–field produced water. Procedia Eng. 2012;42:942–947.

SOEP. (1996). Sable Offshore Energy Project Environmental Impact Statement.

Spitz, L.R. (2003). Advanced Mobile Water Treatment Systems for Treating Coal Bed Methane Produced Water, a paper presented at the 2003 Ground Water Protection Council meeting.

Stephenson, M. T. (1992). A Survey of Produced Water Studies. In J. P. Ray  F. R. Engelhardt (Eds.), Produced Water (pp. 1–11). Boston, MA: Springer US. http://doi.org/10.1007/978-1-4615-2902-6.

Stepnowski, P., Siedlecka, E. M., Behrend, P., Jastorff, B. (2002). Enhanced photo-degradation of contaminants in petroleum refinery wastewater. Water Research, 36(9), 2167–2172. http://doi.org/10.1016/S0043-1354(01)00450-X.

Stewart M. (2008). Disposal Standards. In Surface Production Operations: Design of Oil Handling Systems and Facilities (3rd ed.).

Strømgren, T., Sørstrøm, S.E., Schou, L., Kaarstad, I.,  Aunaas, T., Brakstad, O.G.,  Johansen, Ø. (1995). Acute toxic effects of produced water in relation to chemical composition and dispersion. Mar. Environ. Res. 40:147-169.

Sun, Y., Zhang, Y., Quan, X. (2008). Treatment of petroleum refinery wastewater by microwave-assisted catalytic wet air oxidation under low temperature and low pressure. Separation and Purification Technology, 62, 565–570.

Tang, W. Z. (2004). Physicochemical Treatment of Hazardous Wastes. CRC Press.

Tao, F. T., Pilger, P., Dyke, C. (1993). Reducing aqueous boron concentrations with reverse osmosis membranes operating at a high pH. US Patent 5,250,185.

Taulis, M. (2007). Groundwater characterization and disposal modelling for coal seam gas recovery. Environmental Engineering. Christchurch, New Zealand University of Canterbury. PhD: 334.

Tchobanoglous, G., Burton, F. L., Stensel, H. D., Eddy, M. (2003). Wastewater Engineering: Treatment and Reuse. Retrieved from http://books.google.es/books/about/Wastewater_Engineering_Treatment_and_Reu.html?id=L1MAXTAkL-QC&pgis=1.

Tellez, G. T., & Nirmalakhandan, N. (1992). Bioreclamation of Oilfield Produced Wastewaters: Characterization and Feasibility Study. In Produced Water (pp. 523–533). Springer US.

Tellez, G. T., Nirmalakhandan, N., Gardea-Torresdey, J. L. (2002). Performance evaluation of an activated sludge system for removing petroleum hydrocarbons from oilfield produced water. Advances in Environmental Research, 6(4), 455–470. http://doi.org/10.1016/S1093-0191(01)00073-9.

Texas Coorperative Extension. (2003). Irrigation Water Quality Standards and Salinity Management Strategies.

Tibbetts, P. J. C., Buchanan, I. T., Gawel, L. J., Large, R. (1992). A Comprehensive Determination of Produced Water Composition. In Produced Water (pp. 97–112). Springer US.

Tiburtius, E. R. L., Peralta-Zamora, P., Emmel, A. (2005). Treatment of gasoline contaminated waters by advanced oxidation processes. Journal of Hazardous Materials B, v. 126, p. 86–90.

Tsang, P., Martin, C. (2004). Economic Evaluation of Treating Oilfield Produced Water for Potable Use. In Proceedings of SPE International Thermal Operations and Heavy Oil Symposium and Western Regional Meeting. Society of Petroleum Engineers. http://doi.org/10.2118/86948-MS.

USEPA. (1996). Development Document for Final Effluent Limitations Guidelines and Standards for the Coastal Subcategory of the Oil and Gas Extraction Point Source Category. EPA Number: 821R96023.

Van den Broek, W. M. G. T., Plat, R., Van der Zande, M. J. (2013). Comparison of Plate Separator, Centrifuge and Hydrocyclone. In SPE International Oil and Gas Conference and Exhibition in China. Society of Petroleum Engineers. http://doi.org/10.2118/48870-MS.

Veil, J. A., Puder, M. G., Elcock, D., Redweik, R. J. J. (2004). A White Paper Describing Produces Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane. Water, (January), 87. Retrieved from http://netl.doe.gov/File Library/Research/Energy Analysis/Publications/ProdWater-WhitePaper.pdf.

Veolia water technologies. September 2016. http://technomaps.veoliawatertechnologies.com/opus/en/.

Walling, C., Weilt, T. (1974). The ferric ion catalyzed decomposition of hydrogen peroxide in perchloric acid solution. International Journal of Chemical Kinetcs, 6, 507–516.

Wang, S. (2008). A Comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater. Dyes and Pigments, 76(3), 714–720. http://doi.org/10.1016/j.dyepig.2007.01.012.

Watson, I. C., Morin, O. J., Henthorne, L. (2003). Desalting Handbook for Planners. Journal of Pain Palliative Care Pharmacotherapy, 72(72), 1–310. http://doi.org/10.3109/15360288.2011.620691.

Wicks, Z. (2007). Organic Coatings: Science and Technology. Wiley & Sons, Inc.

Wilf, M., Awerbuch, L., Bartels, C., Mickley, M., Pearce, G., Voutchkov, N. (2007). The Guidebook to Membrane Desalination Technology : Reverse Osmosis, Nanofiltration and Hybrid Systems Process, Design, Applications and Economics.

Xu, P., Drewes, J. E. (2006). Viability of nanofiltration and ultra-low pressure reverse osmosis membranes for multi-beneficial use of methane produced water. Separation and Purification Technology, 52(1), 67–76. http://doi.org/10.1016/j.seppur.2006.03.019.

Yang, Y., Zhang, X., Wang, Z. (2002). Oilfield produced water treatment with surface-modified fiber ball media filtration. Water Science and Technology : A Journal of the International Association on Water Pollution Research, 46(11-12), 165–70.

Yavuz, Y., Koparal, A. S. (2006). Electrochemical oxidation of phenol in a parallel plate reactor using ruthenium mixed metal oxide electrode. Journal of Hazardous Materials B, 136, 296–302.

Younker, J.M., Walsh, M.E. (2014). Bench-scale investigation of an integrated adsorption–coagulation–dissolved air flotation process for produced water treatment. Journal of Environmental Chemical Engineering, 2 (1), 692–697.

Zhao, X., Wang, Y., Ye, Z., Borthwick, A. G. L., Ni, J. (2006). Oil field wastewater treatment in Biological Aerated Filter by immobilized microorganisms. Process Biochemistry, 41(7), 1475–1483. http://doi.org/10.1016/j.procbio.2006.02.006.

Zhong, J., Sun, X., Wang, C. (2003). Treatment of oily wastewater produced from refinery processes using flocculation and ceramic membrane filtration, Sep. Purif.Technol. 32 (2003) 93–98.

Zhou, F. S., Zhao, M. F., Ni, W. X., Dang, Y. S., Pu, C. S., Lu, F. J. (2000). Inorganic polymeric flocculent FMA for purifying oilfield produced water: preparation and uses. Oilfield Chemistry, 17, 256–259.

Zouboulis, A.I., Avranas, A., (2000). Treatment of oil-in-water emulsions by coagulation and dissolved-air flotation, Colloids and Surfaces A: Physicochemical and Engineering Aspects 172, 153-161.

# Chapter 3. Pretreatment of Produced Water for Oil and Grease Removal: Enhanced Flotation / Sedimentation

**Content**

## 3.1. INTRODUCTION

Produced water (PW) is the name given to the water that is brought to the surface along with oil or gas in extraction operations. It includes the formation water (trapped underground) and injection water that are extracted together with the fossil fuel during oil and gas production (Arthur et al, 2011; Fakhru'l-Razi et al, 2009; Neff, 2002; Veil et al, 2004). PW is generated in large amounts (the water to oil ratio is around 3:1) (Khatib and Verbeek, 2002) and has a complex composition that includes organic and inorganic substances, with the main components being salts, free and emulsified oils, phenols, organic acids, benzene, toluene, ethylbenzene and xylene (BTEX), and polycyclic aromatic hydrocarbons (PAHs) (Veil et al, 2004). Among these components, the oil and grease (O&G) fraction, composed of hydrocarbons and fatty acids, is subject to more legislative restrictions for discharge (Khatib and Verbeek, 2002; Yang, 2001). The chemical composition of PW from an average discharge is summarized in Table 3.1.

Table 3.1. Main components of produced water from oilfields (Utvik and Hasle, 2015)

| **Compound group** | **Concentration, mg $L^{-1}$** |
|---|---|
| Salts | Up to 300000 |
| Oil and grease | 15-200 |
| BTEX | 0.7-24 |
| PAH | 0.04-3 |
| Organic Acids | 7-760 |
| Phenols | 0.4-23 |

In addition to its natural components, PW may include chemical additives dosed in drilling, to treat or prevent operational problems and in the oil/water separation process (Arthur et al, 2011; Stephenson, 1992). At present, a large part of PW generated at onshore facilities worldwide is reinjected into the wells. As a result, to avoid plugging, the treatments in onshore oil and gas production operations are mostly designed to remove dispersed O&G and suspended solids. In offshore operations, since the common practice is to discharge the treated PW to the sea, the main treatment objective is to reduce O&G to 30-40 mg $L^{-1}$ depending on the location of the platform and the applicable legislation (e.g. 29 mg $L^{-1}$ in the US, 30 mg $L^{-1}$ in Canada) (Produced water market, 2011; Veil et al, 2004; Williams, 2011). In those cases, conventional PW treatment trains are composed of physical separation technologies such as the API separator, coalescers or hydrocyclones, as it was shown in the chapter 2 (Figure 2.2). These technologies are in most cases incapable of producing an effluent compatible with standards for beneficial water reuse (e.g. industrial processes) (Dores et al, 2012; Hussain et al, 2014).

Advanced water treatment technologies for polishing such as membrane filtration, membrane bioreactor, thermal evaporators or advanced oxidation processes (AOP) can be applied to obtain a secure source of reusable water from treated PW (Dores et al, 2012). Membrane microfiltration and ultrafiltration have been reported as effective processes in oil–water emulsion, although fouling can limit the applicability of membrane treatments (Hilal et al, 2004). Some studies have effectively applied advanced oxidation processes to oil and gas waters (Mota et al, 2008), but a previous treatment, as studied in this chapter, should be carried out to minimize chemical consumption by diminishing suspended solids and organic content.

Due to the complexity of PW and for the reutilization of this wastewater, for generation of high quality water for steam production, and even for other purposes, like irrigation or aquifer recharge, it is not feasible to address their treatment by a single technology. The solution could be the development of integrated processes, i.e. the combination of individual technologies. These techniques could involve a pretreatment, that is studied in the present chapter of the thesis, like dissolved air flotation or settling for reducing the O&G content, optionally followed by membrane ultrafiltration (to remove the residual O&G that remains), an AOP (that will be studied in the next chapter of the thesis) and finally a Reverse Osmosis system for the salts elimination.

Although there are already in the market packaged PW treatment technologies. Most of these solutions are tailormade to meet specific treatment needs for each individual exploitation site. For example, Siemens commercialize AutoShell™ and Monosep™ walnut shell filters (Siemens global website, 2016), to remove oily contaminants from water. However, this solution is only a filtration step that generates a backwash effluent, whose treatment needs to be addressed, and does not produce high quality water able for reuse. CDM has developed a High-Recovery Reverse Osmosis Process (CDM, 2008), for treating PW containing TDS levels up to 20000 mg $L^{-1}$. However, this solution does not offer a consistent pre-treatment for oil removal, so sever fouling events are not prevented. Finally, Veolia water markets treatment systems for high recovery of clean water for reuse or discharge (Veolia webside, 2016), called OPUS™ and OPUS II™, for treatment of water containing high concentrations of silica, organics, hardness, heavy metals, boron and particulates. However, these solutions do not offer a pretreatment to remove oily components.

In this chapter 3, dissolved air flotation (DAF) was selected as one of the pretreatments as conventionally-treated PW still contains low density solids, which this treatment is especially appropriate for removing. The conventional DAF process aims to remove suspended particles from water by bringing them to the surface, and subsequently separate them from the liquid phase. In this process, air is dissolved into water at high pressure in a saturator, and microbubbles are formed by cavitation when water is released into the flotation tank at atmospheric pressure. These microbubbles become attached to the particles, increasing their buoyancy and allowing them to rise to the surface (Al-Shamrani et al, 2002). In many cases, to increase the efficiency of the DAF process, a prior coagulation–flocculation step is carried out (e.g. with ferric chloride) (Zouboulis and Avranas, 2000). The possible limitations of this technology are related to the characteristics of PW. It usually contains natural and added surfactants, leading to oils becoming emulsified and tending to stay in the aqueous phase, which complicates the treatment of this type of water by flotation processes. On the other hand, another characteristic of PW is its high salinity, which can negatively affect flotation since density, dynamic viscosity and surface tension are all higher in seawater than in freshwater, and also due to the lower solubility of air in this kind of matrix (Haarhoff and Edzwald, 2013). In fact, according to other authors, emulsified oils are difficult to treat (Hilal et al, 2004; Hu et al, 2002; Mostefa and Tir, 2004) due to the presence of surfactants. Mostefa and Tir (2004) treated emulsions of cutting oil in water by coupling flocculation (using other chemical coagulants) with electroflotation to separate the oil and decrease COD and turbidity. However, the main disadvantage of this process is the high cost of electrode materials (Hosny, 1996; Ben Mansour and Chalbi, 2006).

In this work, settling was also studied as a promising pretreatment for PW polishing technologies. Sedimentation is a separation in which gravity separates solids from the water due to their different specific weight. This treatment was tested since there are other related industries, such as the olive oil producing industry, which uses it for oily wastewaters treatment (Al-Enazi et al, 2013). As in the flotation pretreatment, the settling was aided by a previous coagulation-flocculation step in order to increase the particle size and thus the settling efficiency.

In the sedimentation process, high turbidity and O&G removals could be achieved although it is a slow process if only the coagulant is used. Since conventional DAF was not effective in removing turbidity, due to the fact that the rising velocity of the bubbles caused floc breakup, as would be explained later, a new process using microspheres instead of air microbubbles has also been studied (with the added advantage of saving the energy required for air injection on a conventional DAF unit). Microspheres are added into the system during the rapid mix stage (coagulation phase), and then incorporated into the floc matrix to drive the flotation process, replacing the use of microbubbles. Microspheres have been used in other studies for the removal of algae (Ometto et al, 2014) but no references for this type of wastewater were found.

In this context, the purpose of the work present in this chapter is to determine the efficacy of four different processes to treat synthetic PW, using the same coagulant. For the flotation experiments (DAF), different concentrations of ferric chloride were tested at different pH levels. In the settling experiments, different coagulant concentrations and settling times were studied. Finally, the efficacy of enhanced dissolved air flotation (E-DAF) was investigated using glass microspheres of limited buoyancy without air injection and using the same process with a subsequent injection of microbubbles.

Although the next treatment after this physical separation is an AOP for the soluble organic compounds elimination, that is studied in chapter 4, some Fenton and photo-Fenton tests are carried out in this chapter 3 too in order to study its application in the polishing of the O&G content of the effluent even further and also as preliminary tests of what is studied in more detail in chapter 4 for the removal of all the soluble compounds such as phenol (which as is shown in this chapter 3, was not eliminated in the previous treatment), taking advantage of the residual iron after these pretreatments.

The classic Fenton reaction interpreted by Haber and Weiss (1934), as cited by Bossmann et al, (1998), consists of an aqueous combination of hydrogen peroxide ($H_2O_2$) and ferrous ions ($Fe^{2+}$), in an acid medium, leading to the decomposition of $H_2O_2$ mainly into a hydroxyl ion and a hydroxyl radical, through the oxidation of $Fe^{2+}$ to $Fe^{3+}$ (Neyens and Baeyens, 2003). Simultaneously, as part of the regular Fenton cycle, $Fe^{2+}$ is regenerated by the reaction between $Fe^{3+}$ and $H_2O_2$ (Kwan and Voelker, 2002; Duesterberg and Waite, 2006). According to Pignatello (1992), UV irradiation strongly accelerates the degradation rate of organic pollutants from Fenton's reagent. Given its sensitivity to UV-Vis radiation for wavelengths above 300 nm, the photolysis of $Fe^{3+}$ enables regeneration of $Fe^{2+}$. Therefore, UV accelerates catalytic Fenton processes when the concentration of $Fe^{2+}$/ $Fe^{3+}$ is lower than $H_2O_2$, where iron reduction is the rate-limiting step.

## 3.2. MATERIALS AND METHODS

### 3.2.1. Synthetic produced water for DAF, Settling and E-DAF treatments

Synthetic PW consisted of an emulsion based on filtered seawater (from the Mediterranean Sea, Barcelona), since in certain locations, the type and concentration of salts is similar to that of seawater, to which 50 mg $L^{-1}$ of olive oil (as oil fraction) and 100 mg $L^{-1}$ of gasoline lubricant (as a grease fraction) were added in order to simulate an approximate concentration of 150 mg $L^{-1}$ of O&G (slightly over the 100 mg $L^{-1}$ of O&G of the effluent from conventional PW treatment trains shown in Figure 2.2). Additionally, 5 mg $L^{-1}$ of phenol (Sigma-Aldrich), as a representative dissolved organic compound found in PW, was added. The emulsion was formed by adding 15 µL of Triton-X-100 (Sigma-Aldrich) surfactant as emulsifier (Younker and Walsh, 2014). This mixture was stirred at 1,600 rpm for 10 min. The average COD, turbidity, phenol, O&G concentration and pH in the simulated PW are presented in Table 3.2 (a).

### 3.2.2. Synthetic produced water for Fenton and photo-Fenton

As the effluent from the treatments that turned out to be more effective, sedimentation and E-DAF, still contained around 30 mg $L^{-1}$ or less of O&G, AOP influents were synthetized with 20 mg $L^{-1}$ of gasoline lubricant and 10 mg $L^{-1}$ of olive oil in order to simulate an approximate concentration of 30 mg $L^{-1}$ of O&G. As phenol was not eliminated in the pretreatment essayed, 5 mg $L^{-1}$ phenol was added again. For the emulsion, 10 µL of Triton-X-100 (Sigma-Aldrich) surfactant was added. This mixture was stirred at 14,000 rpm for 10 min using an Ultra-Turrax homogenizer (IKA, T25) to achieve a more stable and homogeneous emulsion, as the dispersed oil had already been eliminated in the previous treatment, and the remaining fraction could be considered completely emulsified. The average COD, phenol and O&G concentrations and pH in the simulated PW are presented in Table 3.2 (b).

Table 3.2. Average quality parameters of simulated PW used before DAF, settling and E-DAF treatments (a) and before Fenton and photo-Fenton processes (b)

(a)

| **Water Quality Parameter of initial simulated PW used in the study** | **Value** |
|---|---|
| COD (mg $L^{-1}$) | 342.5 |
| Turbidity (NTU) | 120 |
| Phenols (mg $L^{-1}$) | 5 |
| O&G (mg $L^{-1}$) | 167.8 |
| pH | 8 |

(b)

| **Water Quality Parameter of simulated PW before Fenton and photo-Fenton processes** | **Value** |
|---|---|
| COD (mg $L^{-1}$) | 133 |
| Phenols (mg $L^{-1}$) | 5 |
| O&G (mg $L^{-1}$) | 40 |
| pH | 8 |

### 3.2.3. DAF experiments

All experiments were performed using a Platypus™ DAF Jar Tester (Microfloc, Australia) composed of a saturator with a capacity of 1800 mL, where seawater was saturated with compressed air (6 bar) to form an air/water mixture that was released into the jar at atmospheric pressure forming the microbubbles, 2 L jars and vertical stirrers with variable speed for each jar.

Different concentrations of coagulant ($FeCl_3$) between 0 and 150 mg $L^{-1}$ were tested. The experiments were conducted at free pH (not controlled), 5.5 and 8 (these were adjusted with concentrated HCl and/or NaOH).

After adding the emulsion in the jar, the appropriate amount of coagulant was added and pH was adjusted if necessary. Coagulation consisted of a 1-min rapid mix at 200 rpm, followed by a 50-rpm flocculation stage for 9 min and 30 rpm for 10 min. After the coagulation-flocculation process with $FeCl_3$, saturated seawater was injected through a nozzle into the 2 L DAF jar containing a liter of emulsion. Flotation was performed for 8 min after injecting air saturated water at 6 bar and a recycle rate of 20%.

After flotation, a sample was taken and COD, turbidity and phenol were measured and compared with the influent sample.

### 3.2.4. Settling experiments

Each experiment was performed in the same vessel that was used in the flotation experiments. In this case, only the stirring was necessary (for the coagulation-flocculation stage).

Different concentrations of the coagulant, $FeCl_3$, between 10 and 100 mg $L^{-1}$ were tested without pH control to avoid the use of more reagents.

Coagulation consisted of a 1-min rapid mix at 200 rpm, followed by a 50 rpm flocculation stage for 9 min and 30 rpm for 10 min. After this, flocs formed and then settled into a sediment; samples from the supernatant were taken at different times (the maximum decanting time was 90 min).

The same parameters as in the flotation experiments were analyzed; additionally, the content of O&G was determined.

### 3.2.5. E-DAF experiments

Experiments carried out with microspheres and a subsequent air injection were performed using the Platypus™ DAF Jar Tester. In the experiments without air injection, the saturator was not utilized. As a coagulant, different concentrations of iron in the form of $FeCl_3$ were tested (0, 10 and 20 mg $L^{-1}$ of Fe) and a concentration of microspheres between 50-300 mg $L^{-1}$ was used. These thin-walled, hollow glass microspheres were Eccospheres ® IGD101 (Trelleborg, USA), with a mean particle size of 55 microns and a density of 0.19 g $cm^{-3}$.

After adding 1.5 L of synthetic PW to the jar, the appropriate amounts of microspheres and coagulant were added. Coagulation consisted of 2 min of rapid mixing at 200 rpm, followed by a 40 rpm flocculation stage or 90 rpm for 15 min. After this coagulation-flocculation process, in the experiments with air, saturated seawater was injected through a nozzle into the jar containing the emulsion at a recycling rate between 10-22%. After 2 min of flotation, turbidity and concentration of O&G were measured and compared with the influent sample.

### 3.2.6. Fenton and photo-Fenton process

Fenton and photo-Fenton processes were carried out at pH 3 and the reagents used were hydrogen peroxide solution (30% w/w in $H_2O$, with stabilizer) (Sigma-Aldrich, USA) and iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) (Sigma-Aldrich, USA). The Fenton experiments were carried out in 1L stirred topaz bottles (during 6 h or 24 h). In the photo-activated process, the reaction took place inside a Solarbox 3000e (Cofomegra, Italy) equipped with a 2500 W Xenon lamp (Neurtek, Spain) and an outdoor light filter, which allows 290-800 nm wavelengths to pass through. Irradiance was set to 250 W $m^{-2}$ to avoid excessive heating of the sample; the temperature was thereby maintained between 30-35 ºC. The intensity of the radiation from the Xe lamp used in the Solarbox reaching the solution was determined by actinometry, using the Parker method (Hatchard and Parker, 1956), based on the photochemical reduction of the ferrioxalate complex $[Fe(C_2O_4)_3]^{3-}$ to Fe (II) in acid medium. The intensity value resulted 6.5 $10^{-4}$ Einstein $min^{-1}$. These experiments were carried out in opened stirred 1L borosilicate glass jars (Duran, Germany).

### 3.2.7. Analytical methods

The pH measurements were performed using a PH 25 CRISON pH-meter. Turbidity was analyzed using a 2100AN Laboratory Turbidimeter. The Chemical Oxygen Demand (COD) and phenols were determined photometrically using Hach Lange kits, LCK 414 and LCK 345, respectively. The measurement of total iron was carried out using the LCW 902 test, followed by LCK 321 (Hach Lange). Total O&G concentrations were determined by EPA 1664B gravimetric method (EPA, 2010). In accordance with the replicas performed in some experiments, the error associated with the O&G measurements was ± 5 mg $L^{-1}$. Hydrogen peroxide consumption in the Fenton reactions was monitored with QUANTOFIX Peroxide test strips. Residual hydrogen peroxide was neutralized at the end of the experiments with the addition of sodium bisulfite (Sigma-Aldrich) to avoid undesirable reactions.

## 3.3. RESULTS AND DISCUSSION

### 3.3.1. DAF experiments

Figure 3.1 shows the COD, turbidity and phenol removal percentages at different coagulant doses and pH levels. Initial PW has a pH of 8. The addition of $FeCl_3$ causes a reduction of the sample pH. The pH range in the experiments at free pH was 7.9-5.3 when 3-150 mg $L^{-1}$ of coagulant was added. As the resulting pH after adding 100 and 150 mg $L^{-1}$ of coagulant was around 5.5, the experiments at free pH using these two concentrations would be the same as at pH 5.5.

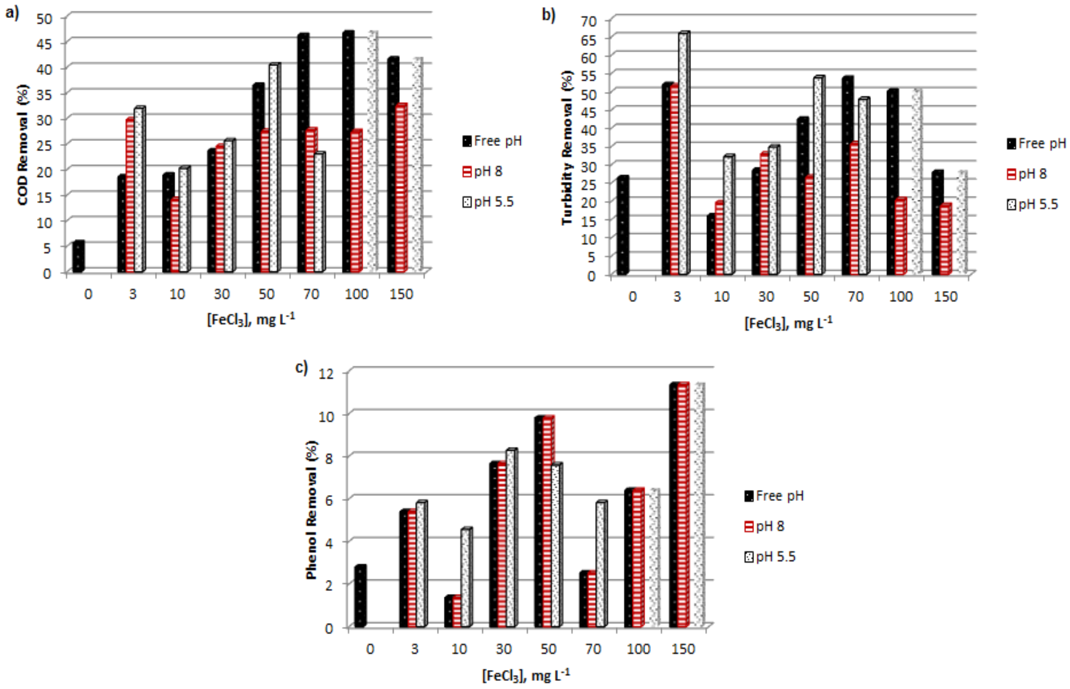


Figure 3.1. a) COD, b) turbidity and c) phenol removal percentages after flotation as a function of the coagulant dose (mg $L^{-1}$) at free pH (between 8-5.3), at pH 8 and 5.5.

As can be observed, higher efficiencies in turbidity and COD removals are achieved when working at free pH or 5.5. This is reasonable, as the optimum pH range for $FeCl_3$ as the coagulant is between 4 and 6 or higher than 8.

A statistical analysis of the presented data was carried out in order to understand the factors affecting the performance of the flotation process, as well as the optimal combination of the factors leading to the highest contaminant removals. In this case, the operational factors considered as playing a role are the coagulant dose and the pH value. The responses that have to be maximized in order to optimize process performance are the COD, turbidity and phenol removal percentages. Figure 3.2 shows the Pareto charts for each response.

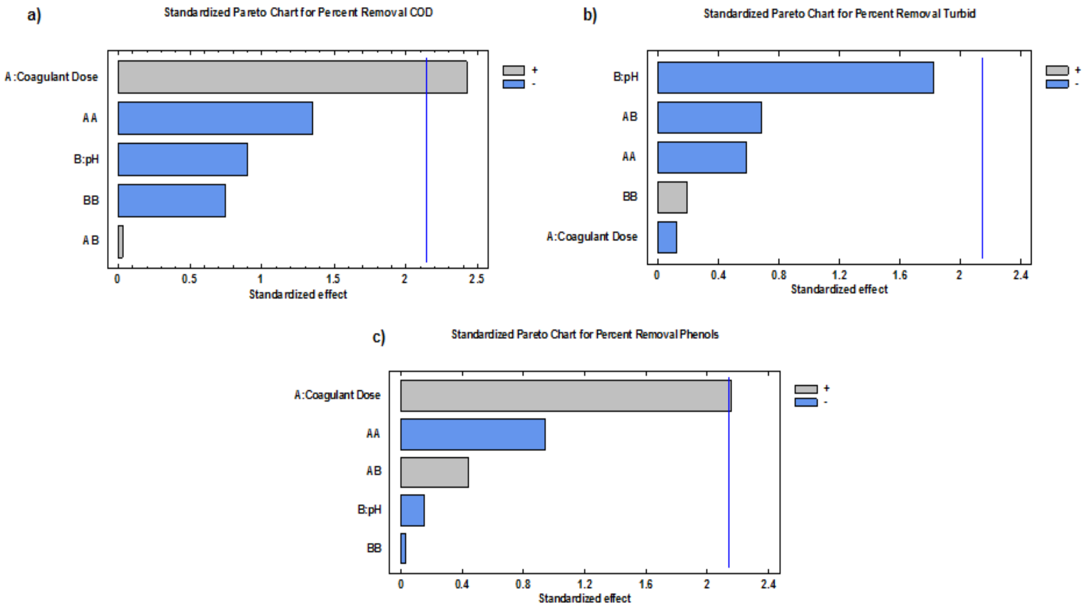


Figure 3.2. Pareto charts for a) COD, b) turbidity and c) phenol removal percentages in the flotation process.

It has been shown that the only operational factor playing a significant role in contaminant removal was the coagulant concentration (Figure 3.2); pH values in the 5.5-7.5 range have no effect on process performance as is also shown in Figure 3.3. Consequently, there would be no need to carry out pH control in the flotation process, which would imply saving reagents costs, as pretreatment for AOP. It is also important to note that the coagulant dose only influenced significantly the removal of COD and phenols, although this component was barely eliminated; and turbidity removal was not significantly affected by different coagulation doses. The result of the optimization analysis is shown in Figure 3.3. As can be seen, the optimal coagulant dose for optimal simultaneous COD and phenol removal was approximately 130 mg $L^{-1}$ of $FeCl_3$ over a wide range of pH values. At this coagulant concentration, the average percentage removals achieved for COD and phenol were 42% and 9%, respectively. As phenol elimination was very low, since its partitioning into the oil droplet phase is low, considering only COD removal, the best result was a 46.2% of COD reduction using 70 mg $L^{-1}$ of $FeCl_3$ at free pH. 53.6% of turbidity removal was achieved under these conditions. However, when focusing on turbidity, with only 3 mg $L^{-1}$ of $FeCl_3$ at free pH, a turbidity elimination of 65% was obtained. Macroscopic observations of the jar test experiments indicated that coagulation was the main treatment mechanism for removal. However, higher levels of COD elimination were not achievable due to the fact that the flocs formed were not consistent and broke when the microbubbles were injected.

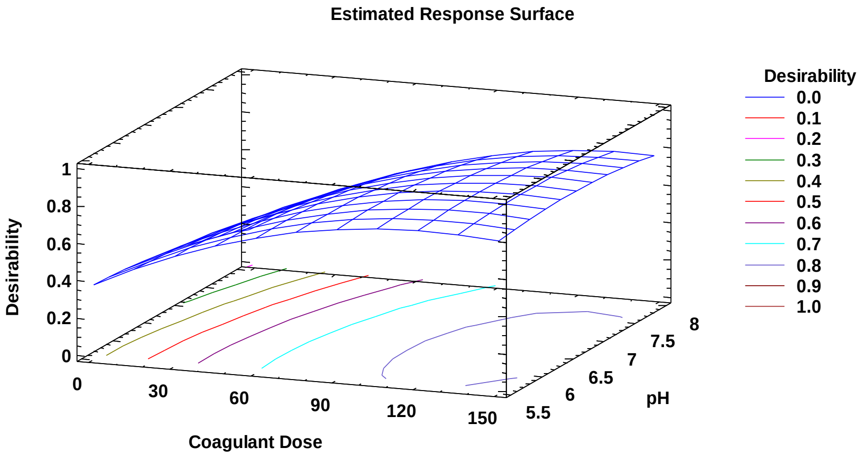


Figure 3.3. Optimization of operational parameters for simultaneous COD and phenol removal in the flotation process.

Younker and Walsh (2014) also removed O&G in synthetic PW below discharge standards using $FeCl_3$ coagulation-DAF and integrating adsorption with organoclay-coagulation-DAF, but starting from a lower initial O&G concentration in their PW, which was simulated according to a different recipe. As in this study, phenol was not eliminated by these treatments.

### 3.3.2. Settling experiments

Preliminary sedimentation tests were carried out with 50 mg $L^{-1}$ of coagulant at pH 8 and without pH control (data not shown). As differences of turbidity and COD were found to be not noticeable when raising the pH at longer sedimentation times, it was decided that the other experiments would be carried out without controlling the pH. A minimum coagulant dose of 30 mg $L^{-1}$ was chosen in the settling experiments, because lower $FeCl_3$ concentrations do not result in apparent sedimentation (data not shown here).

Figure 3.4 shows the COD and turbidity removal percentages at different coagulant doses and settling times. The results for phenol are not shown, the removal of this component remains constant for all process conditions (at an average of 11%). As shown in the Pareto chart (Figure 3.5), phenol removal is not affected by either operational factor.

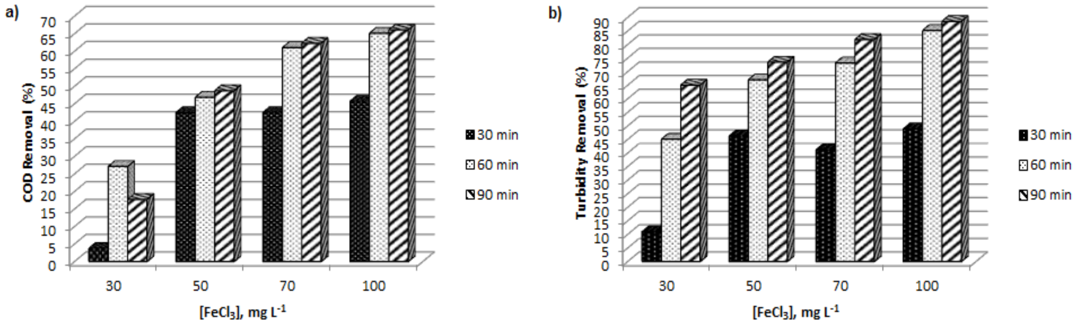


Figure 3.4. a) COD and b) turbidity removal percentages at 30, 60 and 90 min of settling, using 30, 50, 70 and 100 mg L$^{-1}$ of FeCl$_3$ at free pH (7, 6.6, 6.3, 5.9, respectively)

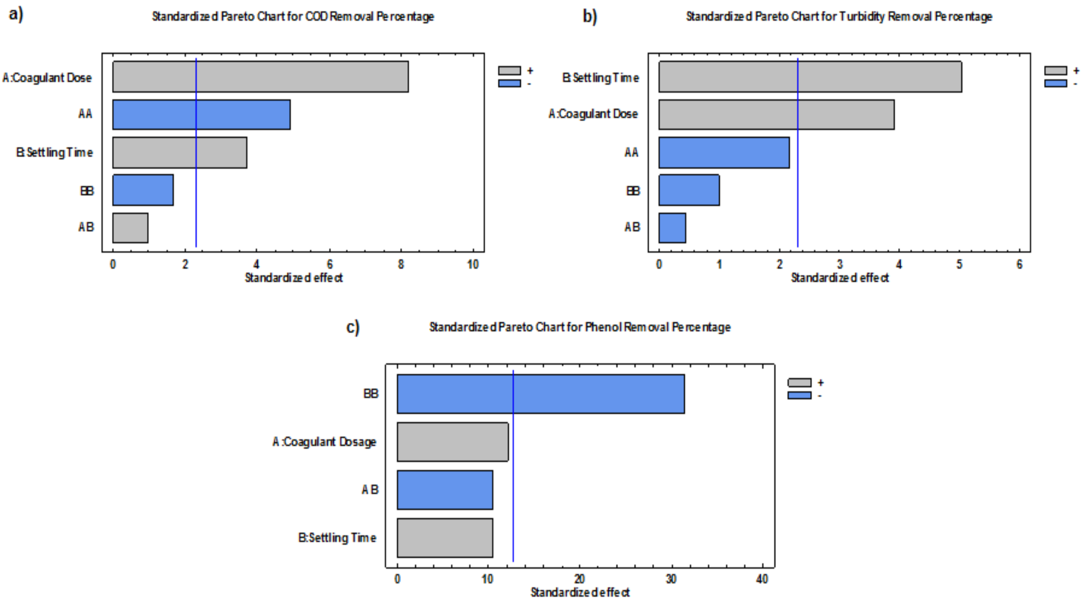


Figure 3.5. Pareto charts for a) COD, b) turbidity and c) phenol removal percentages in the settling process

As the flotation experiments, a statistical analysis of the data presented previously was carried out. In the case of the settling process, the operational factors evaluated were the coagulant concentration and the settling time. The responses that have to be maximized in order to optimize the process performance were, as for flotation, COD, turbidity and phenol removal percentages. Figure 3.5 shows the Pareto charts for each response.

It has been shown that both coagulant concentration and settling time played a significant role in COD and turbidity removal; increasing magnitudes of both operational factors cause an improvement in contaminant removal performance (Figure 3.5). Phenol removal appeared unaffected by either operational factors; as in the flotation experiments, the removal of phenols remained constant for any process conditions (at an average of 11%). According to this, optimization was carried out taking into account only the COD removal percentage. The results of the optimization analysis are shown in Figure 3.6. As can be seen, the optimal coagulant dose for optimal COD removal was approximately 86 mg $L^{-1}$ of $FeCl_3$, while the optimal settling time was 83 min. Under these process conditions, the COD achievable removal percentage was 69%. Under these optimal process conditions for COD removal, the turbidity removal percentage approached 90%; the COD and turbidity removal optimums were very close, potentially pointing to a joint elimination mechanism.

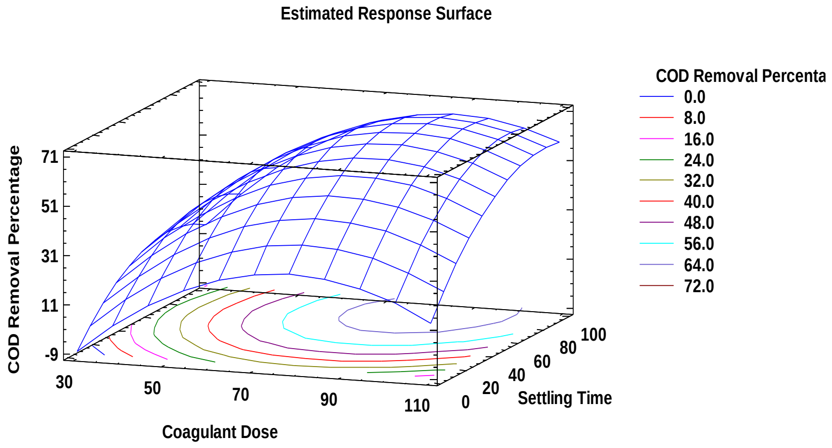


Figure 3.6. Optimization of operational parameters for COD removal in the settling process

Because a higher COD and turbidity removals were achieved with a settling treatment compared to flotation, O&G was also analyzed in this case. Table 3.3 shows the analysis of O&G of the samples at the end of the settling (at 90 min, close to the process optimum). It can be seen that 86% of O&G was removed up to 70 mg $L^{-1}$ or higher; a final concentration of O&G that complies with the legislation (< 30 mg $L^{-1}$ of O&G) was achieved under these conditions. This means that under the optimum conditions in the process (86 mg $L^{-1}$ of coagulant and 83 min of settling time), oils and greases were removed to an acceptable extent from an effluent discharge requirement perspective.

Table 3.3. O&G analysis of the water after 90 min of settling

| **Initial [O&G], (mg $L^{-1}$)** | **[$FeCl_3$], (mg $L^{-1}$)** | **Final [O&G], (mg $L^{-1}$)** | **O&G removal, (%)** |
|---|---|---|---|
| 155.4 | 30 | 51.6 | 66.8 |
| 155.4 | 50 | 31.4 | 79.8 |
| 183.8 | 70 | 25.8 | 86.0 |
| 183.8 | 100 | 25.8 | 86.0 |

After essaying this process, it can be concluded that coagulation was the main separation mechanism for O&G removal in settling and DAF. However, settling appeared to be more effective, unlike DAF, where the microbubbles caused the flocs formed to rupture. Similar results for O&G and turbidity removals were obtained by Younker and Walsh (2016) by adsorption with powdered activated carbon (PAC) and organoclay adsorbents, and like our study, using $FeCl_3$ and settling. For the removal of 5 mg $L^{-1}$ of phenol, the best option was to use high doses of PAC (1000 mg $L^{-1}$). In this work an AOP will be carry out for the removal of dissolved organic compounds.

### 3.3.3. E-DAF experiments

A series of E-DAF experiments were performed. Table 3.4 shows the PW turbidity removal percentages after experiments with and without air injection, and also the O&G removal percentages of selected experiments.

Table 3.4. Turbidity and O&G removals percentages in the flotation experiments with and without air injection, with different doses of microspheres, coagulant and agitation intensity during flocculation, at free pH (pH of 8, 6.9 and 6.5 for 0, 10 mg L$^{-1}$ and 20 mg L$^{-1}$ of iron respectively)

| | | | **Turbidity removal, %** | | **O&G removal, %** | |
|---|---|---|---|---|---|---|
| **Microsphere concentration, (mg L$^{-1}$)** | **Iron concentration, (mg L$^{-1}$)** | **Agitation intensity during flocculation (rpm)** | **Without air** | **With air** | **Without air** | **With air** |
| 50 | 10 | 40 | 74.2 | 61.8 | 77.9 | 65.8 |
| 50 | 10 | 90 | 44.2 | 69.5 | 45.1 | - |
| 50 | 20 | 40 | 66.5 | 73.6 | 72.3 | 75.7 |
| 50 | 20 | 90 | 15.0 | 66.1 | - | - |
| 150 | 10 | 40 | 81.0 | 61.0 | 88.3 | 66.2 |
| 150 | 10 | 90 | 25.8 | 55.5 | - | - |
| 150 | 20 | 40 | 72.9 | 66.7 | - | - |
| 150 | 20 | 90 | - | 62.4 | - | - |
| 300 | 10 | 40 | 62.9 | 72.7 | - | - |
| 300 | 10 | 90 | 68.8 | 51.1 | 83.1 | - |
| 300 | 20 | 40 | 86.2 | 62.3 | 94.3 | 71.7 |
| 300 | 20 | 90 | 83.5 | 64.4 | - | 71.3 |
| 0 | 10 | 40 | - | 15.0 | - | - |
| 0 | 20 | 40 | - | 22.0 | - | - |
| 300 | 20 | 40 | - | 72.2 | - | - |
| 300 | 20 | 30 | 84.2 | | - | - |
| 300 | 0 | 40 | 32.5 | 27.4 | - | - |

A statistical analysis of the turbidity data was carried out in order to determine the factors affecting the performance of both flotation processes and to maximize turbidity removal. The operational studied factors were microsphere concentration (mg $L^{-1}$), iron concentration (mg $L^{-1}$) and flocculation rate (rpm).

A Pareto chart for the experiments with microspheres and without air injection is shown in Figure 3.7. Figure 3.8 shows the estimated response surface setting the iron concentration at which the highest eliminations were obtained according to the statistical model. As can be seen in these figures, the operational factor that affected turbidity removal the most was the agitation intensity during flocculation. Low flocculation rates maximized turbidity removal for the conditions studied. However, with high concentrations of microspheres, fixing 20 mg $L^{-1}$ of iron concentration, the flocculation rate had no influence, as shown in Figure 3.8, so the lowest speed would be advisable to reduce energy consumption. The Pareto chart in Figure 3.7 also shows that the concentration of iron was not significant, but its interaction with the concentration of microspheres was influential, as it was the interaction between the flocculation rate and the microspheres concentration. The maximum turbidity removal according to the statistical model was 87.2%, achieved with a flocculation rate of 40 rpm, a 20 mg $L^{-1}$ of iron dose and a microspheres concentration of 300 mg $L^{-1}$. However, the effect of microspheres and iron concentrations was not very high; depending on the required percentage of removal, it would be therefore possible to significantly lower the concentration of both to optimize operational costs keeping an acceptable removal.

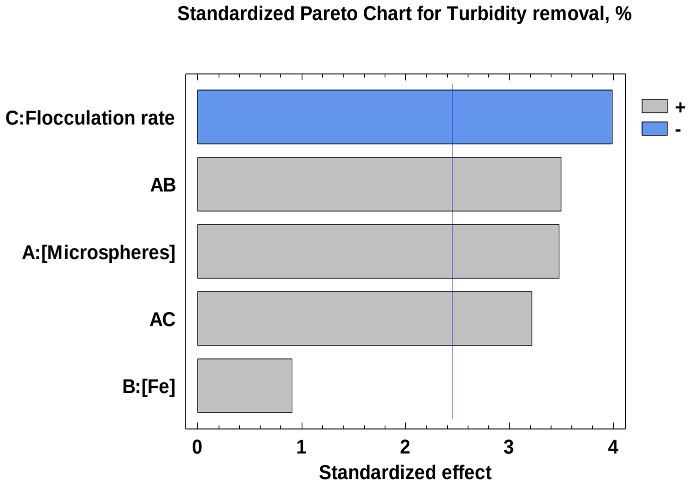


Figure 3.7. Pareto chart for turbidity removal percentage in the flotation experiments with microspheres without air injection.

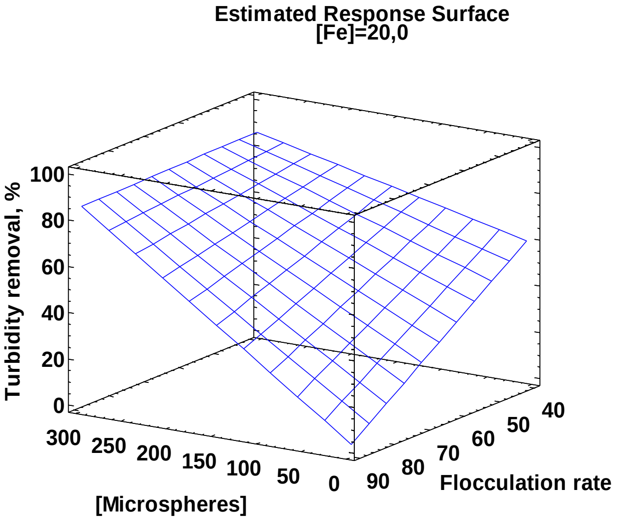


Figure 3.8. Estimated response surface in the flotation experiments with microspheres without air injection.

The Pareto chart for the experiments carried out with microspheres and air injection is shown in Figure 3.9, while Figure 3.10 shows the estimated response surface when setting the flocculation rate at 40 rpm, since it was not statistically significant according to the Pareto chart.

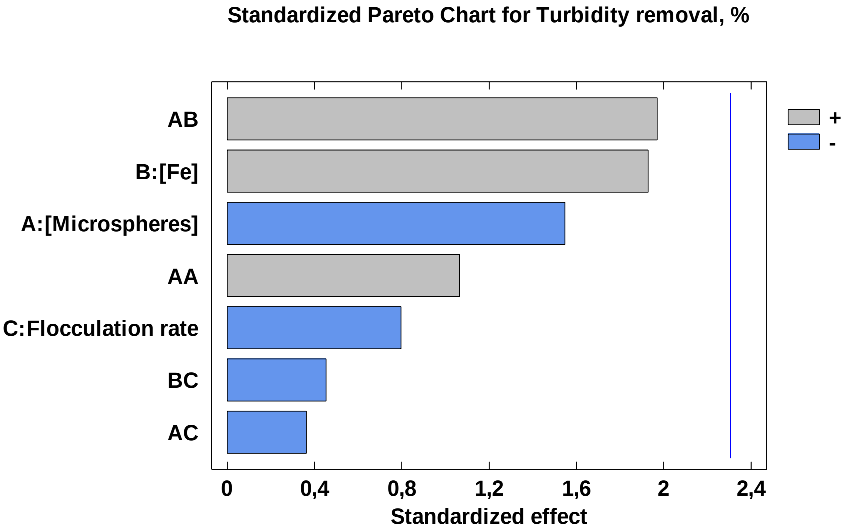


Figure 3.9. Pareto chart for turbidity removal percentage in the experiments with microspheres + air injection

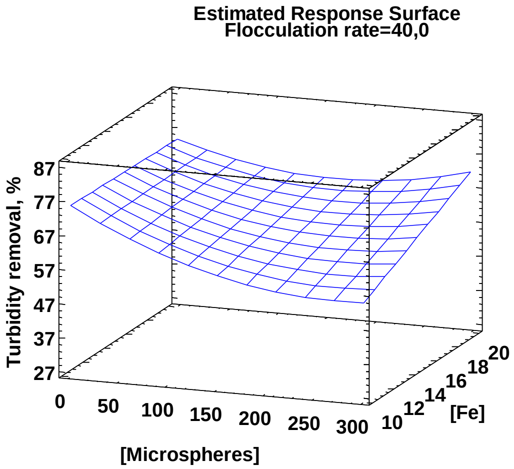


Figure 3.10. Estimated response surface in the experiments with microspheres with air injection

When using microspheres and microbubbles injection, the statistics indicated that the model as fitted explained only 47.9% of the variability in turbidity removal. As can be seen in the Pareto chart, there was no significant operational factor for turbidity elimination. Nevertheless, it was concluded that air injection was not beneficial for turbidity removal.

The elimination percentages ranged from 95% to 45% in O&G removal in the selected experiments, considering both flotation processes. The final O&G concentration of the PW after these treatments was between 10 and 92 mg L$^{-1}$ in the worst case. However, most of the experiments showed a final content between 30-40 mg L$^{-1}$ of O&G, close to the limit of discharge allowed by legislation. As can be seen in Figure 3.11, the final O&G concentration showed a lineal correlation with turbidity (R$^2$= 0.9471); this linear dependence was higher in experiments without air injection.

$$\text{O\&G}\ (mg\ L^{-1})\ = 1.604\ \times Turbidity\ (NTU) - 18.536 \qquad (3.1)$$

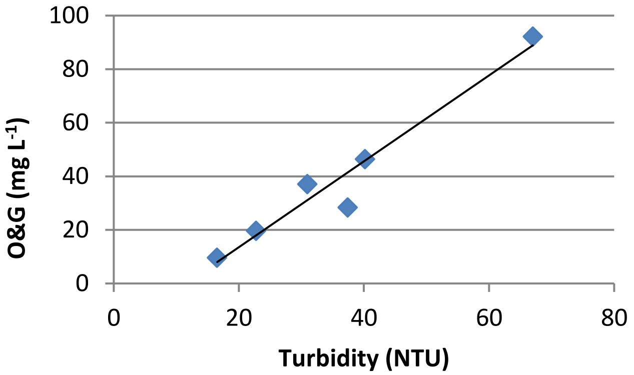


Figure 3.11. Representation of O&G concentration (mg $L^{-1}$) and turbidity (NTU) of the effluent after microsphere flotation without air injection

Given their similar and positive results, settling and E-DAF without air injection could be considered as suitable alternatives for O&G and turbidity removals. While the main drawback of enhanced flotation could be the costs of the microspheres and their recovery, it could be still the most convenient choice in those cases where the space and time required for the settling process are limiting factors.

### 3.3.4. Fenton process

Despite the noticeable removals of turbidity and O&G obtained after settling and the E-DAF processes, the resultant effluent still contained a residual concentration of O&G (O&G values lower than 30 mg $L^{-1}$). In addition, phenol, as a representative of dissolved organic compounds, was not eliminated in these processes. Therefore, further polishing could be suggested. Meanwhile, remaining dissolved iron was also observed. After flotation processes, a maximum of 18 mg $L^{-1}$ of total iron was observed using the highest coagulant concentration and 6 mg $L^{-1}$ with the optimal one. After the best settling process conditions, 1.3 mg $L^{-1}$ of total iron remained in the effluent. Since this reagent is fundamental in Fenton and photo-Fenton reactions, these processes were considered as good alternatives for a polishing treatment to remove the remaining O&G content and other organic substances.

With the influent prepared as described in section 3.2.2, a first set of experiments with different concentrations of hydrogen peroxide, $H_2O_2$, starting with the stoichiometric quantity according to COD ($H_2O_2$/COD (w/w) = 2.12) and up to 10 times more, and Fe (II), were carried out for 6 h. Table 3.5 shows the O&G and phenol removal results of these experiments after this reaction time.

Table 3.5. Fenton experiments and O&G and phenol content of PW after 6 h of reaction, at pH 3

| **Experiment num.** | **$H_2O_2$/COD (w/w)** | **$H_2O_2$ (mg $L^{-1}$)** | **$H_2O_2$/Fe (w/w)** | **$Fe^{2+}$ (mg $L^{-1}$)** | **O&G removal (%)** | **Phenol removal (%)** |
|---|---|---|---|---|---|---|
| 1 | 20.0 | 2660.0 | 20.0 | 133.0 | 10.7 | 75.0 |
| 2 | 12.5 | 1662.5 | 12.5 | 133.0 | 57.6 | 80.0 |
| 3 | 5.0 | 665.0 | 1.0 | 665.0 | 0.0 | 53.4 |
| 4 | 5.0 | 665.0 | 5.0 | 133.0 | 21.8 | 60.0 |
| 5 | 4.5 | 600.0 | 2.0 | 300.0 | 34.6 | 68.0 |
| 6 | 4.5 | 600.0 | 10.0 | 60.0 | 2.1 | 6.0 |
| 7 | 2.1 | 283.0 | 2.0 | 141.5 | 12.7 | 52.4 |
| 8 | 2.1 | 283.0 | 10.0 | 28.3 | 4.8 | 42.6 |

Statistically, the final content of O&G after the Fenton reaction did not follow any trend in terms of the dose of reagents used. However, it could be extracted from the table that the maximum O&G removal achieved after

6 hours of Fenton reaction was 57.6% for experiment 2. When lower concentrations of $H_2O_2$ were used, 34.6% of O&G removal is possible, as seen for experiment 5. Furthermore, it was observed that in all these experiments, more than 100 mg $L^{-1}$ of $H_2O_2$ remained in solution after 6 h. Due to this, some experiments were subsequently performed for 24 h in order to give the process time enough to see if further hydrogen peroxide degradation and O&G and phenol removal was obtained. Table 3.6 shows these results. The essayed hydrogen peroxide in this case ranged from the stoichiometric quantity according to COD ($H_2O_2$/COD (w/w) = 2.12) to 5 times the stoichiometric quantity.

Table 3.6. Fenton experiments and O&G and phenol content of PW after 24 h of reaction, at pH 3

| **$H_2O_2$/COD (w/w)** | **$H_2O_2$, (mg $L^{-1}$)** | **$H_2O_2$/Fe (w/w)** | **$Fe^{2+}$, (mg $L^{-1}$)** | **O&G removal, (%)** | **Phenol removal, (%)** | **Residual $H_2O_2$, (mg $L^{-1}$)** |
|---|---|---|---|---|---|---|
| 10.6 | 1409.8 | 2 | 704.9 | 49.3 | 70 | 0 |
| 10.6 | 1409.8 | 50 | 28.2 | 45.6 | 68 | >>100 |
| 6.4 | 845.9 | 26 | 32.5 | 34.4 | 68 | >100 |
| 2.1 | 282.6 | 2 | 141.3 | 48.5 | 68 | 10 |
| 2.1 | 282.6 | 50 | 5.7 | 46.9 | 65 | >100 |

In general, after 24 h of reaction, no significant differences were obtained in the O&G content of the different experiments compared to shorter experiments, except for the lowest dose of $H_2O_2$ added, 283 mg $L^{-1}$. A greater O&G removal after 24 h was obtained than after 6 h (48.5% versus 12.7%, and 46.9% versus 4.8%, depending on the $Fe^{2+}$ dose). Table 3.6 shows that when a $H_2O_2$/Fe (w/w) ratio of 2 was used, a major consumption of $H_2O_2$ took place, which did not entail to a significant increased O&G removal. Phenol was measured throughout the reaction; this compound concentration decreased from 5 mg $L^{-1}$ to < 1.5 mg $L^{-1}$ in the majority of experiments (a 70% phenol removal, reducing its initial concentration to 50% in the first two min of the reaction).

Further removal of emulsified O&G in this synthetic PW composed by the seawater matrix could be hindered by the presence of salts, since $Cl^-$, $SO_4^{2-}$, $H_2PO_4^-$ /$HPO_4^{2-}$ present in seawater could interfere in the reaction mechanism of the Fenton and photo-Fenton system, reducing the effectiveness of the oxidation system (Lipczynska-Kochany et al, 1995; Lu et al, 1997).

Furthermore, because PW is composed of a heterogeneous mixture, as with the water used in the present study, this prevents the Fenton reagents from mixing well due to the different phases.

### 3.3.5. Photo-Fenton process

Given the results obtained for the Fenton process, the corresponding photo-activated reaction was essayed to compare its efficiency. Coelho and colleagues (2006) combined Fenton and photo-Fenton for the removal of a large quantity of dissolved organic carbon in acid water effluents from oil refineries, since these processes have been found to be more effective for the elimination of dissolved compounds.

The experiments, with the influent prepared as described in section 3.2.2., were performed under simulated solar light, inside a solarbox for 3 h.

The lowest quantities of $H_2O_2$ used in Fenton were employed for the photo-Fenton process; 283 mg $L^{-1}$ and 600 mg $L^{-1}$, with $Fe^{2+}$ doses to obtain $H_2O_2$/Fe (w/w)= 2 and 10. Table 3.7 shows these results; the residual $H_2O_2$ was monitored throughout the reaction time, while the phenol concentration was checked after 3 h.

Table 3.7. Photo-Fenton experiments and O&G and phenol content of the PW after 3 hours of reaction, at pH 3

| **$H_2O_2$/COD (w/w)** | **$H_2O_2$, (mg $L^{-1}$)** | **$H_2O_2$/Fe (w/w)** | **$Fe^{2+}$, (mg $L^{-1}$)** | **O&G removal, (%)** | **Phenol, (mg $L^{-1}$)** | **Residual $H_2O_2$, (mg $L^{-1}$)** |
|---|---|---|---|---|---|---|
| 4.5 | 600 | 2 | 300 | 73.7 | 0.8 | 15 min: >100,<br>1h: >100, 2h: 1,<br>3h:0 |
| 4.5 | 600 | 10 | 60 | 52.9 | 0.4 | 15 min: >100, 1h: >100,<br>2h: 30,<br>3h:5 |
| 2.1 | 283 | 2 | 150 | 30.3 | 0.4 | 15 min: >100,<br>1h: >100,<br>2h: 20,<br>3h: 0 |
| 2.1 | 283 | 10 | 30 | 41.6 | 0.2 | 15 min: >100, 1h: >100,,<br>2h: 10,<br>3h: 0 |

Comparing these results with those after 6 h of the Fenton process, in which the same doses of reagents were used (Table 3.5), it can be concluded that in half of the reaction time used for the Fenton reaction, photo-Fenton consumed all the available $H_2O_2$ yielding higher O&G removal and particularly higher phenol removal, with a maximum phenol elimination of 95.2%. This indicated that the external energy supplied by light radiation could contribute effectively to further oxidize O&G and phenol content, despite the effect of salts and the heterogeneity of the two phases.

Figure 3.12 presents the results of O&G and phenol removal percentages after Fenton and photo-Fenton processes using the same reagent doses.

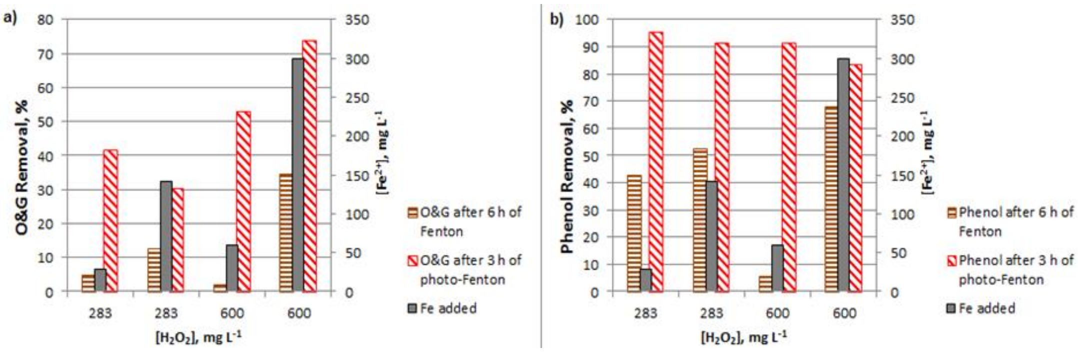


Figure 3.12. a) O&G removal (%) and b) phenol removal (%) with different reagent doses, after 6 h of Fenton and 3 h of photo-Fenton

To check the negative influence of salinity in this process, PW in a milli-Q water matrix (instead of seawater) was synthetized and the experiment adding 600 mg L$^{-1}$ of $H_2O_2$ and 60 mg L$^{-1}$ of Fe was carried out. After 3 h of photo-Fenton the final content of O&G was 14.9 mg L$^{-1}$, i.e., a 66.9% of removal compared with the 52.9% when a seawater matrix was used.

Moraes et al (2004) used the photo-Fenton process in saline synthetic PW, concluding that $Fe^{3+}$ ions react with $Cl^-$ ions, forming $FeCl^{2+}$ complexes, which in the presence of UV radiation may give rise to $Cl_2^{\bullet -}$ radicals (lower oxidation potential than the $HO^{\bullet}$).

According to these results, the combination of settling or E-DAF and the photo-Fenton process could be suggested as a suitable polishing process for the reuse of PW.

## 3.4. CONCLUSIONS

The experiments performed and the subsequent data analysis have shown that DAF processes and settling are good pretreatment options for reducing O&G and turbidity. Further polishing can be obtained with a subsequent advanced oxidation process.

For flotation experiments, the coagulant dose only affected removal of COD, while pH levels did not impact on the process performance; this meant that pH control would not be necessary in this type of pretreatment. As phenol was barely eliminated, the optimal coagulation concentration taking into account the COD removal was 70 mg $L^{-1}$ to achieve 46.2% of COD elimination. Under these conditions, 53.6% of turbidity removal was obtained. Higher levels of removals were not achieved with this treatment since microbubbles break the formed flocs.

In the settling process, the removal of COD and turbidity were significantly affected by coagulant dosage and settling time. Phenol removal was not influenced by any operational parameter, as in flotation. The optimal process conditions were 86 mg $L^{-1}$ of coagulant concentration and 83 min of settling time, leading to a 69% COD removal percentage and 90% turbidity removal. Comparison of these pretreatments showed that higher COD and turbidity removals were achieved by settling (86% of O&G was also eliminated with this pretreatment).

Precisely due to the fact that the rising velocity of the microbubbles caused floc breakup, a new process using microspheres instead of air microbubbles was also studied. This enhanced DAF or E-DAF removed 87.2% of PW turbidity and 94% of O&G (similar to the settling treatment but requiring less operation time), using 57.9 mg $L^{-1}$ of coagulant, 300 mg $L^{-1}$ of microspheres and a flocculation rate of 40 rpm.

In E-DAF experiments it was observed that the turbidity reduction of PW was correlated to its O&G concentration depletion. High O&G removal percentages were achieved (up to 90% of elimination) with this process, comparable with settling. The use of microspheres in the flotation without the injection of microbubbles was shown to be more effective for the removal of turbidity and O&G (which also implies lower energy consumption).

After these treatments, in order to polish the O&G content of the effluent even further and to remove the phenol (component chosen as the representative of dissolved organic compounds found in PW), Fenton and photo-Fenton reactions were essayed. With the Fenton reaction a maximum O&G elimination of 57.6 % was achieved, and phenol was removed by up to 80%, adding 1,662.5 mg $L^{-1}$ $H_2O_2$ and 133 mg $L^{-1}$ Fe, at pH 3. After 24 h of reaction, the O&G content decreased, but not significantly compared to a 6-h treatment. Phenol removal did not change after longer reaction times, since the elimination of this component mainly occurs in the first minutes of reaction.

The difficulty in removing emulsified O&G in this synthetic PW could be due to the salts contained in this water, which hinder the effectiveness of Fenton process. Furthermore, because this water is composed of a heterogeneous mixture, this can prevent Fenton reagents from mixing properly.

The photo-Fenton process with solar radiation for 3 h showed that all $H_2O_2$ was consumed and a higher fraction of O&G content was eliminated (73.7% of removal adding 600 mg $L^{-1}$ $H_2O_2$ and 300 mg $L^{-1}$ Fe at pH 3), compared to the conventional Fenton process. In the case of phenol, up to 95.2% was eliminated.

According to these results, the combination of settling and the photo-Fenton process could be suggested as a suitable polishing process for the reuse of PW if the reaction time is not a limiting factor. The settling could be substituted by E-DAF technology, without air injection, when there are limitations regarding reaction volumes and times.

## 3.5. REFERENCES

Al-Enazi, M.M., El-Khateeb, M.A., El-Bahrawy, A.Z., 2013. Combining Chemical Treatment and Sand Filtration for the Olive Mill Wastewater Reclamation. Life Science Journal, 10(3), 583-592.

Al-Shamrani, A.A., James, A., Xiao, H., 2002. Separation of oil from water by dissolved air flotation. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 209(1), 15–26.

Arthur, J.D., Dillon, L.W., Drazan, D.J., 2011. Management of Produced Water From Oil and Gas Wells. Working Document of the NPC North American Resource Development Study. 32 pages.

Ben Mansour, L., Chalbi, S., 2006. Removal of oil from oil/water emulsions using electroflotation process. Journal of Applied Electrochemistry 36 (5), 577–581.

Bossmann, S. H., Oliveros, E., Göb, S., Siegwart, S., Dahlen, E. P., Payawan, L., Braun, A. M., 1998. New Evidence against Hydroxyl Radicals as Reactive Intermediates in the Thermal and Photochemically Enhanced Fenton Reactions. The Journal of Physical Chemistry A, 102(28), 5542 5550.

CDM, 2008. Produced Water Technical Breakthrough http://content.cdm.com/webinarregistration/Produced%20Water%20Treatment%20Brochure.pdf.

Coelho, A., Castro, A.V., Dezotti, M., Sant'Anna Jr., G.L., 2006. Treatment of petroleum refinery sourwater by advanced oxidation processes. Journal of Hazardous Materials B, 137, 178–184.

Dores, R., Hussain, A., Katebah, M., Adham, S., 2012. Using Advanced Water Treatment Technologies To Treat Produced Water From The Petroleum Industry. SPE International.

Duesterberg, C.K., Waite, T.D., 2006. Process optimization of fenton oxidation using kinetic modeling. Environmental Science and Technology 40 (13), 4189–4195.

Environmental Protection Agency Method 1664, Revision B: n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel n-Hexane Extractable Material (SGT-HEM; Non-Polar Material) by Extraction and Gravity. USA: EPA, 2010.

Fakhru’l-Razi, A., Alireza, P., Luqman, C.A., Dayang, R.A.B., Sayed, S.M., Zurina, Z.A., 2009. Review of technologies for oil and gas produced water treatment. Journal of Hazardous Materials, 170, 530–551.

Haarhoff, J., Edzwald, J.K., 2013. Adapting dissolved air flotation for the clarification of seawater. Desalination, 311, 90–94.

Hilal, N., Busca, G., Hankins, N., Mohammad, A. W., 2004. The use of ultrafiltration and nanofiltration membranes in the treatment of metal-working fluids. Desalination 167, 227–238.

Hosny, A.Y., 1996. Separating oil from oil-water emulsions by electroflotation technique. Separation Technology 6, 9–17.

Hu, X. G., Bekassy-Molnar, E., Vatai, G., 2002. Study of ultrafiltration behaviour of emulsified metalworking fluids. Desalination 149 (1–3), 191–197.

Hussain, A., Minier-Matar, J., Janson, A., Gharfeh, S., Adham, S., 2014. Advanced Technologies For Produced Water Treatment And Reuse. IPTC 2014: International Petroleum Technology Conference.

Khatib, Z., Verbeek, P., 2002. Water to value-produced water management for sustainable field development of mature and green fields, in: SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Kuala Lumpur, Malaysia, 20–22 March, 2002.

Kwan, W.P., Voelker, B. M., 2002. Decomposition of hydrogen peroxide and organic compounds in the presence of dissolved iron and ferrihydrite. Environmental Science and Technology 36(7), 1467–1476.

Lipczynska-Kochany, E., Sprah, G., Harms, S., 1995. Influence of some groundwater and surface waters constituents on the degradation of 4-chlorophenol by the Fenton reaction. Chemosphere 30(1), 9–20.

Lu, M.C., Chen, J.N., Chang, C.P., 1997. Effect of inorganic ions on the oxidation of dichlorvos insecticide with Fenton's reagent. Chemosphere 35(10), 2285–2293.

Moraes, J.E.F., Quina, F., Nascimento, C.A.O., Silva, D.N., Chiavone-Filho, O., 2004. Treatment of Saline Wastewater Contaminated with Hydrocarbons by the Photo-Fenton Process. Environ. Sci. Technol., 38, 1183-1187.

Mostefa, N. M., Tir, M., 2004. Coupling flocculation with electroflotation for waste oil/water emulsion treatment. Optimization of the operating conditions. Desalination 161(2), 115–121.

Mota, A.L.N., Albuquerque, L.F., Beltrame, L.T.C.; Chiavone-Filho, A., Machulek JR., A., Nascimento, C.A.O., 2008. Advanced Oxidation Processes and their Application in the Petroleum Industry: A review. Brazilian Journal of Petroleum and Gas 2, 122-142.

Neff, J.M., 2002. Bioaccumulation in Marine Organisms: Effect of Contaminants from Oil Well Produced Water. Elsevier Science Publishers, Amsterdam. 452 pages.

Neyens, E., Baeyens, J., 2003. A review of classic Fenton's peroxidation as an advanced oxidation technique. Journal of Hazardous Materials 98 (1–3), 33–50.

Ometto, F., Pozza C., Whitton R., Smyth B., Gonzalez Torres A., Henderson RK., Jarvis P., Jefferson B., Villa R., 2014. The impacts of replacing air bubbles with microspheres for the clarification of algae from low cell-density culture. Water Research, 53, 168-179.

Pignatello, J. J. (1992). Dark and photoassisted iron(3+)-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. Environmental Science & Technology, 26(5), 944–951.

Produced Water Market, 2011. Opportunities in the oil, shale and gas sectors in North America. Global Water Intelligence Publication.

Siemens (visited in 2016), http://www.energy.siemens.com/hq/en/industries-utilities/oil-gas/products-systems-solutions/water-solutions/produced-water-treatment.htm.

Stephenson, MT; (1992). A Survey of Produced Water Studies, In: Produced Water, Ray J.P. and Englehart F.R. editors. Plenum Press, New York.

Utvik, T.I.R., Hasle, J.R., 2015. Recent Knowledge About Produced Water Composition and the Contribution From Different Chemicals to Risk of Harmful Environmental Effects. Journal of Petroleum Technology, 54(12), 67–69.

Veil, J.A., Pruder, M.G., Elcock, D., Redweik, J., 2004. A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane. Prepared for the U.S. Department of Energy, Energy Technology Laboratory.

Veolia, (visited in 2016). http://www.veoliawaterst.com/opus/en/

Williams D., 2011. Turning Water into oil: Desalination: a process to enhance world oil resources. IDA World Congress, Perth, Australia, September 2011.

Yang M., 2001. Measurement of Oil in Produced Water. Produced Water, Environmental Risks and Advances in Mitigation Technologies, Lee K. and Neff J. editors. Springer Science+Business Media, LLC 2011.

Younker, J.M., Walsh, M.E., 2014. Bench-scale investigation of an integrated adsorption–coagulation–dissolved air flotation process for produced water treatment. Journal of Environmental Chemical Engineering 2 (1), 692–697.

Younker, J.M., Walsh, M.E., 2016. Effect of adsorbent addition on floc formation and clarification, Water Research (2016), doi: 10.1016/j.watres.2016.03.044.

Zouboulis, A.I., Avranas, A., 2000. Treatment of oil-in-water emulsions by coagulation and dissolved-air flotation, Colloids and Surfaces A: Physicochemical and Engineering Aspects 172, 153-161.

# Chapter 4. Produced Water Treatment by Advanced Oxidation Processes

## Content

## 4.1. INTRODUCTION

Produced water (PW) is the name given to the water that is brought to the surface along with oil or gas in extraction operations. It includes the formation water (trapped underground) and injection water that are extracted together with the fossil fuel during oil and gas production (Arthur et al., 2011; Fakhru'l-Razi et al., 2009; Neff, 2002; Veil et al., 2004). PW is generated in large amounts (the water to oil ratio is around 3:1) (Khatib and Verbeek, 2002) and has a complex composition that includes organic and inorganic substances, with the main components being salts, free and emulsified oils, phenols, organic acids, benzene, toluene, ethylbenzene and xylene (BTEX), and polycyclic aromatic hydrocarbons (PAHs) (Veil et al, 2004). Among these components, the oil and grease (O&G) fraction, composed of hydrocarbons and fatty acids, is subject to legislative restrictions for discharge and/or reuse (Khatib and Verbeek, 2002). US EPA Method 1664 defines O&G as “the mixture of those components of PW that are extractable in hexane at pH 2 or lower and remain after vaporization of the hexane”. Therefore, this would include dispersed oil and water soluble organics except low molecular weight phenols (which are highly soluble in water), low molecular weight acids (which are soluble in water and volatile) and BTEX (which are highly volatile).

The chemical composition of PW from an average discharge is summarized in Table 4.1.

Table 4.1. Main components of produced water from oilfields (Utvik and Hasle, 2015)

| **Compound group** | **Concentration, mg L$^{-1}$** |
|---|---|
| Salts | Up to 300000 |
| O&G | 15-200 |
| BTEX | 0.7-24 |
| PAHs | 0.04-3 |
| Organic Acids | 7-760 |
| Phenols | 0.4-23 |

The previous chapter was focused in the O&G fraction and some processes as enhanced dissolved air flotation (E-DAF) were studied as pretreatments for the O&G removal in PW (Jiménez et al., 2017). After that first stage, PW with an O&G content below the requirements for discharging was obtained, but the treatment efficiency is not enough when the aim is to reuse the treated water, since the rest of the components, mainly the dissolved organic compounds, are not eliminated in this pretreatment. Therefore, the objective in this work (chapter 4) is the removal of these components contained in PW by advanced oxidation processes (AOPs).

Due to the complexity of PW and for the reutilization of this wastewater, e.g. for generation of high quality water for steam production, and even for other purposes, like irrigation or aquifer recharge, it is not feasible to address their treatment by a single technology. The solution could be the development of integrated processes, i.e. the combination of individual technologies. These techniques could involve E-DAF or settling (Jiménez et al., 2017), optionally followed by membrane ultrafiltration (to remove the residual O&G that remains), an AOP (that will be studied in the present chapter) and finally a Reverse Osmosis system for the salts elimination.

Although there are already in the market packaged PW treatment technologies, most of these solutions are tailormade to meet specific treatment needs for each individual exploitation site. For example, Siemens commercializes AutoShell™ and Monosep™ walnut shell filters (Siemens global website, 2016), to remove oily contaminants from water. However, this solution is only a filtration step that generates a backwash effluent, whose treatment needs to be addressed, and does not produce high quality water able for reuse. CDM has developed a High-Recovery Reverse Osmosis Process (CDM, 2008), for treating PW containing TDS levels up to 20000 mg $L^{-1}$. However, this solution does not offer a consistent pre-treatment for oil removal, so sever fouling events are not prevented. Finally, Veolia Water offers treatment systems for high recovery of clean water for reuse or discharge (Veolia website, 2016), called OPUS™ and OPUS II™, for treatment of water containing high concentrations of silica, organics, hardness, heavy metals, boron and particulates. However, these solutions do not offer a pretreatment to remove oily components.

This study was carried out to compare the performance of different AOPs such as photocatalysis, photo-Fenton, Fenton and ozonation in the removal of dissolved organics from PW, to include one of these processes within the integrated treatments solution for the PW polishing.

Currently, in the oil and gas industry, biological treatment is able to remove some compounds. However, the efficiency of the biological process is inadequate when water contains highly toxic recalcitrant compounds (Mota et al., 2008), as for example BTEX and phenols.

AOPs are technologies characterized by the generation of hydroxyl radicals, which are highly reactive and non-selective towards the oxidation of toxic organic compounds completely or partially to carbon dioxide and water. This destruction is the advantage of the AOPs in contrast to other processes, sometimes leading only to the transfer of contaminants from one phase to another (Sinha et al., 2007).

**Photocatalysis** counts on the acceleration of a photoreaction by the presence of a catalyst. Heterogeneous photocatalysis is a process in which two phases, solid and liquid, are present. The solid phase is a catalyst, usually a semiconductor. The molecular orbital of semiconductors has a band structure. The bands of interest in photocatalysis are the valence band (VB) and the conduction band (CB), which is commonly characterized by band gap energy (Ebg). The semiconductors may be photoexcited to form electron-donor sites (reducing sites) and electron-acceptor sites (oxidising sites), providing great scope for redox reaction. When the semiconductor is illuminated with light ($h\upsilon$) of greater energy than that of the band gap, an electron is promoted from the VB to the CB, leaving a positive hole ($h^+_{vb}$) in the VB and an electron ($e^-_{cb}$) in the CB. If charge separation is maintained, the electron and hole may migrate to the catalyst surface, where they participate in redox reactions with sorbed species. Specially, $h^+_{vb}$ may react with surface-bound $H_2O$ or $OH^-$ to produce the hydroxyl radical and $e^-_{cb}$ is picked up by oxygen to generate superoxide radical anion ($O_2^{\cdot -}$), as indicated in the following equations 4.1-4.3:

absorption of efficient photons by titania ($h\upsilon \geq Ebg = 3.2$ ev):

$TiO_2 + h\upsilon \rightarrow e^-_{cb} + h^+_{vb}$ (4.1)

formation of superoxide radical anion:

$O_2 + e^-_{cb} \rightarrow O_2$ (4.2)

neutralization of OH- group into $^{\cdot}OH$ by the hole:

$(H_2O \Leftrightarrow H^+ + OH^-)_{ads} + h^+_{vb} \rightarrow {}^{\cdot}OH + H^+$ (4.3)

It has been suggested that the hydroxyl radical ($^{\cdot}OH$) and superoxide radical anions ($O_2^{\cdot -}$) are the primary oxidizing species in the photocatalytic oxidation processes (Nath et al, 2012). These oxidative reactions result in the degradation of the pollutants as shown in the following equations 4.4-4.5:

oxidation of the organic pollutants via successive attack by $^{\cdot}OH$ radicals:

$R + {}^{\cdot}OH \rightarrow R'^{\cdot} + H_2O$ (4.4)

or by direct reaction with holes:

$R + h^{+} \rightarrow R^{\cdot +} \rightarrow$ degradation products (4.5)

For oxidation reactions to occur, the VB must have a higher oxidation potential than the material under consideration. The redox potential of the VB and the CB for different semiconductors varies between +4.0 and -1.5 volts versus Normal Hydrogen Electrode (NHE) respectively. The VB and CB energies of the $TiO_2$ are estimated to be +3.1 and -0.1 volts, respectively, which means that its band gap energy is 3.2 eV and therefore absorbs in the near UV light ($\lambda$<387 nm). Many organic compounds have a potential above that of the $TiO_2$ valence band and therefore can be oxidized. In contrast, fewer organic compounds can be reduced since a smaller number of them have a potential below that of the $TiO_2$ conduction band (Haque et al., 2012).

**Fenton** reaction consists of an aqueous combination of hydrogen peroxide ($H_2O_2$) and ferrous ions ($Fe^{2+}$), in an acid medium, leading to the decomposition of $H_2O_2$ mainly into a hydroxyl ion and a hydroxyl radical, through the oxidation of $Fe^{2+}$ to $Fe^{3+}$ (Neyens and Baeyens, 2003). Simultaneously, as part of the regular Fenton cycle, $Fe^{2+}$ is regenerated by the reaction between $Fe^{3+}$ and $H_2O_2$ (Duesterberg and Waite, 2006; Kwan and Voelker, 2002).

The principal reactions from the Fenton mechanism are shown in the following equations (Gallard and De Laat, 2001; Garrido-Ramírez et al., 2010; Walling, 1975):

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + {}^{\bullet}OH$ // $E_a$=39.5 kJ mol$^{-1}$; k=76 M$^{-1}$ s$^{-1}$ (4.6)

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + O_2H^{\bullet} + H^+$ //$E_a$=126 kJ mol$^{-1}$; k= 0.001-0.01 M$^{-1}$ s$^{-1}$ (4.7)

Hydroxyl radicals may be scavenged by reaction with $Fe^{2+}$ or with $H_2O_2$ (Chamarro et al., 2001; Lu et al., 1999; Torrades et al., 2003):

$^{\bullet}OH + Fe^{2+} \rightarrow OH^- + Fe^{3+}$ (4.8)

$^{\bullet}OH + H_2O_2 \rightarrow O_2H^{\bullet} + H_2O$ (4.9)

Hydroxyl radicals may react with organics starting a chain reaction (Bianco et al., 2011; Dercová et al., 1999):

$^{\bullet}OH + RH \rightarrow H_2O + R^{\bullet}$ , RH = organic substrate (4.10)

$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \rightarrow$ products of degradation (4.11)

Ferrous ions and radicals are produced during the reactions as shown below (Lu et al., 1999):

$H_2O_2 + Fe^{3+} \Leftrightarrow H^+ + FeOOH^{2+}$ (4.12)

$FeOOH^{2+} \rightarrow O_2H^{\bullet} + Fe^{2+}$ (4.13)

$O_2H^{\bullet} + Fe^{2+} \rightarrow O_2H^- + Fe^{3+}$ (4.14)

$O_2H^{\bullet} + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^+$ (4.15)

The efficiency of this process depends mainly on $H_2O_2$ concentration, $Fe^{2+}/H_2O_2$ ratio, temperature, pH and treatment time. The oxidizing potential of the hydroxyl radical is pH dependent, and varies from E0 =1.8 V at neutral pH to +2.7 V in acidic solutions (El-Morsi et al., 2002). Operating pH of the system has been observed to significantly affect the degradation of pollutants (Benitez et al., 2001; Kang and Hwang, 2000; Lin and Lo, 1997; Nesheiwat and Swanson, 2000). The degree of oxidation of organics with Fenton's reagent is maximum when the pH lies in the interval pH 3–5 (Lin and Lo, 1997; Lunar et al., 2000). Hydrogen peroxide is most stable in the range of pH 3–4, but the decomposition rate is rapidly increased with increasing pH above 5. Thus, the acidic pH level around 3 is usually optimum for Fenton oxidation (Gogate and Pandit, 2004; Neyens and Baeyens, 2003). Besides, the system reactivity decreases with increasing pH above the value of 3, due to a decrease in concentration of dissolved iron that precipitates as ferric hydroxide.

The reagent concentrations is indeed especially important due to the fact that an excess of them could cause counterproductive increase in the kinetics of undesirable reactions. For example, an excess of $H_2O_2$ produces a deceleration of a few orders of magnitude in the process, due to too rapid oxidation of $Fe^{2+}$ to $Fe^{3+}$. This could also increase the formation of hydroperoxyl radicals according to reaction 4.9, scavenging the hydroxyl radicals jeopardizing the oxidation of the hypothetical organic load.

Inorganic species such as $Cl^-$, $SO_4^{2-}$, $H_2PO_4^-$/ $HPO_4^{2-}$, etc., could affect also the global reaction rates of Fenton process as has been reported in previous literature. They can cause three different effects: i) complexing reactions with $Fe^{2+}$ and $Fe^{3+}$ (reducing the photoactivity of the system (Pignatello et al., 2006)); ii) precipitating reactions that reduce dissolved active $Fe^{3+}$; iii) hydroxyl radicals scavenging that favors the formation of other inorganic radicals less reactive (Bacardit et al., 2007; Pignatello et al., 2006) and subsequent oxidation reactions with those species.

In the **photo-Fenton** process, OH radicals are generated by the reactions of Fe ions with $H_2O_2$ and/or light energy (Pignatello et al. 2006). In other words, the efficiency of the photo-Fenton oxidative degradation process is controlled by the iron redox cycle consisting of three reactions, i.e. the Fenton reaction (reaction 4.6), the photo-Fenton reaction (reaction 4.16) and the Fenton-like reaction (reaction 4.7) as shown in Figure 4.1 (Baba et al., 2015). Organic ligands often accelerate or decelerate the photo-Fenton process. For example, carboxylic acids are frequently formed as intermediates in the degradation of organic pollutants by the photo-Fenton oxidative degradation process (Kavitha and Palanivelu, 2004; Oturan et al. 2008; Wang et al. 2011; Xiao et al. 2014). They will react with iron and form iron complexes ($Fe^{2+}$-ligands and $Fe^{3+}$-ligands), which can undergo direct mineralization to $CO_2$ under UV visible radiation and may affect the degradation rate.

$$Fe^{3+} + H_2O_2 + h\upsilon \rightarrow Fe^{2+} + OH^{\bullet} + H^{+} \qquad (4.16)$$

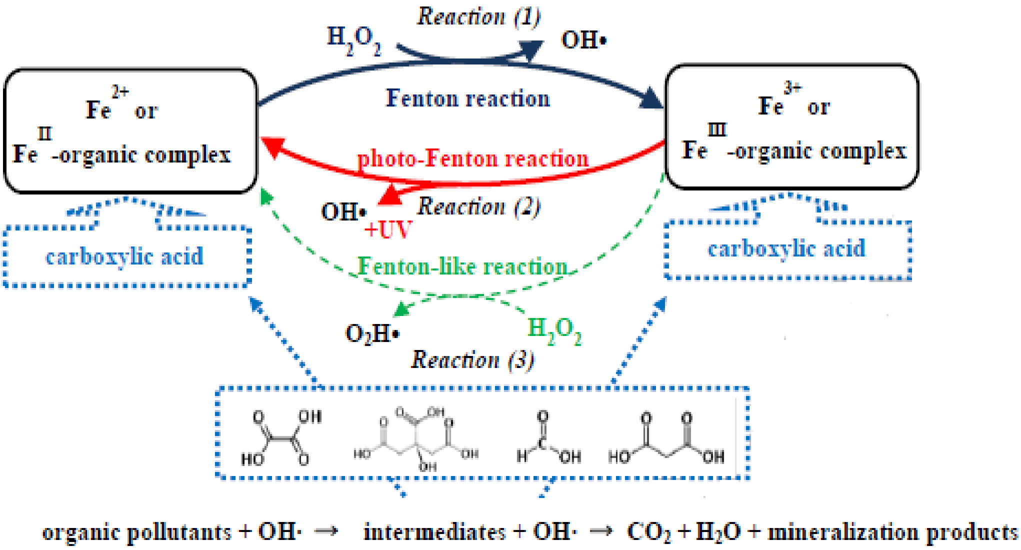


Figure 4.1. Iron redox cycle and OH radical generation in the photo-Fenton oxidative degradation process (Baba et al. 2015)

OH radicals can also be formed only with $H_2O_2$/UV. UV radiation is absorbed by $H_2O_2$, splitting the $H_2O_2$ molecule into two OH radicals (Crittenden et al., 1999).

According to Pignatello (1992), the photo-Fenton process accelerates the degradation rate of organic pollutants from Fenton's reagent. Given its sensitivity to UV-Vis radiation for wavelengths above 300 nm, the photolysis of $Fe^{3+}$ enables regeneration of $Fe^{2+}$. Therefore, UV accelerates catalytic Fenton processes when the concentration of $Fe^{2+}$/$Fe^{3+}$ is lower than $H_2O_2$, where iron reduction is the rate-limiting step. The $Fe(OH)^{2+}$ ion absorbs light at wavelengths up to about 410 nm.

It should be noted that the oxidation potential of perhydroxyl radical ($O_2H^{\bullet}$) formed by the Fenton-like reaction (4.7) is weak compared with that of the hydroxyl radical, and the influence of the Fenton-like reaction on the reduction of $Fe^{3+}$ is less than that of the photo-Fenton reaction.

More detailed studies of the pH dependence of the photo-Fenton reaction have shown that the optimum pH range is ca. pH 3. The reason for this pH dependence becomes clear when one examines the speciation of $Fe^{3+}$ as a function of pH and the absorption spectra of the relevant $Fe^{3+}$ species. At $pH < 2$, the dominant species is hexaquoiron(III), $Fe(H_2O)_6^{3+}$ [or simply $Fe^{3+}$ for convenience], which absorbs weakly in the ultraviolet above 300 nm. At $pH > 3$, freshly prepared solutions of $Fe^{3+}$ are supersaturated with respect to formation of colloidal iron hydroxide, $Fe(OH)_3$ and prone to precipitation of hydrated iron oxides upon standing for a prolonged period. At pH 3, however, the predominant Fe(III) species present in aqueous solution is $Fe(H_2O)_5(OH)^{2+}$ [or simply $Fe(OH)^{2+}$], which absorbs throughout much of the ultraviolet spectral region.

Studies of the photochemistry of $Fe(OH)^{2+}$ have shown that $Fe(OH)^{2+}$ undergoes a relatively efficient photoreaction to produce $Fe^{2+}$ and the hydroxyl radical:

$$Fe(OH)^{2+} + h\upsilon \rightarrow Fe^{2+} + {}^{\bullet}OH \qquad (4.17)$$

Thus, irradiation of the Fenton reaction not only regenerates $Fe^{2+}$, the crucial catalytic species in the Fenton reaction (reaction 4.6), but also produces an additional hydroxyl radical, the species responsible for the degradation of organic material. As a consequence of these two effects, the photo-Fenton process is faster than the conventional thermal Fenton process. Moreover, since $Fe^{2+}$ is regenerated by light with decomposition of water (equations 4.16-4.17) rather than $H_2O_2$ (reaction 4.18), the photo-Fenton process consumes less $H_2O_2$ and requires only catalytic amounts of $Fe^{2+}$.

$Fe^{3+} + H_2O_2 + H_2O \rightarrow Fe^{2+} + H_3O^{+} + OH_2^{\bullet}$ (4.18)

At the end of the reaction, if necessary, the residual $Fe^{3+}$ can be precipitated as iron hydroxide by increasing the pH. Any residual hydrogen peroxide that is not consumed in the process will spontaneously decompose into water and molecular oxygen and is thus a "clean" reagent in itself. These features make homogeneous photo-Fenton based AOPs the leading candidate for cost efficient, environmental friendly treatment of industrial effluents on a small to moderate scale (Pignatello et al., 2006).

**Ozone** has a high reduction potential (2.07 V), and can react slowly and directly with an organic substrate (direct pathway) (Augugliaro et al., 2006). However, the use of ozone is only characterized as an AOP when it decomposes to generate hydroxyl radicals (indirect pathway) (e.g. Equation 4.19 and 4.20), and can be catalyzed by hydroxyl ions ($HO^{-}$) in alkaline medium or by transition metal cations (Augugliaro et al., 2006; Pera-Titus et al., 2004; Straehelin and Hoigné, 1985).

$2O_3 + 2H_2O \rightarrow 2\ OH^{\bullet} + O_2 + 2HO_2^{\bullet}$ (4.19)

$3O_3 + OH^{-} + H^{+} \rightarrow 2\ OH^{\bullet} + 4\ O_2$ (4.20)

In practice, both direct and indirect oxidation reactions will take place. One kind of reaction will dominate, depending on various factors, such as temperature, pH and chemical composition of the water. To determine the role $^{\bullet}OH$ radicals play in ozone oxidation, the rate of ozone versus the rate of $OH^{\bullet}$ radicals is used. When ozone is applied in water, this value varies between $10^{-6}$ and $10^{-9}$. During the ozone process, this value will be about $10^{-8}$ in the second phase.

Direct reactions:

Ozone can act as a 1,3-dipole, an electrophilic agent and a nucleophilic agent during reactions. These three types of reactions usually occur in solutions that contain organic pollutants.

*Cyclo addition (Criegee mechanism)*:

Consequentially to its dipolar structure, an ozone molecule can undergo a 1-3 dipolar cyclo addition with unsaturated compounds (double or triple bonds). This leads to the formation of a compound called ‘ozonide’ (I), as is shown in Figure 4.2.

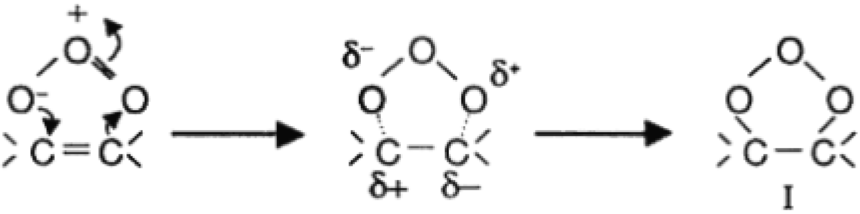


Figure 4.2. Dipolar cyclo addition (Lenntech, 2016)

In a protonic solution, such as water, primary ozonide disintegrates into an aldehyde, a keton or a zwitter ion, as is shown in Figure 4.3. The zwitter ion will eventually be disintegrated further into hydrogen peroxide and carboxyl compounds.

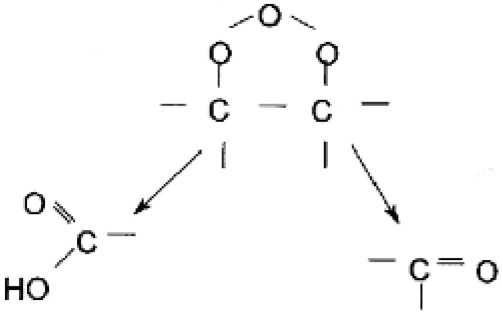


Figure 4.3. Disintegration of ozonide (Lenntech, 2016)

*Electrophilic reactions*:

Electrophilic reactions occur in molecular solutions that have a high electronic density and mainly in solutions that contain a high level of aromatic compounds. Aromatic compounds that are substituted by electron donors (such as OH and $NH_2$), have a high electronic density on the carbon compounds in ortho and para position. Consequentially, in these positions aromatic compounds react actively with ozone. As example, the reaction between ozone and phenol is shown in Figure 4.4.

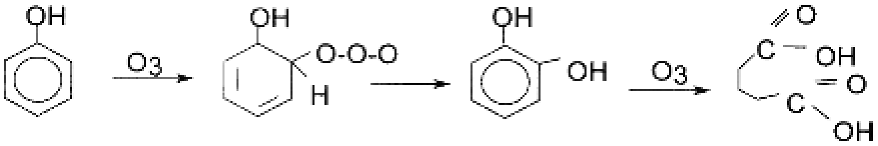


Figure 4.4. Reaction between phenol and ozone

Nucleophilic reactions mainly take place where there is a shortage of electrons and particularly at carbon compounds that contain electron-retreating groups, such as –COOH and -$NO_2$.

Indirect reactions:

Contrary to those of ozone, OH-radical reactions are largely non-selective. Indirect reactions in an ozone oxidation process can be very complex. An indirect reaction takes place according to the following steps:

1. Initiation
2. Radical chain-reaction
3. Termination

*1. Initiation*

The first reaction that takes place is accelerated ozone decomposition by a type of initiator. This can be an OH-molecule (reaction 4.21):

$O_3 + OH^- \rightarrow O_2^{\bullet -} + HO_2^{\bullet}$ ($k=10\ M^{-1}\ s^{-1}$) (4.21)

This radical has an acid/ base equilibrium of pKa = 4.8. Above this value, this radical no longer splits, because it forms a superoxide radical (reaction 4.22):

$HO_2^{\bullet} \Leftrightarrow O_2^{\bullet -} + H^+$ (pKa = 4.8) (4.22)

*2. Radical chain-reaction*

Now, a radical chain-reaction takes place, during which OH-radicals are formed. The reaction mechanism is as follows:

$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2$ $(k=1.9\ 10^{9}\ M^{-1}\ s^{-1})$ (4.23)

For pH < ≈ 8: $O_3^{\bullet-} + H^{+} \Leftrightarrow HO_3^{\bullet}$ $(k_{4.22}=5\ 10^{10}\ M^{-1}\ s^{-1};\ k\text{-}_{4.22}=3.3\ 10^{2}\ M^{-1}\ s^{-1})$ (4.24)

$HO_3^{\bullet} \rightarrow OH^{\bullet} + O_2$ (4.25)

For pH > ≈ 8: $O_3^{\bullet-} \Leftrightarrow O^{\bullet-} + O_2$ $(k_{4.25}=2.1\ 10^{3}\ M^{-1}\ s^{-1};\ k\text{-}_{4.22}=3.3\ 10^{9}\ M^{-1}\ s^{-1})$ (4.26)

$O^{\bullet-} + H_2O \rightarrow OH^{\bullet} + OH^{-}$ $(k= 10^{8} - 2\ 10^{9}\ M^{-1}\ s^{-1})$ (4.27)

No matter the pH, it can be seen water ends up in the generation of hydroxyl radicals that will contribute to the oxidation of the organic matter. Furthermore, ozone itself is susceptible to react with hydroxyl radicals leading to the formation of hydroperoxide radical that starts the cycle all over again.

$O_3 + OH^{\bullet} \rightarrow O_2H^{\bullet} + O_2$ (4.28)

This chain-reaction can be maintained even by organic substances that can act as promoters. When a promoter reacts with $OH^{\bullet}$, it transform it into hydroperoxide radicals, such as in reaction 4.29, that again start the cycle all over again. At the same time, the promoter is oxidized and degraded.

$H_2R + OH^{\bullet} + O_2 \rightarrow R + O_2H^{\bullet} + H_2O$ (4.29)

*3. Termination*

The completion of the chain reaction is reached when the radicals react with intermediates or no promoting organic substances. In those cases, reaction does not lead to formation of hydroperoxide species, as it happens in the following reactions with alkalinity content of the solution:

$OH^{\bullet} + CO_3^{2-} \rightarrow OH^{-} + CO_3^{-}$ (4.30)

$OH^{\bullet} + HCO_3^{2-} \rightarrow OH^{-} + HCO_3^{-}$ (4.31)

Or when radical species react between themselves

$OH^{\bullet} + O_2H^{\bullet} \rightarrow O_2 + H_2O$ (4.32)

Ozonation is a well-established technology for water treatment, especially drinking water, and it has been the focus of attention in literature in the last few years as an option for advanced wastewater treatment (Pera-Titus et al., 2004). Ozone ($O_3$) is an expensive oxidant since requires energy to generate it (Pera-Titus et al., 2004) but its ability to mineralize organic matter, alone or in combination with $H_2O_2$, may be attractive for wastewater reuse purposes (Rodríguez et al., 2008). The efficiency of $O_3$ is extremely dependent on gas-liquid mass transfer, which is impeded by the low solubility of ozone in aqueous solution, as reported by Gogate and Pandit (2004). The efficacy of ozone in degrading organic compounds is improved when combined with $H_2O_2$, UV radiation or ultrasound.

Moving to the objective of the present chapter, there are studies that apply AOPs to degrade some components individually or/and not contained in a complex matrix like this PW. The particularity of this study is the application of the AOPs to degrade different types of components that are together in a seawater matrix composed by a high and heterogeneous concentration of salts. Chemical species such as carbonate and bicarbonate ions (Andreozzi et al., 1999) can react with the hydroxyl radicals. Also, according to Aljabri (2015), seawater is a complicated mixture that contains various organics and inorganics components that might result in the formation of organic by-products, which might cause the increase in the total organic carbon after photocatalysis. Besides, there are recalcitrant compounds present in this PW, as acetic acid having a low reaction rate for radicals and are hard to decompose (Park and Lee, 2008). Degradation of acetic acid in wastewater is difficult due to its refractory characteristics and consequently very few study reports are available for this (Sinha et al., 2007) and some of them achieved its conversion but after many hours of treatment (Ogata et al., 1981).

## 4.2. MATERIALS AND METHODS

### 4.2.1. Synthetic produced water

In this study, PW was synthetized according to the bibliographic data of oilfields PW, taking into account the main groups of components of which this PW is composed (BTEX, PAHs, organic acids and phenols) and its concentrations (Table 2.1 of chapter 2 and Table 4.1). The oil and grease group was not added since it was removed in the previous pretreatment (studied in chapter 3: settling or E-DAF), so the processes studied in this chapter are focused in the removal of the dissolved organic compounds in the PW.

PW was synthetized in a seawater matrix (from the Mediterranean Sea, Barcelona), where 10 mg $L^{-1}$ toluene and 10 mg $L^{-1}$ xylene were added as representatives of the BTEX group, 3 mg $L^{-1}$ naphthalene (from a more concentrated dissolution prepared with a minimal quantity of Triton-X-100 (Sigma-Aldrich) surfactant and agitation to dissolve naphthalene) as representative of the PAHs group, 150 mg $L^{-1}$ acetic acid (Panreac, Spain) and 10 mg $L^{-1}$ malonic acid (Sigma-Aldrich) as representatives of the acids group, and 10 mg $L^{-1}$ phenol. This synthetic PW has a chemical oxygen demand (COD) and total organic carbon (TOC) of ca. 262 mg $L^{-1}$ and 92 mg $L^{-1}$ respectively, and a pH of 4.95. The value of toxicity $EC_{50}$ (% v/v) is 10%.

Figure 4.5 (a) shows the identification of the components from gas chromatography-mass spectrometry (GC-MS) contained in the initial prepared sample of PW. Starting from the left, the first peak corresponds to toluene; the second one is the orthoxylene that comes close to another peak which is a mixture of meta and para xylene, phenol and naphthalene. The malonic and acetic acids, besides the phenol, are analyzed in the HPLC (Figure 4.5 (b)).

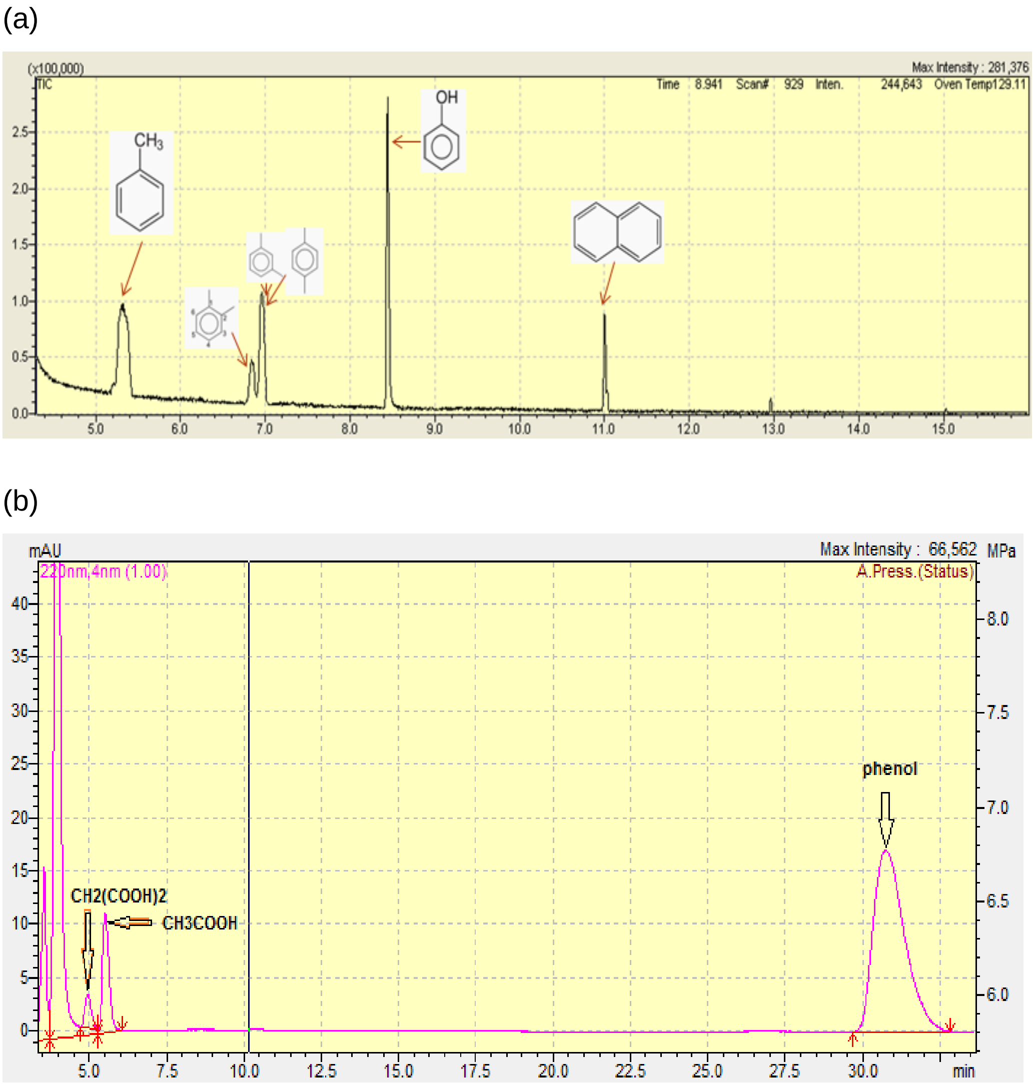


Figure 4.5. a) Toluene, xylene, phenol and naphthalene from GC-MS and b) Malonic acid, acetic acid and phenol from HPLC, contained in the initial PW

### 4.2.2. Photo-Fenton experiments

Photo-Fenton reactions were carried out at pH 3 (by acidification with HCl) and the reagents used were hydrogen peroxide solution (30% w/w in $H_2O$, with stabilizer) (Sigma-Aldrich, USA) and iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) (Sigma-Aldrich, USA). Photo-Fenton experiments were carried out in a 1-L container made of borosilicate glass of 86 mm high and 157 mm diameter (Duran, Germany) with magnetic stirring.

The reaction took place inside a solar simulator (Solarbox 3000e, Cofomegra, Italy) (SB) equipped at the top with a 2500 W Xenon lamp (Neurtek, Spain) and an outdoor light filter, which allows 290-800 nm wavelength to pass through. Irradiance was set to 250 W $m^{-2}$. The intensity of the radiation from the Xe lamp used in the SB reaching the solution was determined by actinometry, using the Parker method (Hatchard and Parker, 1956), based on the photochemical reduction of the ferrioxalate complex $[Fe(C_2O_4)_3]^{3-}$ to Fe (II) in acid medium. The reduction takes place with a quantum yield of 1-1.2 mol $Einstein^{-1}$ in the range of wavelengths between 250-450 nm (Goldstein and Rabani, 2008). The concentration of Fe (II) over time was followed by the o-phenanthroline method (Zuo, 1995), based on the formation of a colored complex between Fe (II) in solution and 1,10-phenanthroline in acid medium acetic acid / acetate at pH 3-4. The absorbance was measured at 510 nm. The intensity value resulted in $6.5\ 10^{-4}$ Einstein $min^{-1}$.

Inside the SB, there was enough space to perform two experiments at the same time.

Figure 4.6 shows a photography of the SB.

Figure 4.6. Solar simulator (Solarbox 3000e, Cofomegra, Italy)

Photo-Fenton (PF) experiments were carried out in the SB adding to the sample the stoichiometric quantity of $H_2O_2$ according to COD ($H_2O_2$/COD (w/w) = 2.12) and 2 times more, and a dose of Fe (II) to achieve the relations $H_2O_2$/Fe (II) (w/w) = 2 and 10 according to Table 4.2.

Table 4.2. Reagents doses in the photo-Fenton experiments in the SB

| **Exp PF** | **$H_2O_2$/COD (w/w)** | **$H_2O_2$, mg $L^{-1}$** | **$H_2O_2$/Fe (w/w)** | **$Fe^{2+}$, mg $L^{-1}$** |
|---|---|---|---|---|
| 1 | 2.1 | 557 | 2 | 278.4 |
| 2 | 2.1 | 557 | 10 | 55.7 |
| 3 | 2.1 | 557 | 20 | 28.0 |
| 4 | 4.5 | 1179 | 2 | 589.5 |
| 5 | 4.5 | 1179 | 10 | 117.9 |

### 4.2.3. Fenton with temperature

As in the photo-Fenton experiments, Fenton (F) reactions were carried out at pH 3 and the reagents used were hydrogen peroxide solution (30% w/w in $H_2O$, with stabilizer) (Sigma-Aldrich, USA) and iron(II) sulfate heptahydrate ($FeSO_4·7H_2O$) (Sigma-Aldrich, USA). As is shown in Table

4.3, the concentrations of reagents added were the same as in photo-Fenton experiments numbers 1 and 2, in which the stoichiometric $H_2O_2$ quantity was used. The Fenton experiments were carried out in 1-L stirred topaz bottles to avoid the light influence and with magnetic stirring. The temperature essayed for these experiments was room temperature (20ºC), 40ºC and 70ºC.

Table 4.3. Reagents doses and temperature in the Fenton experiments (comparing with the photo-Fenton experiments 1 and 2)

| **Exp F** | **$H_2O_2$, mg L$^{-1}$** | **$Fe^{2+}$, mg L$^{-1}$** |
|---|---|---|
| 1 at 20ºC | 557 | 278.4 |
| 1 at 40ºC | 557 | 278.4 |
| 1 at 70ºC | 557 | 278.4 |
| 2 at 20ºC | 557 | 55.7 |
| 2 at 40ºC | 557 | 55.7 |
| 2 at 70ºC | 557 | 55.7 |

### 4.2.4. Photocatalytic experiments

Photocatalytic (PC) experiments were carried out in the solar simulator (Solarbox 3000e, Cofomegra, Italy) and with 4x 15 W UVA lamps (300-400 nm, with a maximum at 360-365 nm) (Philips TL-D BLB). Solarbox is shown in Figure 4.6 and UVA lamps in Figure 4.7.

The intensity of the total radiation from the UVA lamps determined by actinometry, using the Parker method (Hatchard and Parker, 1956), was 1.3 $10^{-4}$ Einstein min$^{-1}$.

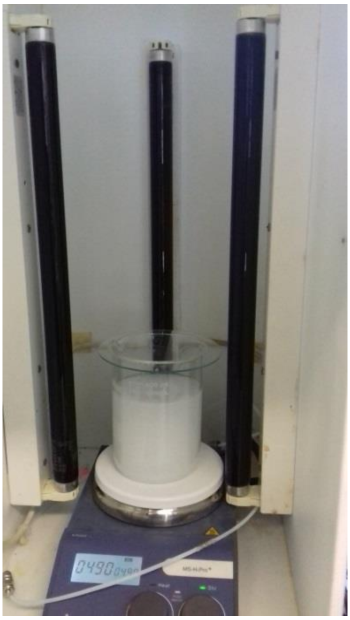


Figure 4.7. UVA lamps

Aeroxide® P25 (Acros Organics, Belgium) was used as a commercially available $TiO_2$ photocatalyst. This product was analyzed by X-ray diffraction and is composed of anatase (87.6%) and rutile (12.4%). The crystallite size was: anatase 16.9 nm and rutile 30 nm.

The experiments performed using the UVA lamps were started by adding 100 mg $L^{-1}$ P25 at free pH with and without 1500 mg $L^{-1}$ $H_2O_2$, and an experiment was carried out using PW synthetized in a milli-Q water matrix (instead of seawater) to test the effect of the salts. Also, experiments were realized by adding 500 mg $L^{-1}$ P25 at free pH, 6.25 (the pH of zero point of charge of $TiO_2$ P25) (Korman et al., 1991), 8 and 3.

Photocatalysis experiments were also carried out in the SB by adding 100 mg $L^{-1}$ P25 and 500 mg $L^{-1}$ P25 with and without 1500 mg $L^{-1}$ $H_2O_2$.

Table 4.4 shows the photocatalytic experiments tested with the UVA lamps and the SB, the reagent doses and pH initial.

Table 4.4. Light source (lamp), reagent doses and initial pH of the photocatalytic experiments

| **Exp PC** | **Light source** | **P25, mg L$^{-1}$** | **$H_2O_2$, mg L$^{-1}$** | **Initial pH** |
|---|---|---|---|---|
| 1 | UVA | 100 | 0 | Free (4.95) |
| 2 | UVA | 100 | 1500 | Free (4.95) |
| 3 | UVA | 500 | 0 | Free (4.95) |
| 4 | UVA | 500 | 0 | 6.25 |
| 5 | UVA | 500 | 0 | 8 |
| 6 | UVA | 500 | 0 | 3 |
| 7 | SB | 100 | 0 | Free (4.95) |
| 8 | SB | 100 | 1500 | Free (4.95) |
| 9 | SB | 500 | 0 | Free (4.95) |
| 10 | SB | 500 | 1500 | Free (4.95) |

### 4.2.5. Ozonation

The ozonation reactions were performed in a 1.5 L glass reactor containing 1 L of PW at ambient conditions (25 ± 2ºC) and atmospheric pressure. The ozone generated by an ozone generator (ANSEROS COM-AD-02) from pure $O_2$ (50 L h$^{-1}$) was passed through the solution maintaining a constant production of $O_3$. The $O_3$ flow added was determined by iodometry and productions between 1.59 and 5.7 g h$^{-1}$ were measured. An $O_3$ trap containing 20 g L$^{-1}$ potassium iodide (Sigma-Aldrich, USA) solution was connected in order to collect the $O_3$ gas passing through the reactor unreacted. Figure 4.8. shows the equipment used for the ozonation.

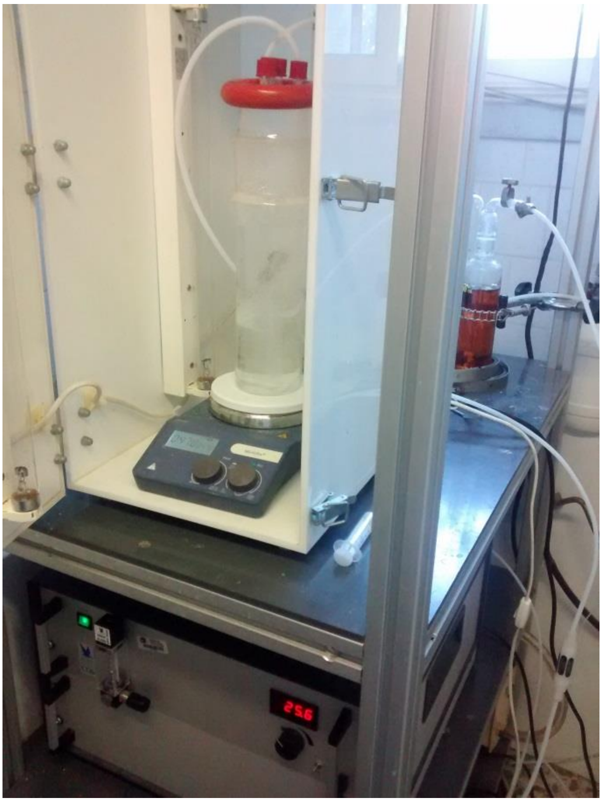


Figure 4.8. Ozone generator and equipment for ozonation experiments

First a stripping experiment was carried out, passing 50 L $h^{-1}$ $O_2$ (without $O_3$), which will be the flow rate used in all the experiments, through the sample during 2 h.

Secondly, some experiments were carried out by passing different $O_3$ flows (between 1.59 g $h^{-1}$ and 5.7 g $h^{-1}$ $O_3$) at free pH and at pH 8.

With 1.59 g $h^{-1}$ $O_3$, some ozonation tests were carried out to compare with the previous photo-Fenton and Fenton experiments, by adding $H_2O_2$ and $Fe^{2+}$ ($FeSO_4 \cdot 7H_2O$) in the same concentrations than experiment PF 1 (557 mg $L^{-1}$ $H_2O_2$ and 55.7 mg $L^{-1}$ $Fe^{2+}$) at pH 3, free pH (4.95) and 8.

Experiments were also conducted at free pH and pH 8 with 1.59 g $h^{-1}$ $O_3$ with different doses of $H_2O_2$ (557, 1000 and 1500 mg $L^{-1}$ $H_2O_2$).

After that, keeping 1500 mg $L^{-1}$ $H_2O_2$ at free pH, different $O_3$ productions were tested: 1.59 g $h^{-1}$, 2.8 g $h^{-1}$, 4 g $h^{-1}$, 4.8 g $h^{-1}$ and 5.7 g $h^{-1}$ $O_3$. The experiment with 5.7 g $h^{-1}$ $O_3$ was also tested with 3000 mg $L^{-1}$ $H_2O_2$.

Finally, once the amount of $O_3$ and $H_2O_2$ were optimized, tests were performed at pH 10 to check if this pH improved the elimination.

Table 4.5 shows the ozonation experiments performed.

Table 4.5. Reagents and initial pH in the ozonation experiments

| **Exp** | **pH** | **$O_3$, g $h^{-1}$** | **$H_2O_2$, mg $L^{-1}$** | **$Fe^{2+}$, mg $L^{-1}$** |
|---|---|---|---|---|
| 1 | 4.95 (free) | 1.59 | - | - |
| 2 | 4.95 (free) | 2.8 | - | - |
| 3 | 4.95 (free) | 4.0 | - | - |
| 4 | 4.95 (free) | 4.8 | - | - |
| 5 | 4.95 (free) | 5.7 | - | - |
| 6 | 8 | 1.59 | - | - |
| 7 | 8 | 4.0 | - | - |
| 8 | 8 | 5.7 | - | - |
| 9 | 4.95 (free) | 1.59 | 557 | - |
| 10 | 4.95 (free) | 1.59 | 1000 | - |
| 11 | 4.95 (free) | 1.59 | 1500 | - |
| 12 | 8 | 1.59 | 557 | - |
| 13 | 8 | 1.59 | 1000 | - |
| 14 | 8 | 1.59 | 1500 | - |
| 15 | 3 | 1.59 | 557 | 55.7 |
| 16 | 4.95 (free) | 1.59 | 557 | 55.7 |
| 17 | 8 | 1.59 | 557 | 55.7 |
| 18 | 4.95 (free) | 1.59 | 1500 | - |

| | | | | |
|---|---|---|---|---|
| 19 | 4.95 (free) | 2.8 | 1500 | - |
| 20 | 4.95 (free) | 4.0 | 1500 | - |
| 21 | 4.95 (free) | 4.8 | 1500 | - |
| 22 | 4.95 (free) | 5.7 | 1500 | - |
| 23 | 4.95 (free) | 5.7 | 3000 | - |
| 24 | 8 | 4.0 | 1500 | - |
| 25 | 10 | 4.0 | 1500 | - |
| 26 | 10 | 4.0 | 1000 | - |
| 27 | 10 | 4.0 | 3000 | - |
| 28 | 10 | 4.0 | - | - |

### 4.2.6. Analytical Methods

The pH measurements were performed using a PH 25 CRISON pH-meter. COD was determined photometrically using Hach Lange kit LCK 414. $H_2O_2$ consumption in the processes was monitored with QUANTOFIX Peroxide test strips. Residual $H_2O_2$ was neutralized at the end of the experiments with the addition of sodium bisulfite (Sigma-Aldrich) to avoid undesirable reactions. TOC concentrations were measured by a Shimadzu 5000-A TOC analyzer.

For the analysis of components such as the acids and phenol an HPLC system (LC Shimadzu 2010) equipped with a diode array detector (DAD) was used. For the separation of the analytes, a Mediterranea HPLC column (C18, 2.1 × 150 mm, 3.5 μm, Teknokroma, USA) was used at a temperature of 40°C. Isocratic program was used with a flow rate of 0.8 mL min$^{-1}$ mobile phase (deionized water at pH 2.2). The DAD wavelength was set at 220 nm.

Other components such as BTEX, naphthalene and phenol were analyzed by Gas chromatography coupled to mass spectrometry (GC-MS) using a

GC-MS 2010 of Shimadzu with a Zebron ZB-5 column using a splitless injection mode of 0.5 μL of sample.

Samples with $TiO_2$ or iron were previously filtered through 0.20 μm Phenex Nylon filter membranes before TOC, GC and HPLC analysis.

Ecotoxicological evaluation was performed on initial PW as well as selected samples after the AOP treatment using Vibrio fischeri, as test organisms to evaluate acute aquatic toxicity according to the basic test methodology developed for the equipment Microtox 5000. The principle used for the determination of toxicity is the inhibition of luminescence emitted by the bacteria when in contact with the sample. The basic test was performed in duplicate for a control sample and applying four dilutions of the initial concentration of each sample (5, 11, 22 and 45%), except for the samples treated with ozone/$H_2O_2$ where the 81.9% basic test was applied. Exposure time was 15 minutes, and $EC_{50,15\,min}$ (% v/v) was calculated with the software of the equipment. Toxicity can be classified using $EC_{50}$ values as established by Calleja et al. (1986) and consists of four toxicity classes (1–4): Class 1, when $EC_{50} \leq < 25\%$ (very toxic); as Class 2, when $<25\% < EC_{50} < 75\%$ (toxic); as Class 3, when $EC_{50} = 75\%$ (slightly toxic); and Class 4, when $EC_{50} > 75\%$ (non-toxic).

## 4.3. RESULTS

### 4.3.1. Photocatalysis

Adsorption tests in the dark were performed firstly, with 100 and 500 mg $L^{-1}$ P25 at free pH, with and without the addition of 1500 mg $L^{-1}$ $H_2O_2$. The results showed that until 2 hours, there was between 4-13% of TOC removal because of the adsorption of the organic matter to the titania and this percentage increased at longer times. $H_2O_2$ did not seem to produce any effect on the adsorption rate.

Figure 4.9 shows the photocatalysis experiments carried out using the UVA lamps. First, 100 mg $L^{-1}$ of catalyst P25 was added to the sample. Figure 4.9 (a) shows the TOC removal percentages using this catalyst concentration, where it can be seen that the TOC removal is very low (8%), even if 1500 mg $L^{-1}$ $H_2O_2$ (10 times more than the amount of acetic acid (w/w), which as it will be shown later is the most recalcitrant compound) is added.

Besides, to test the effect of the salts contained in the PW, a photocatalytic experiment with 100 mg $L^{-1}$ P25 was carried out using PW synthetized in a milli-Q water matrix (instead of seawater). In this case, TOC removal showed a better linear correlation with the time, achieving a 20% mineralization degree. It was confirmed that salts contained in the seawater influence the TOC removal, probably because some ions present such as chlorides are responsible for scavenging photoinduced radicals (e.g., hydroxyl or superoxide radicals) from the $TiO_2$ surface, limiting the destruction of organic molecules by photocatalysis (Kim et al. 2010).

Figure 4.9 (b) shows the TOC removal results using a higher P25 concentration and different initial pHs. TOC removal with 500 mg $L^{-1}$ P25 is slightly higher than with 100 mg $L^{-1}$ P25 but only a maximum of 15% of removal is achieved at free pH after 6 h. pH does not seem to have influence in the process.

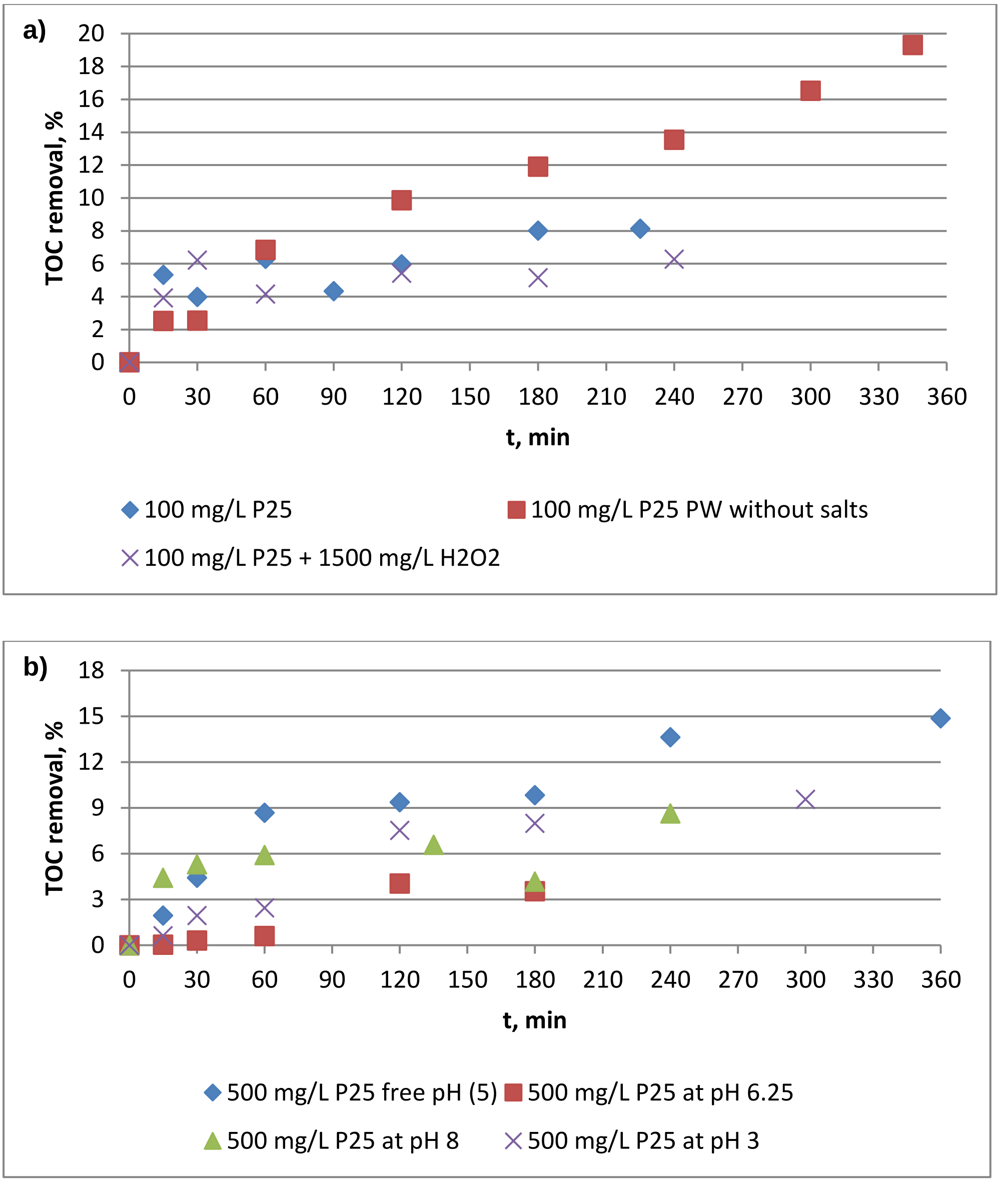


Figure 4.9. TOC removal percentages in photocatalytic experiments using the UVA lamps with a) 100 mg $L^{-1}$ P25 and b) 500 mg $L^{-1}$ P25

Photocatalysis experiments were also carried out in the SB. Figure 4.10 shows the results of TOC removal. As it was obtained using the UVA lamps, when 100 mg $L^{-1}$ P25 was added, there was hardly any TOC elimination. With this dose, TOC and phenol removals in the SB were 9.8% and 50%, respectively, after 240 min. When 500 mg $L^{-1}$ P25 was added, TOC and phenol removals were 18% and 100%, respectively, after 240 min. The rest of the PW compounds were also analyzed after this photocatalysis process and it was obtained that BTEX and naphthalene were removed, a maximum of 70% of malonic acid was eliminated but there was no degradation of acetic acid, so this process is not effective for the PW treatment. The addition of $H_2O_2$ did not improve the process. Table 4.6 summarizes the TOC and the components eliminations after 240 min achieved with photocatalysis by adding 100 mg $L^{-1}$ and 500 mg $L^{-1}$ P25 in the SB, where the results were moderately better than with the UVA equipment, probably because the intensity of the radiation from the Xe lamp used in the SB is higher according to the actinometric tests, and the configuration of the lamp on the top in the SB allows sample to take better profit of the light better.

Toxicity ranges expressed as $EC_{50}$ for the samples treated with photocatalysis were between 13-16%.

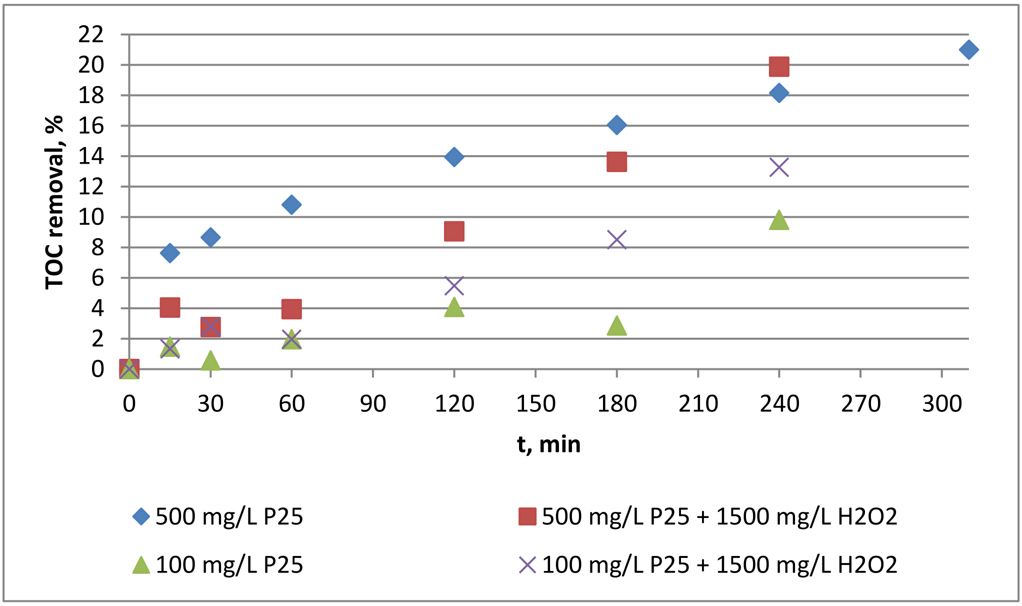


Figure 4.10. TOC removal percentages in photocatalytic experiments using the solarbox

Table 4.6. TOC and compounds removal percentages in the photocatalysis after 4 h using the SB and doses of 100 and 500 mg $L^{-1}$ P25

| **Dose of P25, mg $L^{-1}$** | **TOC removal, %** | **BTEX removal, %** | **Naphthalene removal, %** | **Phenol removal, %** | **Malonic acid removal, %** | **Acetic acid removal, %** |
|---|---|---|---|---|---|---|
| 100 | 9.8 | 100 | 100 | 50 | 30 | 0 |
| 500 | 18.0 | 100 | 100 | 100 | 70 | 0 |

### 4.3.2. Photo-Fenton

Table 4.7 shows the results of the TOC removal percentages in the photo-Fenton (PF) experiments with the SB after 90 min (since as shown in Figure 4.13, TOC did not decrease with a longer time), as well as the degradation percentages of BTEX, naphthalene, phenol and organic acids after 90 min. It was observed that most of the phenol disappeared during the first minutes of reaction.

Photo-Fenton experiments were performed in the SB because the intensity of the radiation from the Xe lamp used in the SB is higher than that of the UVA lamps, the configuration of the lamp on the top in the SB allows sample to take better profit of the light better and because iron compounds can absorb radiation up to ca. 550 nm.

As intermediates, it was found by the GC analysis than an aromatic compound containing nitrogen and benzaldehyde were formed during the process in similar concentrations in all these photo-Fenton experiments for the same time of reaction and the concentration of these compounds increased over time. Due to the formation of more intermediates (difficult to identify but which are detected by HPLC), TOC did not decrease. As example, Figure 4.11 shows these intermediates in the experiment PF 1 after 3 h of reaction and in Figure 4.12 the identification of malonic acid (that after 3 h is almost eliminated) and acetic acid.

Table 4.7. Photo-Fenton experiments in the solarbox with different dose of reagents and removal percentages obtained after 90 min (and 2 min in the case of phenol)

| **Exp PF** | **$H_2O_2$/COD (w/w)** | **$H_2O_2$, mg $L^{-1}$** | **$H_2O_2$/Fe (w/w)** | **$Fe^{2+}$, mg $L^{-1}$** | **TOC remov, %** | **BTEX remov, %** | **Naphthalene remov, %** | **Phenol remov, %** | | **Malonic acid remov, %** | **Acetic acid remov, %** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | **2 min** | **90 min** | | |
| 1 | 2.1 | 557 | 2 | 278.4 | 6.9 | 100 | 100 | 93.4 | 100 | 66 | 0 |
| 2 | 2.1 | 557 | 10 | 55.7 | 16.5 | 100 | 100 | 83.7 | 100 | 89 | 0 |
| 3 | 2.1 | 557 | 20 | 28.0 | 12 | 100 | 100 | 90.1 | 100 | 80 | 0 |
| 4 | 4.5 | 1179 | 2 | 589.5 | 8 | 100 | 100 | 97.5 | 100 | 55 | 0 |
| 5 | 4.5 | 1179 | 10 | 117.9 | 15.6 | 100 | 100 | 91.1 | 100 | 82 | 0 |

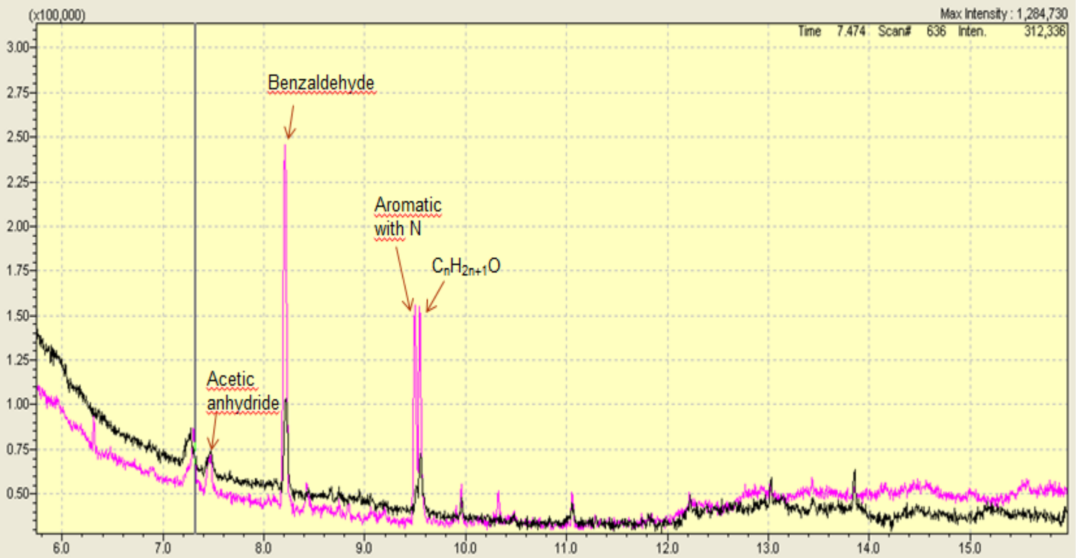


Figure 4.11. Intermediates formed in the PF 1 after 3 h (analyzed by GC-MS)

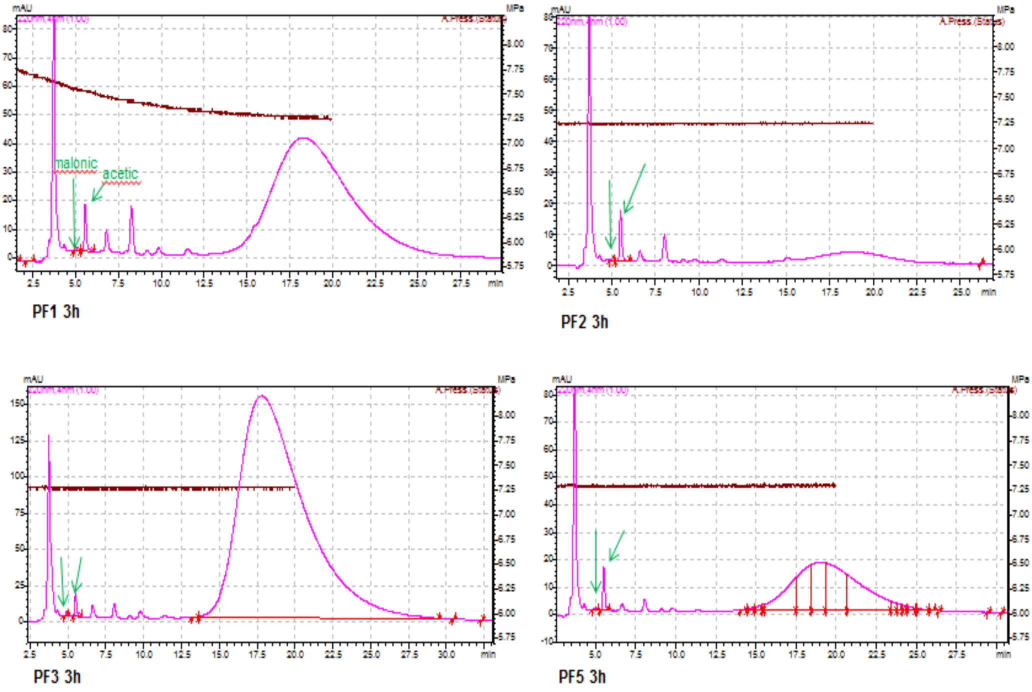
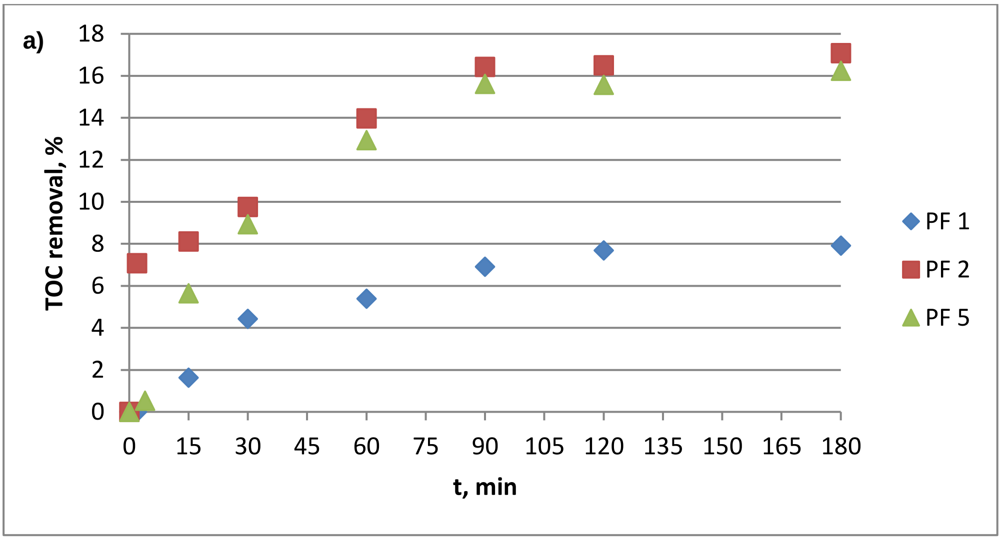


Figure 4.12. Malonic and acetic acids in PF 1,2,3,5 (analyzed by HPLC)

TOC was monitored at different times during the photo-Fenton reaction. Figure 4.13 (a) shows these TOC removal percentages for the experiments 1, 2 and 5, as well as the residual $H_2O_2$ that remained 3 (b). TOC analysis was monitored during 3 h of reaction, but as can be seen, after 90 min was stopped.

With the photo-Fenton process the only component that did not decrease its concentration is the acetic acid. TOC elimination was low due to the formation of intermediates during the photo-Fenton reaction. For the studied conditions, the optimum $H_2O_2$/Fe (w/w) was 10, with the least dose of oxidant, 557 mg $L^{-1}$, which after 2 h of reaction was consumed, obtaining a 16.5% of TOC removal after 90 min, similar to the TOC removal percentage achieved by Aljubourya et al. (2015) in the photo-Fenton process of petroleum wastewater using 1000 mg $L^{-1}$ $H_2O_2$ and 40 mg $L^{-1}$ Fe after 180 min. Higher removals obtained by other authors are due to the fact that the composition of the wastewater was different, no including recalcitrant compounds such as the acetic acid found in this PW (Coelho et al., 2006).



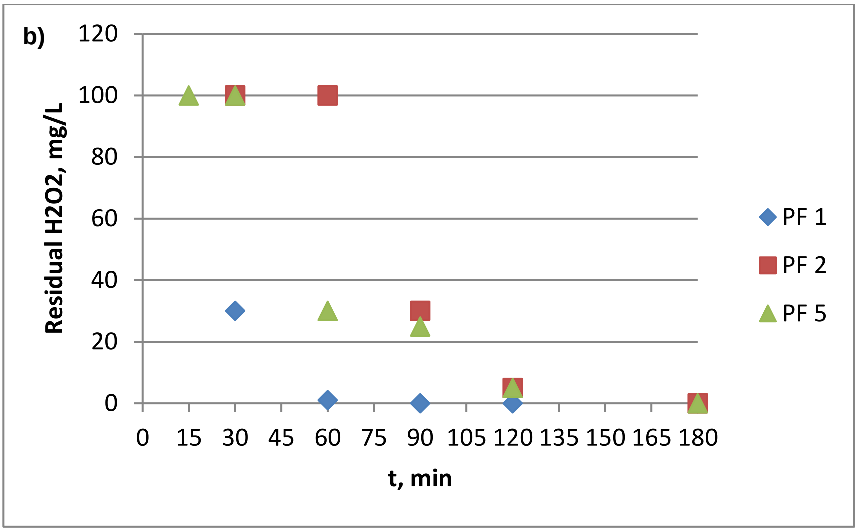


Figure 4.13. a) TOC removal percentages at different times during the photo-Fenton experiments 1, 2 and 5. b) Residual $H_2O_2$ during the photo-Fenton experiments 1, 2 and 5

Toxicity ranges expressed as $EC_{50}$ for the samples treated with photo-Fenton were <10%.

### 4.3.3. Fenton

Fenton (F) experiments were carried out by adding the same quantities of reagents than in the photo-Fenton experiments 1 and 2. These doses were 557 mg $L^{-1}$ $H_2O_2$, that was the minimum oxidant concentration, with 278.4 mg $L^{-1}$ Fe (F1) and 55.7 mg $L^{-1}$ Fe (F2). Fenton reactions were carried out at an initial pH 3 and at temperature of ca. 20ºC (room temperature), 40ºC and 70ºC. Figure 4.14 shows the results of TOC removal percentages of these experiments. As in the case of photo-Fenton process, almost all the malonic acid was possibly removed but its quantification was not possible due to the formation of formic and oxalic acids, that appear at the same retention time than malonic acid. These components may also have been formed in the photo-Fenton process but as they form photoactive complexes with iron (Baba et al., 2015) were not detected.

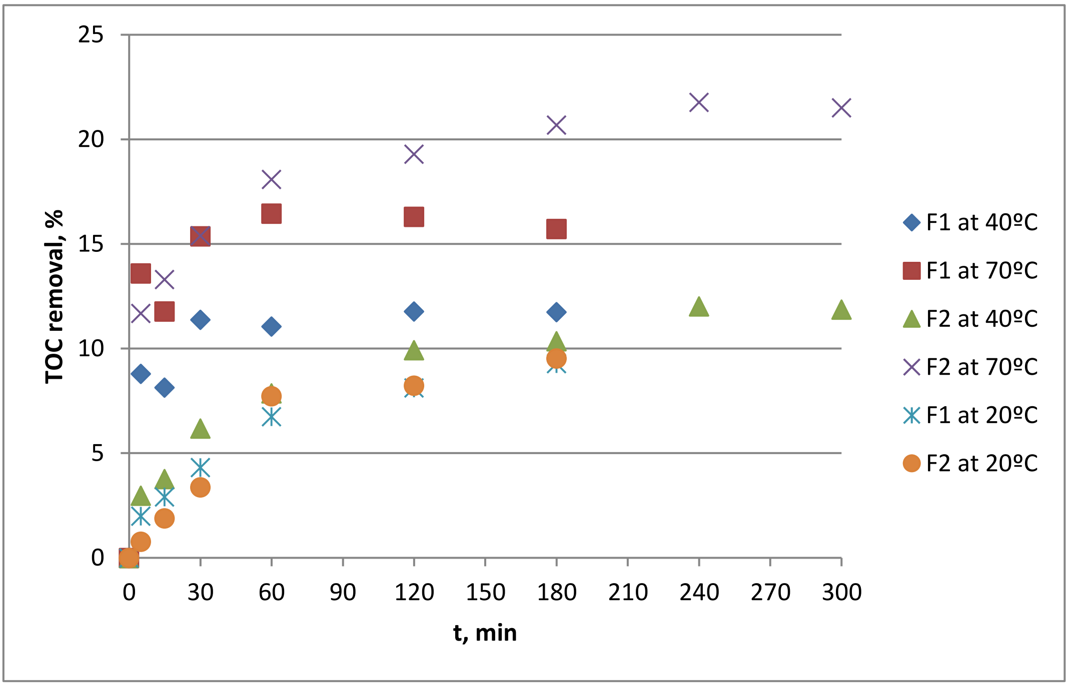


Figure 4.14. TOC removal percentages at different times during the Fenton reactions at 40ºC and 70ºC

As can be observed, TOC removal was slightly higher for the high temperature Fenton experiments. The temperature had more influence than the iron dose, so by adding 557 mg L$^{-1}$ $H_2O_2$ and 55.7 mg L$^{-1}$ Fe (F2), 18% of TOC removal was achieved after 60 min of reaction at 70ºC, but $H_2O_2$ was not consumed within 5 h of monitoring. Comparing with the photo-Fenton processes using the same doses of reagents, it was obtained that temperature has more influence than light in the TOC decrease. As in the case of photo-Fenton, BTEX, naphthalene and phenol were rapidly eliminated but no acetic acid removal occurred and intermediate compounds were also formed. Table 4.8 summarizes the eliminations in these Fenton experiments after 2 h of reaction.

Table 4.8. Fenton experiments and removal percentages obtained after 2 h of reaction

| **Exp F** | **$H_2O_2$, mg $L^{-1}$** | **$Fe^{2+}$, mg $L^{-1}$** | **TOC removal, %** | **BTEX removal, %** | **Naphthalene removal, %** | **Phenol removal, %** | **Malonic acid removal, %** | **Acetic acid removal, %** |
|---|---|---|---|---|---|---|---|---|
| 1 at 20ºC | 557 | 278.4 | 8.1 | 100 | 100 | 100 | - | 0 |
| 1 at 40ºC | 557 | 278.4 | 11.8 | 100 | 100 | 100 | - | 0 |
| 1 at 70ºC | 557 | 278.4 | 15.7 | 100 | 100 | 100 | - | 0 |
| 2 at 20ºC | 557 | 55.7 | 8.2 | 100 | 100 | 100 | - | 0 |
| 2 at 40ºC | 557 | 55.7 | 11.9 | 100 | 100 | 100 | - | 0 |
| 2 at 70ºC | 557 | 55.7 | 21.5 | 100 | 100 | 100 | - | 0 |

### 4.3.4. Ozonation

In previous tests with oxygen, it was found than BTEX and naphthalene were eliminated simply by striping with $O_2$ flow by passing 50 L $h^{-1}$ $O_2$ (without $O_3$) during 2 h, remaining the phenol and the acids.

First ozonation experiments were carried out with different $O_3$ productions between 1.59-5.7 g $h^{-1}$ $O_3$ (1.59 g $h^{-1}$, 2.8 g $h^{-1}$, 4 g $h^{-1}$, 4.8 g $h^{-1}$ and 5.7 g $h^{-}$1) through 1 L PW, and after 2 h, it was obtained that for initial pH of 5 (free pH) and 8, the TOC removals were around 17% in all the cases.

Phenol was eliminated by ozonation during the first minutes, but the acids remained after the 2 h of treatment.

Toxicity ranges expressed as $EC_{50}$ for the samples treated with ozonation were between 12-20%.

To enhance the formation of hydroxyl radicals (OH·), $H_2O_2$ was used in conjunction with $O_3$, since the hydroxyl radical is a stronger oxidant than molecular $O_3$ alone. First experiments were carried out by using 1.59 g $h^{-1}$ $O_3$ and adding 557 mg $L^{-1}$ $H_2O_2$ and 55.7 mg $L^{-1}$ Fe to compare with the photo-Fenton and Fenton experiments which were carried out previously. These tests were performed at initial pH 3, 8 and free (4.95). Figure 4.15 shows these results. It was observed that when Fe was added at pH 3 the result was worse, since TOC removals at initial pH 3, at free pH and pH 8 after 2 h were 16.3%, 21.8% and 31.7%, respectively. If only 557 mg $L^{-1}$ $H_2O_2$ was added at free pH in the ozonation, the elimination was 25.1%, so the addition of Fe in the ozonation is not necessary and even detrimental when $Fe^{2+}$ is added at acidic pH, probably because $O_3$ may be consumed in the oxidation of $Fe^{2+}$ to $Fe^{3+}$. At basic pH, there are more hydroxide ions present that act as an initiator for the decay of $O_3$ to form $HO_2^-$ which react with another $O_3$ molecule to form a radical $^{\bullet}OH$. These radicals introduce other reactions with ozone, causing more radicals to be formed.

In all these experiments more than 10 mg $L^{-1}$ $H_2O_2$ remained after 2 h reaction.

Figure 4.15 also shows the TOC removal percentages of the ozonation experiments with 1.59 g $h^{-1}$ $O_3$ and different doses of $H_2O_2$: 557 mg $L^{-1}$, 1000 mg $L^{-1}$ and 1500 mg $L^{-1}$ at free pH and at pH 8 to test if a higher pH or $H_2O_2$ dose enhanced the process. However, it was obtained that the improvement of the process did not depend significantly on these variables, so the next step was to increase the ozone production.

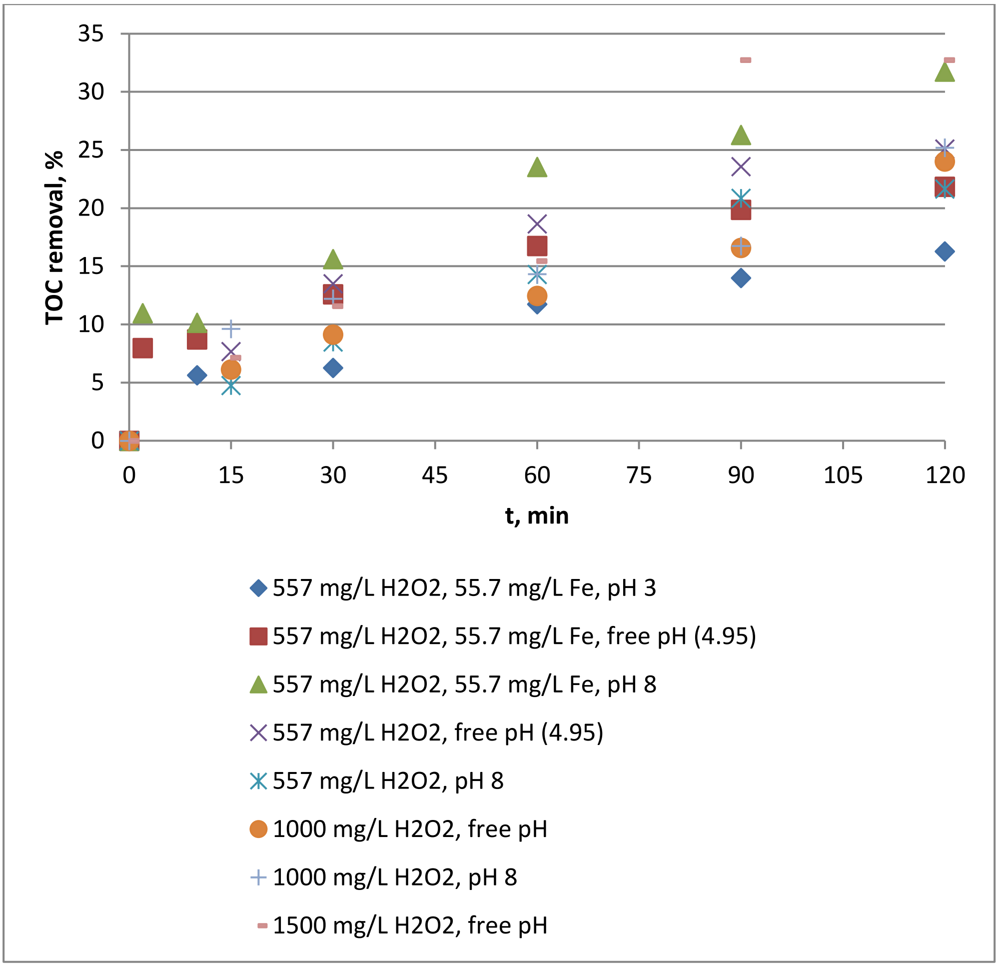


Figure 4.15. TOC removal percentages at different times during the ozonation experiments with 1.59 g $h^{-1}$ $O_3$

Figure 4.16 shows the TOC removal percentages, fixing 1500 mg $L^{-1}$ $H_2O_2$ and initial free pH, with different $O_3$ production rates: 1.59 g $h^{-1}$, 2.8 g $h^{-1}$, 4 g $h^{-1}$, 4.8 g $h^{-1}$ and 5.7 g $h^{-1}$ $O_3$. After 2 h of treatment, the TOC eliminations achieved were 32.7%, 36.8%, 49.6%, 56.1% and 40.3%, respectively. For these conditions, all the components in PW were eliminated, including part of the acetic acid (that is not removed by the rest of AOPs).

By passing 4 g h$^{-1}$, 4.8 g h$^{-1}$ and 5.7 g h$^{-1}$ $O_3$, all the $H_2O_2$ was consumed after 90 min.

It can be seen than TOC removal increases with the $O_3$ production but with the maximum flow rate, 5.7 g h$^{-1}$ $O_3$, the TOC goes down again, so a test was performed increasing the $H_2O_2$ dose up to 3000 mg L$^{-1}$ but the same elimination was achieved than with 1500 mg L$^{-1}$ $H_2O_2$ and 4 g h$^{-1}$ $O_3$.

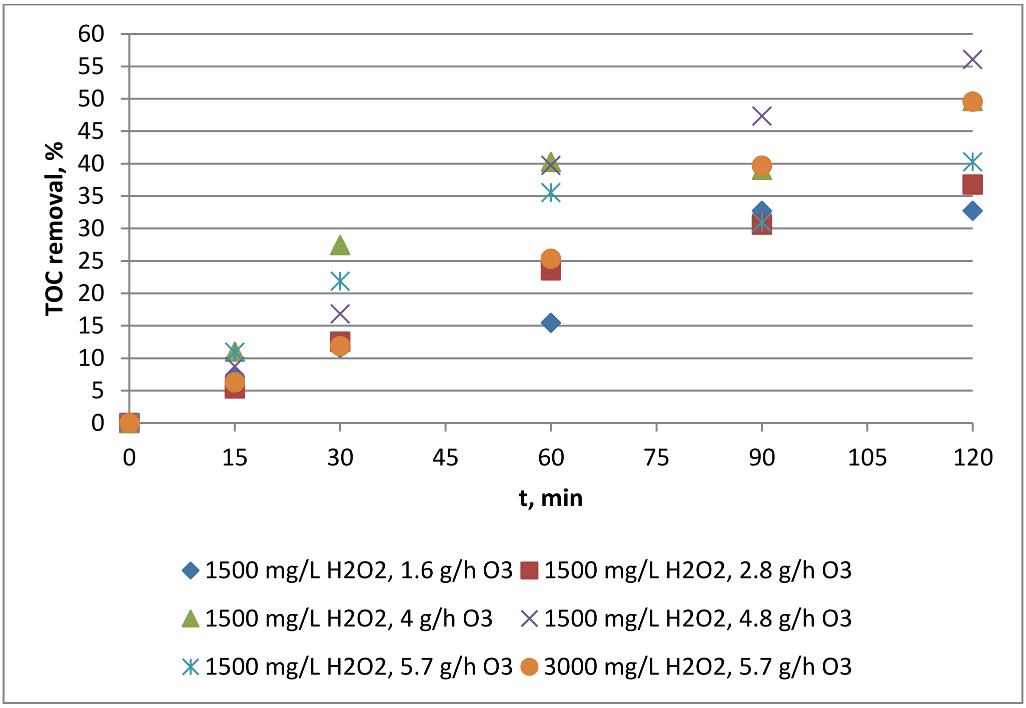


Figure 4.16. TOC removal percentages at different times during the ozonation experiments at free pH with different $O_3$ flows (1.6-5.7 g h$^{-1}$) and 1500 mg L$^{-1}$ $H_2O_2$, and 3000 mg L$^{-1}$ $H_2O_2$ with 5.7 g h$^{-1}$ $O_3$

Taking as optimum concentrations 1500 mg L$^{-1}$ $H_2O_2$ and 4 g h$^{-1}$ $O_3$ (to avoid too much $O_3$ consumption), the effect of initial pH was tested by doing the experiment at pH 8 and pH 10. Figure 4.17 shows these results. As observed, there is hardly any difference between doing the ozonation at pH 4.95 and 8, but at pH 10, removals are higher. This may be because when pH is close to pKa value for the $H_2O_2$ (11.6), the equilibrium is more displaced towards the formation of the hydroperoxide anion ($HO_2^-$). Moreover, at pH 10, there are more $OH^-$ present in the media than at free pH and pH 8. Both anions, $HO_2^-$ and $OH^-$, react rapidly with the $O_3$ to form hydroxyl and superoxide radicals (Beltrán, 2004). In addition, the $O_3$ decomposition kinetics, and therefore oxidation, is dependent on pH, and is higher at pHs between 8.5 and 11, while at neutral and slightly acidic pH, the $O_3$ decomposition kinetics is slower.

The highest elimination was achieved at pH 10 with 1500 mg $L^{-1}$ $H_2O_2$ and 4 g $h^{-1}$ $O_3$ after 2 h. The graph also compares the ozonation at initial pH 10, by passing 4 g $h^{-1}$ $O_3$ without adding $H_2O_2$ (where the maximum TOC removal was 42.6%), with 3000 mg $L^{-1}$ $H_2O_2$ (with a TOC removal of 58.6%) and 1000 mg $L^{-1}$ $H_2O_2$ (with a TOC removal of 56.3%), but the optimal condition was still 1500 mg $L^{-1}$ $H_2O_2$ where the TOC removal was 74% and the acetic acid removal was 77.8% (remaining 33.3 mg $L^{-1}$). In these ozonation experiments the rest of PW components that had been added were eliminated. Intermediates were not found by GC analysis. By the HPLC, intermediate acids compounds were found but were difficult to separate since they appear in the same peak that salts contained in the synthetic PW.

In this optimum experiment, the $H_2O_2$ was consumed after 1 h and the final pH after 2 h of process was 8.4.

Toxicity ranges expressed as $EC_{50}$ for the samples treated with ozone and $H_2O_2$ were between 40-57% (so they resulted less toxic than with the other AOPs).

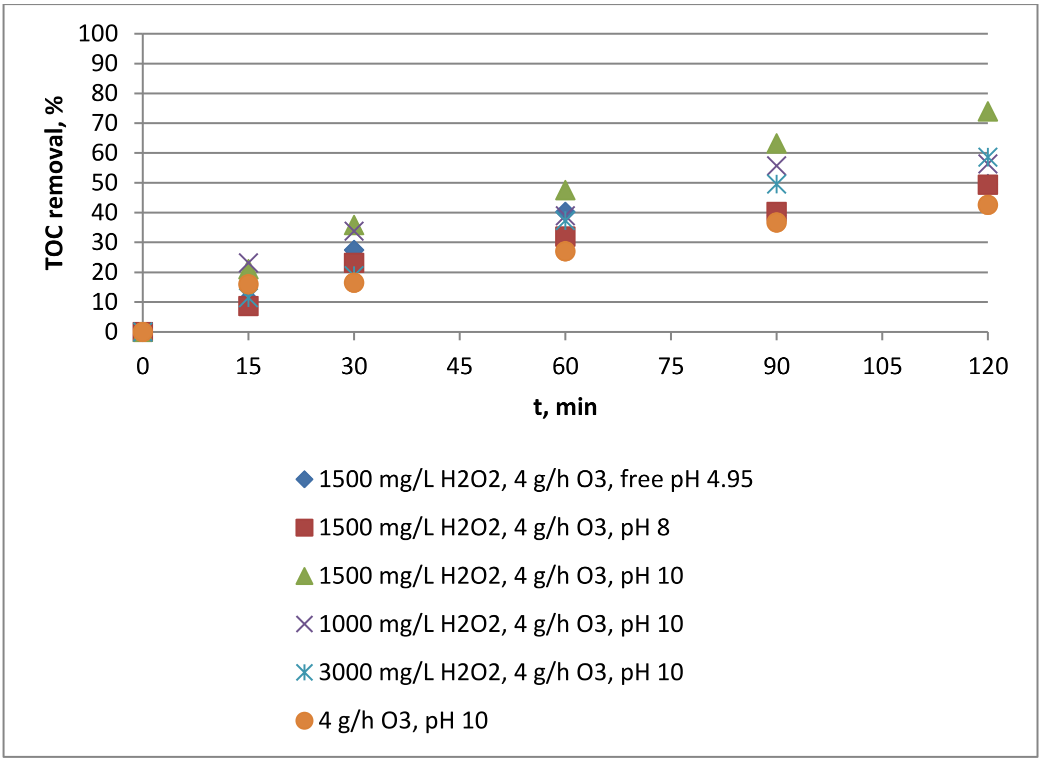


Figure 4.17. TOC removal percentages at different times during the ozonation experiments with 4 g $h^{-1}$ $O_3$

According to these results, the best option for the treatment of PW is the ozonation combined with $H_2O_2$ at pH 10, where 74% of TOC removal was achieved with 1500 mg $L^{-1}$ $H_2O_2$ and 4 g $h^{-1}$ $O_3$ after 2 h. The only component that was not totally eliminated was the acetic acid, although its concentration decreased a 77.8%, in contrast to the other AOPs tested, where no removal occurred. In addition, as $H_2O_2$ was consumed, treated PW did not contain any residual substance that had to be removed in a later treatment, as the iron sludge obtained after Fenton and photo-Fenton processes or the $TiO_2$ catalyst in photocatalysis. Besides, the final pH that is obtained is within the established limits for discharge and reutilization of water.

As the only component that is not totally eliminated is the acetic acid and there are seawater salts present in the PW, for some possible reuses of this water, e.g. as irrigation, the next and final step would be a reverse osmosis to eliminate the salts and besides the rejection of an additional 50% of acetic acid (Aquatechnology, 2016).

## 4.4. CONCLUSIONS

Different AOPs such as photocatalysis, photo-Fenton, Fenton and ozonation were studied to include one of these processes within the integrated treatments solution for the PW polishing that is composed by E-DAF or settling, possibly followed by membrane ultrafiltration, an AOP and finally a Reverse Osmosis system.

In all these AOPs, BTEX and naphthalene were removed.

Photocatalysis was not effective for the treatment of PW, since under solar radiation and by adding 100 mg $L^{-1}$ P25, TOC and phenol removals were 9.8% and 50%, respectively, after 4 h and by adding 500 mg $L^{-1}$ P25, TOC and phenol removals were 18% and 100%, respectively, after 4 h. Besides, malonic acid remains and there is no degradation of acetic acid.

With photo-Fenton process under solar radiation at pH 3 and by adding 557 mg $L^{-1}$ $H_2O_2$ and 55.7 mg $L^{-1}$ Fe, a 16.5% of TOC removal was achieved after 90 min. With this process phenol is completely eliminated and malonic acid was removed in a 89% but not the acetic acid, and additional intermediates as benzaldehyde were formed.

With the Fenton process at 70ºC adding also 557 mg $L^{-1}$ $H_2O_2$ and 55.7 mg $L^{-1}$ Fe, a 18% of TOC removal was achieved after 60 min. Comparing with the photo-Fenton processes and using the same doses of reagents, it was observed that temperature had more influence than light in the TOC decrease. As in the case of photo-Fenton, BTEX, naphthalene and phenol were rapidly eliminated but no acetic acid removal occurred and intermediate compounds were also formed.

Higher eliminations were obtained by ozonation combined with $H_2O_2$. Although TOC removal is still low (17%) and there is not degradation of acetic acid by passing only $O_3$, its combination with $H_2O_2$ produced better results and acetic acid began to be eliminated. At free pH, 50% of TOC removal was achieved after 2 h by adding 4 g $h^{-1}$ $O_3$ and 1500 mg $L^{-1}$ $H_2O_2$ and a 56% by adding 4.8 g $h^{-1}$ $O_3$ and 1500 mg $L^{-1}$ $H_2O_2$. For these conditions all the components in PW were eliminated, including a 70% of acetic acid (45 mg $L^{-1}$ remains). $H_2O_2$ was consumed in these processes between 60-90 min of reaction and the final pH of the treated PW was around 7.6. The optimum result was obtained with 4 g $h^{-1}$ $O_3$ and 1500 mg $L^{-1}$ $H_2O_2$ at initial pH 10, where 74% of TOC removal was achieved after 2 h and the acetic acid elimination was 77.8%. $H_2O_2$ was consumed within 60 min and the final pH of this effluent was 8.4.

## 4.5. REFERENCES

Al Jabri, H., Feroz, S., 2015. The Effect of Combining $TiO_2$ and ZnO in the Pretreatment of Seawater Reverse Osmosis Process. International Journal of Environmental Science and Development, Vol. 6, No. 5.

Aljubourya, A., Al Deen, D., Palaniandy, P., Aziz, H.B.A., Feroz, S., 2015. Comparative study of advanced oxidation processes to treat petroleum wastewater. Hung. J. Ind. Chem. 43, 97-101.

Andreozzi, R., Caprio, V., Insola, A., Marotta, R., 1999. Advanced oxidation processes (AOP) for water purification and recovery. Catalysis Today, v. 53, p. 51–59, Aquatechnology (visited in 2016). https://www.aquatechnology.net/reverse_osmosis.html

Arthur, J.D., Dillon, L.W., Drazan, D.J., 2011. Management of Produced Water From Oil and Gas Wells. Working Document of the NPC North American Resource Development Study. 32 pages.

Augugliaro, V., Litter, M., Palmisano, L., Soria, J., 2006. The combination of heterogeneous photocatalysis with chemical and physical operations: A tool for improving the photoprocess performance. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, v. 7, p. 127–144.

Baba, Y., Yatagai, T., Harada, T., Kawase, Y., 2015. Hydroxyl radical generation in the photo-Fenton process: Effects of carboxylic acids on iron redox cycling. Chem. Eng. J. 277, 229-241.

Bacardit, J., Stötzner, J., Chamarro, E., Esplugas, S., 2007. Effect of salinity on the photo-fenton process. Ind. Eng. Chem. Res., 46 (23), pp 7615–7619.

Beltrán, F.J. (2004). Ozone reaction kinetics for water and wastewater systems. Boca Raton, Fla.: Lewis Publishers.

Benitez, F.J., Acero, J.L., Real, F.J., Rubio, F.J., Leal A.I., 2001. The Role of Hydroxyl Radicals for the Decomposition of p-hydroxy Phenylacetic Acid in Aqueous Solutions. Water Research, Vol. 35, No. 5, pp. 1338-1343, ISSN 0043-1354.

Bianco, B., Michelis, I., Vegliò, F., 2011. Fenton treatment of complex industrial wastewater: Optimization of process conditions by surface response method. Journal of Hazardous Materials, Vol. 186, pp. 1733–1738, ISSN 0304-3894.

Calleja, A., Baldasano, J.M., Mulet, A., 1986. Toxicity analysis of leachates from hazardous wastes via Microtox and Daphnia magna. Toxicity Assessment: An International Quarterly, 1 (1), 73-83.

CDM, 2008. Produced Water Technical Breakthrough http://content.cdm.com/webinarregistration/Produced%20Water%20Treatment%20Brochure.pdf

Chamarro, E., Marco, A., Esplugas, S., 2001. Use of Fenton reagent to improve organic chemical biodegradability. Water Research, Vol. 35, No. 4, pp. 1047–1051, ISSN 0043-1354.

Coelho A., Castro AV, Dezotti M, Sant'Anna GL Jr., 2006. Treatment of petroleum refinery sourwater by advanced oxidation processes. Journal of Hazardous Materials B 137, 178–184.

Crittenden, J.C., Hu, S., Hand, D.W., Green, S.A., 1999. A kinetic model for H2O2/UV process in a completely mixed batch reactor, Water. Res. 33, 2315–2328.

Dercová, K., Vrana, B., Tandlich, R., Šubová, L., 1999. Fenton’s type reaction and chemical pretreatment of PCBs. Chemosphere, Vol. 39, No. 15, pp. 2621–2628, ISSN 0045-6535.

Duesterberg, C.K., Waite, T.D., 2006. Process optimization of fenton oxidation using kinetic modeling. Environmental Science and Technology 40 (13), 4189–4195.

El-Morsi, T.M., Emara, M.M., Abd El Bary, H.M.H., Abd-El-Aziz, A.S., Friesen, K.J., 2002. Homogeneous degradation of 1,2,9,10-tetrachlorodecane in aqueous solutions using hydrogen peroxide, iron and UV light. Chemosphere, Vol. 47, pp. 343–348, ISSN 0045-6535.

Fakhru'l-Razi, A., Alireza, P., Luqman, C.A., Dayang, R.A.B., Sayed, S.M., Zurina, Z.A., 2009. Review of technologies for oil and gas produced water treatment. Journal of Hazardous Materials, 170, 530–551.

Gallard, H., De Laat, J., 2001. Kinetics of oxidation of chlorobenzenes and phenyl-ureas by Fe(II)/ $H_2O_2$ and Fe(III)/$H_2O_2$. Evidence of reduction and oxidation reactions of intermediates by Fe(II) or Fe(III). Chemosphere, Vol. 42, pp. 405–413, ISSN 0045-6535.

Garrido-Ramírez, E.G., Theng, B.K.G, Mora, M.L., 2010. Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions — A review. Applied Clay Science, Vol. 47, pp. 182–192, ISSN 0169-1317.

Gogate, P. R., Pandit, A. B., 2004. A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. Advances in Environmental Research, v. 8, n. 3-4, p. 501-551, 2004.

Haque, M.M., Bahnemann, D., Muneer, M., 2012. Photocatalytic Degradation of Organic Pollutants: Mechanisms and Kinetics, Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update, Dr. Tomasz Puzyn (Ed.), InTech, DOI: 10.5772/34522.

Jiménez, S., Micó, M.M., Arnaldos, M., Ferrero, E., Malfeito, J.J., Medina, F., Contreras, S., 2017. Integrated processes for produced water polishing: Enhanced flotation/sedimentation combined with advanced oxidation processes. Chemosphere, 168, 309-317.

Kang, Y.W., Hwang, K.Y., 2000. Effects of Reaction Conditions on the Efficiency in the Fenton Process. Water Research, Vol. 34, No. 10, pp. 2786-2790, ISSN 0043-1354.

Kavitha, V., Palanivelu, K., 2004. The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol, Chemosphere 55, 1235-1243.

Khatib, Z., Verbeek, P., 2002. Water to value-produced water management for sustainable field development of mature and green fields, in: SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Kuala Lumpur, Malaysia, 20–22 March, 2002.

Kim, M.J., Choo, K.H., Park, H.S., 2010. Photocatalytic degradation of seawater organic matter using a submerged membrane reactor, J. Photochem. Photobiol. A Chem. 216, 215–220.

Kormann, C., Bahnemann, D.W., Hoffman, M.R., 1991. Photolysis of chloroform and other organic molecules in aqueous titanium dioxide suspensions. Environ.Sci.Technol. 25, 494-500.

Kwan, W.P., Voelker, B. M., 2002. Decomposition of hydrogen peroxide and organic compounds in the presence of dissolved iron and ferrihydrite. Environmental Science and Technology 36(7), 1467–1476.

Lin, S.H., Lo, C.C., 1997. Fenton Process for Treatment of Desizing Wastewater. Water Research, Vol. 31, No. 8, pp. 2050-2056, ISSN 0043-1354.

Lu, M.C., Chen, J.N., Chang, C.P., 1999. Oxidation of dichlorvos with hydrogen peroxide using ferrous ion as catalyst. Journal of Hazardous Materials, Vol. B65, pp. 277–288, ISSN 0304-3894.

Lunar, L., Sicilia, D., Rubio, S., Rez-Bendito, D., Nickel, U., 2000. Degradation of Photographic Developers by Fenton's Reagent: Condition

Optimization and Kinetics for Metol Oxidation. Water Research, Vol. 34, No. 6, pp. 1791-1802, ISSN 0043-1354.

Mota A. L. N., Albuquerque L. F., Beltrame L. T. C., Chiavone-Filho O., Machulek Jr.A., Nascimento C. A. O., 2008. Advanced oxidation processes and their application in the petroleum industry. Brazilian Journal of Petroleum and Gas, Vol. 2, n. 3, p. 122-142.

Nath, R. K., Zain, M. F. M., Kadhum, A. A.H., 2012. New Material LiNbO3 for photocatalytically improvement of indoor air- an overview. Advances in Natural and Applied Sciences, 6, n. 7, 1030-1035.

Neff, J.M., 2002. Bioaccumulation in Marine Organisms: Effect of Contaminants from Oil Well Produced Water. Elsevier Science Publishers, Amsterdam. 452 pages.

Nesheiwat, F.K., Swanson, A.G., 2000. Clean Contaminated Sites using Fenton's Reagent. Chemical Engineering Progress, Vol. 96, No. 4, pp. 61-66, ISSN 0360-7275.

Neyens, E., Baeyens, J., 2003. A review of classic Fenton's peroxidation as an advanced oxidation technique. Journal of Hazardous Materials 98 (1–3), 33–50.

Ogata, Y., Tomizawa, K., Takagi, K., 1981. Photo-oxidation of formic, acetic, and propionic acids with aqueous hydrogen peroxide. Can. J. Chem. 59, 14.

Oturan, M.A., Pimentel, M., Oturan,N., Sires, I., 2008. Reaction sequence for the mineralization of the short-chain carboxylic acids usually formed upon cleavage of aromatics during electrochemical Fenton treatment, Electrochim. Acta 54, 173-182.

Park, J.Y., Lee, I.H., 2009. Decomposition of acetic acid by advanced oxidation processes. Korean J. Chem. Eng. 26(2), 387-391.

Pera-Titus, M., García-Molina, V., Baños, M. A., Giménez, J., Esplugas, S., 2004. Degradation of chlorophenols by means of advanced oxidation processes: a general review. Applied Catalysis B: Environmental, v. 47, p. 219–256.

Pignatello, J.J., 1992. Dark and photoassisted iron(3+)-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. Environmental Science & Technology, 26(5), 944–951.

Pignatello, J., Oliveros, E., MacKay, A., 2006. Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry. Critical Reviews in Environmental Science and Technology, 36, 1-84.

Rodríguez, A., Rosal, R., Perdigón-Melón, J.A., Mezcua, M., Agüera, A., Hernando, M.D., 2008. Ozone-based technologies in water and wastewater treatment. The handbook of environmental chemistry, Vol. 5. Berlin Heidelberg: Springer-Verlag.

Siemens (visited in 2016), http://www.energy.siemens.com/hq/en/industries-utilities/oil-gas/products-systems-solutions/water-solutions/produced-water-treatment.htm.

Sinha, A., Chakrabarti, S., Chaudhuri, B., Bhattacharjee, S., Ray, P., 2007. Oxidative degradation of strong acetic acid liquor in wastewater emanating from hazardous industries. Industrial & Engineering Chemistry Research 46, pp. 3101-3107.

Straehelin, S., Hoigné, J., 1985. Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions. Environ. Sci. Technol., v. 19, p. 1209–1212.

Torrades, F., Pérez, M., Mansilla, H.D., Peral, J., 2003. Experimental design of Fenton and photo-Fenton reactions for the treatment of cellulose bleaching effluents. Chemosphere, Vol. 53, pp. 1211–1220, ISSN 0045-6535.

Utvik, T.I.R., Hasle, J.R., 2015. Recent Knowledge About Produced Water Composition and the Contribution From Different Chemicals to Risk of Harmful Environmental Effects. Journal of Petroleum Technology, 54(12), 67–69.

Veil, J.A., Pruder, M.G., Elcock, D., Redweik, J., 2004. A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane. Prepared for the U.S. Department of Energy, Energy Technology Laboratory.

Veolia, (visited in December, 2016). http://www.veoliawaterst.com/opus/en/

Walling, C., 1975. Fenton's reagent revisited. Accounts of Chemical Research, Vol. 8, pp. 125–131, ISSN 0001-4842.

Wang, A., Li, Y.Y., Estrada, A.L., 2011. Mineralization of antibiotic sulfamethoxazole by photoelectron-Fenton treatment using activated carbon fiber cathode and under UVA irradiation, Appl. Catal. B Environ. 102, 378-386.

Xiao, D., Guo, Y., Lou, X., Fang, C., Wang, Z., Liu, J., 2014. Distinct effects of oxalate versus malonate on the iron redox chemistry: Implications for the photo-Fenton reaction, Chemosphere 103, 354-358.

Zuo, Y., 1995. Kinetics of photochemical/chemical cycling of iron coupled with organic substances in cloud and fog droplets”. Geochimica et Cosmochimica Acta, 59, 3123-3130.

# Chapter 5. Reverse Osmosis Membranes Cleaning Waters Treatment for Reutilization Purposes. Part I: Application of Fenton Process

**Content**

## 5.1. INTRODUCTION

Reverse Osmosis (RO) is the most common membrane based desalination option in seawater desalination, dominating in the Mediterranean area (Fritzmann et al. 2007). RO membrane enables the separation of salts and inorganic molecules, as well as organic molecules with a molecular weight greater than approximately 100 Da through a semi-permeable membrane thanks to a pressure gradient. A typical seawater RO (SWRO) desalination process includes seawater intake, pretreatment, a RO system, and post-treatment. Before the RO process, the usual pretreatment consists on coagulation, flocculation, media filtration, and cartridge filter (Young et al. 2009).

Despite this pretreatment, in normal operation, RO membranes can become fouled by mineral scale, biological matter, colloidal particles and insoluble organic constituents (Chesters et al. 2011; Dow Water & Process Solutions, 2011; Melián, 2015; Mitra et al. 2009; Pontié et al. 2005; Shirazi et al. 2010). These deposits on the membrane surfaces cause loss in normalized permeate flow, loss of normalized salt rejection, or both (Dow Water & Process Solutions, 2011; Mohammadi et al. 2002). There are several cleaning scenarios in desalination plants; basic cleanings for regular maintenance; acid cleaning against severe inorganic scaling; biocide injection for the conservation of RO modules in plant shutdowns (Dow Water & Process Solutions, 2011; Jiménez, 2016) and its posterior flushing when restarting. Table 5.1 shows various scenarios present in desalination plants. To characterize these scenarios have been used a liquid chromatography with organic carbon detection equipment, a total organic carbon analyzer and a gas chromatography mass spectrometry headspace injection equipment between others (Navea et al. 2016). The defined scenarios are:

- Scenario 1: Organic fouling in the first element of a reverse osmosis rack.

- Scenario 2: Organic fouling in the first element of a reverse osmosis rack with presence of inorganic fouling coming from a coagulation process.
- Scenario 3: Inorganic fouling in the first element of a reverse osmosis rack because of aluminum and iron silicates with the presence of organic fouling.
- Scenario 4: Cleaning water coming from a basic CIP of the pretreatment process.
- Scenario 5: Water coming from module membrane conservation of plant shutdowns using biocides based on isothiazolones.

Table 5.1. Composition of some scenarios of cleaning wastewaters present in desalination plants (Navea et al. 2016)

| **Scenario** | **Composition** |
|---|---|
| Scenario 1 | • 7.67 mg $L^{-1}$ potato anioinic modified starch (= 1.65 mg $L^{-1}$ C)<br>• 200 mg $L^{-1}$ $Na_4$-EDTA<br>• 150 mg $L^{-1}$ lauryl sulphate<br>• pH 10.32 |
| Scenario 2 | • Idem scenario 1<br>• 0.52 mg $L^{-1}$ Fe |
| Scenario 3 | • 2.42 mg $L^{-1}$ potato anionic modified starch (= 0.54 mg $L^{-1}$ C)<br>• 200 mg $L^{-1}$ $Na_4$-EDTA<br>• 150 mg $L^{-1}$ lauryl sulphate<br>• 4.60 mg $L^{-1}$ Fe<br>• 9.56 mg $L^{-1}$ Si<br>• 3.56 mg $L^{-1}$ Al<br>• pH 10.32 |

| | |
|---|---|
| Scenario 4 | • 4000 mg $L^{-1}$ ECO(VERMICUC) (aprox. 21.5 mg $L^{-1}$ C)<br>• 750 µg $L^{-1}$ de trihalomethanes<br>• 270 mg $L^{-1}$ free chlorine<br>• pH 8.56<br>• 8.3 mS $cm^{-1}$ |
| Scenario 5 | • 1000 mg $L^{-1}$ biocide based on isothiazolones<br>• Desactivation of biocide with bisulphite |

Alkaline cleaning with permeate water pump cycles and soaking are commonly used against the organic fouling of the membranes. These operations generate a significant amount of wastewater (Dow Water & Process Solutions, 2011; Jiménez, 2016) that will be treated in this study (scenario 1, according to Table 5.1). This volume is particularly significant in those RO plants where organic fouling is specially common, for example those located where algal blooms are a typical phenomenon. This cleaning water nowadays is finally discharged to a neutralization tank and then is resent to the sea or the public sewer system. It contains organic matter detached from the membrane and cleaning products, such as chelating agents (e.g. salts of ethylenediaminetetraacetate (EDTA) or citric acid), and surfactants (e. g. Sodium Lauryl Sulfate (SLS) also known as Sodium Dodecyl Sulfate (SDS), an anionic surfactant); and it has an alkaline pH (Ang et al. 2011; Jiménez, 2016; Singh et al. 2015). As the cleaning solution is prepared from permeate water, this effluent has low salinity; therefore it could be reused once the pH is neutralized and the mentioned organic matter is removed, as irrigation water or in other stages of the process, contributing to the concept of a zero liquid discharge osmosis desalination plant.

Basic cleaning is usually executed for regular maintenance of the RO system and different scenarios can be determined due to the fact that depending on the position of the membrane in the whole plant, its fouling or its scaling can be more or less severe, so the resulting cleaning effluent can be more or less rich on organic matter. This work focuses in particular on the effluent resulting from regular cleaning of the organic fouling of the first module of a RO rack; this scenario implies the highest volumes of generated wastewater and its content of detached organic matter is expected to be the maximum. According ACCIONA Agua company operational practices, the resulting effluent of this cleaning contains the organic matter which was adhered to the membrane, together with the common reagents used in this process, such as tetrasodium ethylenediaminetetraacetate ($Na_4$-EDTA) and sodium dodecyl sulfate (SDS) as cleaning reagents, as is usually recommended by the manufacturer of the membranes (Dow Water & Process Solutions, 2011). Regarding its reuse, the most important parameter to control could be the SDS content, because this surfactant is an emerging contaminant (Stuart et al. 2012) and is susceptible to be contemplated as target compound in the future through the implementation of the wastewater discharge legislation EU Directive 2013/39/UE, and regional regulations on sea discharge MAH/285/2007 (which accepts a maximum level of 6 mg $L^{-1}$ for anionic surfactants, expressed as sodium lauryl sulfate). In relation to the rest of the organic matter content, there is no European legislation framework for reuse purpose. The Spanish regulation (Royal Decree 1620/2007) does not include organic matter content limits for reuse in irrigation, and it concentrates the limitations mainly on the content on biological and inorganic parameters, as it is also contemplated in the World Health Organization (WHO) and the Food and Agricultural Organization (FAO) reuse guidelines, in which probably the countries possessing reuse regulations are based (Choukr-Allah et al. 2012). The US Environmental Protection Agency (US EPA, 2012) recommends concentrations below 10 mg $L^{-1}$ biochemical oxygen demand (BOD) if food crops are intended for human consumption and will be consumed raw, and 30 mg $L^{-1}$ BOD for processed food crops or crops which are not consumed by humans, including fodder, fiber, and seed crops, or to irrigate pasture land, commercial nurseries, and sod farms.

In this chapter, Fenton process is studied as a plausible treatment for the organic load removal of the RO membranes cleaning waters in desalination plants. Fenton reaction consists of a combination of hydrogen peroxide ($H_2O_2$) and ferrous ions ($Fe^{2+}$), in an acid medium, leading to the decomposition of $H_2O_2$ mainly into radicals, mainly hydroxyl radical that possesses a high oxidation potential and therefore can oxidize organic molecules (Neyens and Baeyens, 2003). Among the Advanced Oxidation Processes (AOPs), Fenton reaction was chosen because of the low cost of iron, the ease of use of $H_2O_2$ and its harmless decomposition to the environment (Jones, 1999).

Previous studies revealed information on the different AOPs for the degradation of SDS and other anionic-based surfactants (Chitra et al. 2014; Kiran et al. 2013 ). Fenton process was also applied by Bandala et al. (2007) and Chitra et al. (2014) for the degradation of SDS, although it showed that reaction using sunlight, $Fe^{2+}$, and $H_2O_2$ (solar photo-Fenton) was faster.

On the other hand, $Na_4EDTA$, is a synthetic chelating agent found in the cleaning waters. Suárez et al. (2013) achieved a recovery of 90% using nanofiltration when the $Na_4EDTA$ concentration in water was nearly 0.2% w/w. There are also studies based in the degradation of EDTA by AOPs (Chitra et al. 2013; Rekab et al. 2014). The results from the comparative study on the kinetics of EDTA degradation carried out by Chitra et al. (2013), revealed that the reaction using UV, ultrasound, $Fe^{2+}$ and $H_2O_2$ was faster than that obtained in any of the other tested processes. Fenton and photo-Fenton experiments at pH 3 were performed by Ghiselli et al. (2014) under similar conditions to study the degradation of EDTA. With

Fenton process, TOC removal was very low at the end of 4 h for all experiments, they reached a maximum of 31.9% removal in the case of 1:1 EDTA:$Fe^{2+}$ ratio. In addition, some by-products formed in this process, in particular oxalic acid, can accumulate in the reaction media due to its refractory nature to Fenton's reagent.

However, no references were found regarding the degradation of these two components coexisting in the same matrix, as they are present in the cleaning waters of this work, nor the possibility of treating these effluents that are generated in large volumes in the desalination plants and that could have application, e.g. for irrigation.

## 5.2. MATERIALS AND METHODS

### 5.2.1. Cleaning waters

Cleaning effluents were simulated for this work.

Based on laboratory analyses from autopsies of first position RO modules from the seawater desalination plant in Sureste (Tenerife, Spain), organic fouling was estimated (see Figure 5.1). This data was obtained through the measurement by LC-OCD, and resulted around 4.12 g C per module (Navea et al. 2016). Besides, it was observed that the predominant fraction of organic matter corresponded to biopolymers (Figure 5.2). According to this, an anionic modified potato starch from Cargill (C flake 35704) was chosen for simulating the organic content. Currently this product is marketed under the name Anifloc (Nova Casanova MCM S.L., Spain). As shown in Figure 5.2, this starch practically only supplies organic carbon from the fraction of biopolymers, considered the predominant fraction in the solid from the organic fouling of a RO module (Nguyen et al. 2012). Thus it was obtained that 100 mg $L^{-1}$ of starch corresponds to 22.4 mg $L^{-1}$ of dissolved organic carbon.

Figure 5.1. Image of organic fouling deposited on the membrane

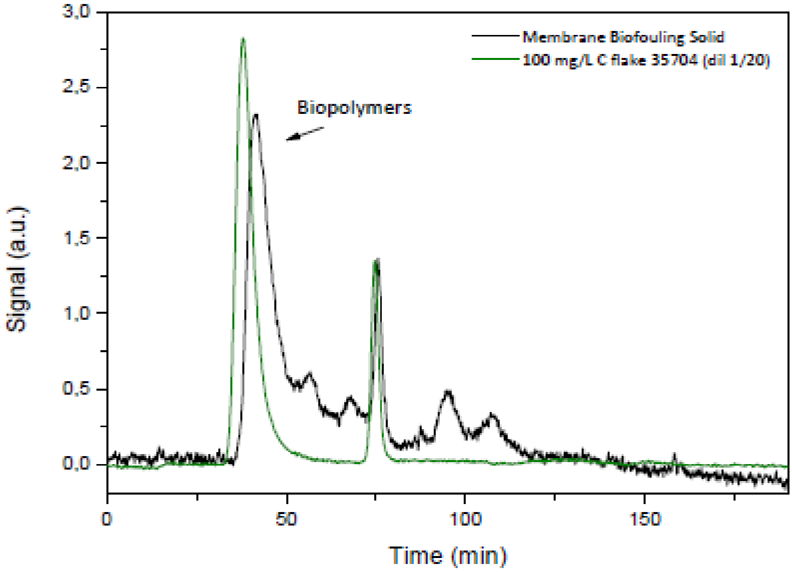


Figure 5.2. LC-OCD chromatograms of the solid content of the membrane and 100 mg $L^{-1}$ modified anionic potato starch (C flake 35704) with a 1:20 dilution.

In an average desalination plant with 100 tubes of RO modules per rack, 250 $m^3$ of water is used for the basic cleaning against organic fouling.

According to the manufacturer instructions (Dow Water & Process Solutions, 2011), this cleaning solution contains $Na_4$-EDTA (0.2%), NaOH, SDS (0.1-0.2%) and HCl. After a basic cleaning, a 100 $m^3$ acidic displacement is always performed. Both 250 and 100 $m^3$ volumes are stored in the same neutralization tank, and its combination is the effluent that finally should be treated. Table 5.2 shows the composition of the synthetic effluent prepared for this study based on that described scenario.

Table 5.2. Composition of cleaning water including initial chemical oxygen demand (COD), total organic carbon (TOC) and biological oxygen demand ($BOD_5$).

| **Quality Parameter of the simulated cleaning water** | **Value** |
|---|---|
| $Na_4$-EDTA (Sigma-Aldrich, USA) (mg $L^{-1}$) | 200.0 |
| SDS (Sigma-Aldrich, USA) (mg $L^{-1}$) | 150.0 |
| Anionic modified potato starch from Cargill (C flake 35704) (mg $L^{-1}$) | 7.4 (1.65 mg C $L^{-1}$) |
| pH | 10.3 |
| COD (mg $L^{-1}$) | 414.0 |
| TOC (mg $L^{-1}$) | 134.5 |
| $BOD_5$ (mg $L^{-1}$) | 3.1 |

### 5.2.2. Fenton experiments

Fenton reactions were carried out at pH 3 and the reagents used were hydrogen peroxide solution (30% w/w in $H_2O$, with stabilizer) (Sigma-Aldrich, USA), iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) (Sigma-Aldrich, USA) and hydrochloric acid (HCl) (Panreac, Spain) to acidify. The Fenton experiments were carried out in 1L topaz bottles, to avoid light influence, made of borosilicate glass (Duran, Germany) and with magnetic stirring.

Stoichiometric $H_2O_2$ required for the oxidation of organic matter was calculated as reported by Kim and colleagues (1997), who considered that the stoichiometric ratio $H_2O_2$ / COD (w) must be 2.125. Therefore in this work, $H_2O_2$ concentration ranged between 800 mg $L^{-1}$ ($H_2O_2$ / COD (w)= 1.9, close to the stoichiometric quantity according to the COD at Table 1) and 8280 mg $L^{-1}$ ($H_2O_2$ / COD (w) =20), and $Fe^{2+}$ (as $FeSO_4 \cdot 7H_2O$) from 50 mg $L^{-1}$ to 16560 mg $L^{-1}$ were added.

Samples were withdrawn at 15, 157 and 300 min of the reaction and TOC was analyzed.

### 5.2.3. Analytical methods

pH measurements were performed using a PH 25 CRISON pH-meter. COD was determined photometrically using Hach Lange kit LCK 414. H2O2 consumption in the Fenton reactions was monitored semi-quantitatively with QUANTOFIX Peroxide test strips (Macherey-Nagel). Residual $H_2O_2$ was neutralized after samples withdrawal with the addition of sodium bisulfite (Sigma-Aldrich) to quench Fenton reaction. TOC concentrations were measured using a GE Total Organic Carbon Analyzer, Sievers Innovox model. Biochemical Oxygen Demand after five days ($BOD_5$) was measured according to the standard method (SM 5210-D) using an Oxitop system (VELP Scientifica).

## 5.3. RESULTS

Table 5.3 shows the Fenton experiments carried out with different doses of $H_2O_2$ and $Fe^{2+}$, and TOC results after 15 min, 157 min and 300 min of reaction.

In all samples more than 100 mg $L^{-1}$ of residual $H_2O_2$ remained, except in experiments 15 and 19, whose ratio $H_2O_2$ / Fe (w/w) was approximately 2, in which about 3 mg $L^{-1}$ $H_2O_2$ were left after 157 min of reaction and was undetectable after 300 min.

Table 5.3. Fenton experiments of cleaning waters at pH 3 and TOC concentrations after 15 min, 157 min and 300 min of reaction.

| **Experim num** | **$H_2O_2$/ COD (w/w)** | **$H_2O_2$ (mg $L^{-1}$)** | **$H_2O_2$/Fe (w/w)** | **$Fe^{2+}$ (mg $L^{-1}$)** | **TOC (mg $L^{-1}$) 15 min** | **TOC (mg $L^{-1}$) 157 min** | **TOC (mg $L^{-1}$) 300 min** |
|---|---|---|---|---|---|---|---|
| 1 | 5.0 | 2070 | 5.00 | 414 | 116.0 | 63.8 | 57.3 |
| 2 | 12.5 | 5175 | 12.50 | 414 | 113.0 | 57.7 | 45.5 |
| 3 | 20.0 | 8280 | 20.00 | 414 | 102.0 | 48.0 | 41.6 |
| 4 | 5.0 | 2070 | 0.24 | 8487 | 104.7 | 100.6 | 99.7 |
| 5 | 12.5 | 5175 | 0.61 | 8487 | 67.9 | 67.6 | 65.6 |
| 6 | 20.0 | 8280 | 0.98 | 8487 | 63.0 | 57.9 | 58.0 |
| 7 | 5.0 | 2070 | 0.13 | 16560 | 103.6 | 110.1 | 105.4 |
| 8 | 12.5 | 5175 | 0.31 | 16560 | 94.6 | 95.5 | 92.6 |
| 9 | 20.0 | 8280 | 0.50 | 16560 | 78.4 | 77.9 | 78.7 |
| 10 | 20.0 | 8280 | 27.60 | 300 | 123.0 | 60.1 | 56.0 |
| 11 | 20.0 | 8280 | 82.80 | 100 | 131.5 | 64.9 | 52.7 |
| 12 | 12.5 | 5175 | 5.18 | 1000 | 85.0 | 72.8 | 55.7 |
| 13 | 12.5 | 5175 | 17.25 | 300 | 128.4 | 64.4 | 58.3 |
| 14 | 12.5 | 5175 | 51.75 | 100 | 132.2 | 65.3 | 56.6 |
| 15 | 4.8 | 2000 | 2.00 | 1000 | 106.8 | 85.4 | 69.2 |
| 16 | 4.8 | 2000 | 6.67 | 300 | 154.6 | 96.2 | 91.2 |
| 17 | 4.8 | 2000 | 20.00 | 100 | 148.8 | 146.9 | 101.5 |
| 18 | 4.8 | 2000 | 40.00 | 50 | 159.8 | 157.8 | 124.6 |
| 19 | 2.9 | 1200 | 2.40 | 500 | 106.7 | 126.7 | 71.9 |
| 20 | 2.9 | 1200 | 12.00 | 100 | 142.6 | 134.1 | 96.3 |
| 21 | 2.9 | 1200 | 24.00 | 50 | 135.5 | 134.8 | 136.6 |
| 22 | 1.9 | 800 | 2.67 | 300 | 128.6 | 108.4 | 84.9 |
| 23 | 1.9 | 800 | 16.00 | 50 | 131.2 | 135.0 | 128.8 |

TOC removal in most experiments presented an asymptotic behavior. Figure 5.3 shows the final TOC of the sample at different reaction times for three experiments. As can be seen, after 157 min, the most part of the organic content was removed, after that time there was barely a decrease in TOC. This indicated the presence of an organic fraction recalcitrant and resistant to the Fenton reaction.

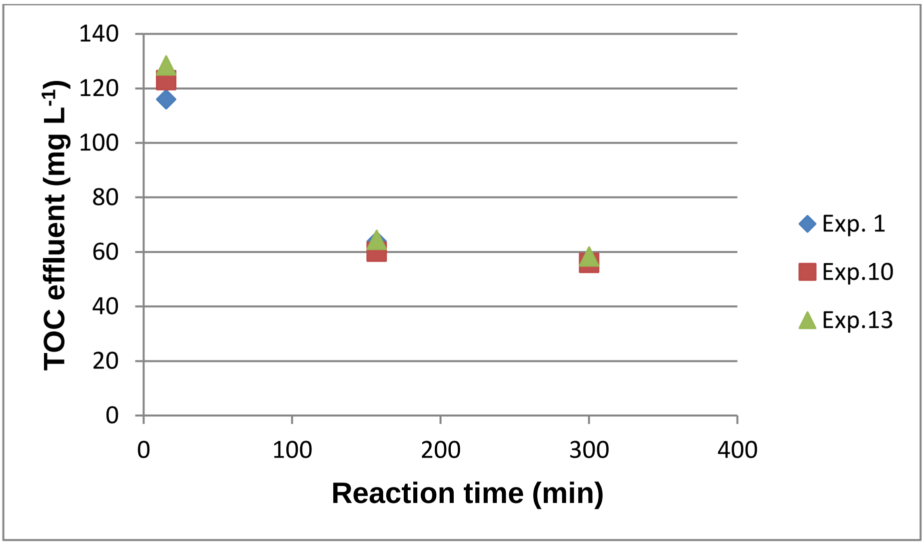


Figure 5.3. Content of TOC after 15, 157 and 300 min of reaction

A statistical analysis of the presented data was carried out in order to understand the factors affecting the performance of the Fenton process, as well as the optimal combination of the operating variables leading to the highest contaminant removals. In this case, the operational factors studied as playing a role are the $H_2O_2$ and $Fe^{2+}$ added concentrations, and the response that has to be maximized in order to optimize the process performance is the TOC removal percentage at different times.

Figure 5.4 (a) shows the Pareto chart for the TOC in the effluent after 15 min of reaction with the factors that have significant effects. As can be seen, during the first minutes of reaction, the decrease of the TOC was favored by the amount of $H_2O_2$ and Fe added, although as it can be observed in the response surface in Figure 5.4 (b), an excessive addition of iron was unfavorable. According to the statistical program, TOC of the effluent decreases with increasing dose of $Fe^{2+}$ until 10177 mg $L^{-1}$ (resulting a minimal TOC concentration of 59.9 mg $L^{-1}$ using this $Fe^{2+}$ dose and 8280 mg $L^{-1}$ $H_2O_2$). With higher additions of $Fe^{2+}$, final TOC value rises again, showing the negative effect of an excess of this reagent for the possible activation of undesired secondary reactions.

The requirement of high doses of iron may be due to the presence of EDTA, a chelating agent that forms complexes with Fe. Although hydroxyl radicals can be produced with the pair Fe-EDTA (Engelmann et al. 2003; Singh and Hider, 1988; Walling et al. 1975), chelation can retard the regeneration reaction of $Fe^{2+}$ ion, scavenge $HO^{\bullet}$ or produce ferryl species instead of the desired hydroxyl radicals (Pignatello et al. 2006), reducing then the efficiency of the process.

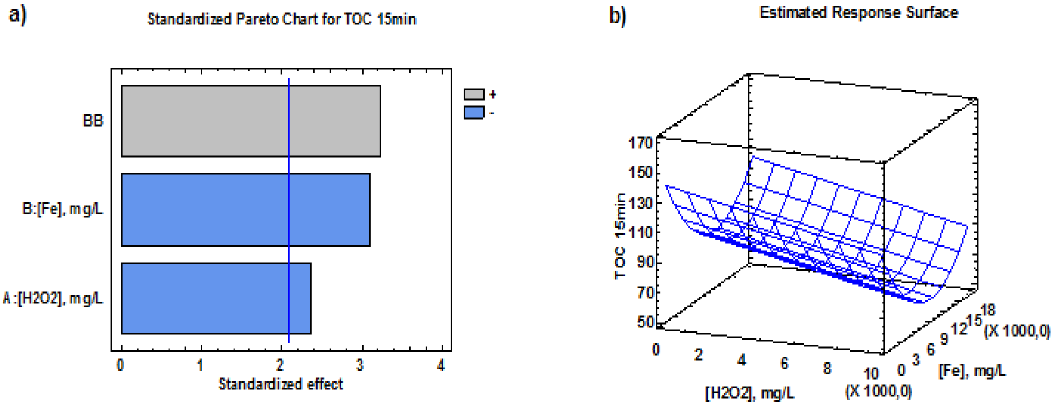


Figure 5.4. a) Pareto chart and b) response surface for the TOC value after 15 min of Fenton reaction

Figure 5.5 shows the Pareto chart for the TOC in the effluent after 157 min of Fenton reaction, in this case, without discarding the statistically insignificant factors. The only factor that influences the TOC after this time is the $H_2O_2$ concentration. This factor resulted favorable for TOC reduction.

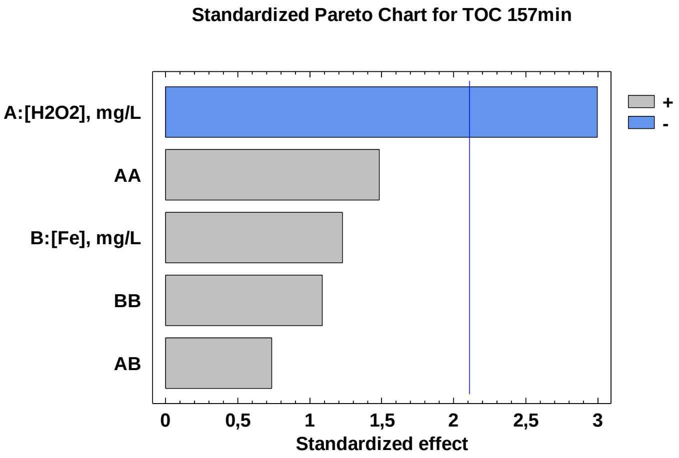


Figure 5.5. Pareto chart for the TOC value after 157 min of Fenton reaction

Figure 5.6 shows the corresponding results after 300 min of Fenton reaction. As can be noted, the initial concentration of $H_2O_2$ remained favorable for the TOC decrease, but not the iron concentration since when $H_2O_2$ dose is low in relation to iron concentration, iron can participate in other secondary reactions, instead than with $H_2O_2$.

That is, for rapid organic matter degradation is necessary the use of high doses of both reagents, achieving within 15 min a maximum TOC removal of 53.3%; while when longer reaction times are applied, only $H_2O_2$ has influence, and 64.4% of TOC would be removed by adding 8280 mg $L^{-1}$ $H_2O_2$ and 414 mg $L^{-1}$ $Fe^{2+}$ after 157 min. After 300 min, a TOC removal of

67.5% would be achieved with the lowest dose of $Fe^{2+}$ (8280 mg $L^{-1}$ of $H_2O_2$ and 50 mg $L^{-1}$ of $Fe^{2+}$), according to the statistical model obtained.

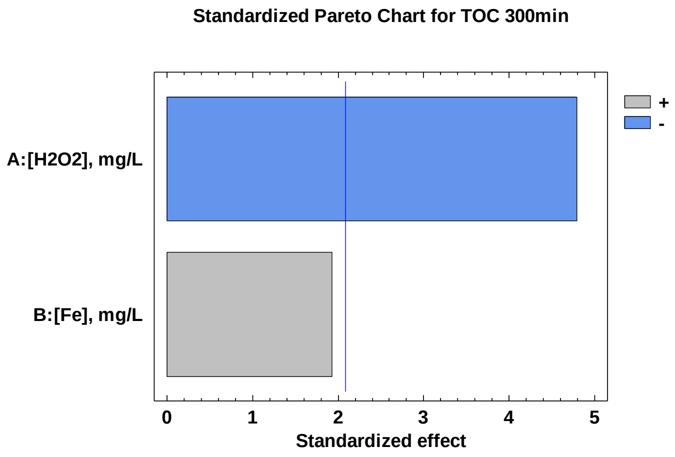


Figure 5.6. Pareto chart for the TOC value after 300 min of Fenton reaction

Given that the optimum contact time for this process is 157 min, more statistical analysis was performed regarding those results. In Figure 5.7 (a) and (b), the Pareto chart and the response surface, respectively, of the TOC after 157 minutes of reaction are shown, but including the ratio $H_2O_2$ / $Fe^{2+}$ (w/w) as operational factor instead of $Fe^{2+}$ initial concentration. In this response surface is observed more clearly that after 157 min of reaction, decrease in TOC is favored by the addition of high doses of $H_2O_2$ and low ratio $H_2O_2$ / $Fe^{2+}$, obtaining a minimum TOC value when the $H_2O_2$ concentration is above 4000 mg $L^{-1}$. This concentration could be considered as the optimal, since higher concentrations hardly change the TOC value. The optimal $H_2O_2$ / $Fe^{2+}$ ratio (w/w) is between 1 and 20, thereby to minimize the consumption of $Fe^{2+}$, the ratio 20, that corresponds to 200 mg L$^{-1}$ of Fe$^{2+}$ is chosen. According to the statistical model, the maximum TOC removal that is obtained with this process is 67%. The experiment with the optimal conditions (4000 mg L$^{-1}$ $H_2O_2$ and 200 mg L$^{-1}$ Fe$^{2+}$) was carried out and was obtained, in fact, a TOC removal of 65% after 157 min, confirming the results predicted by the statistical analysis. BOD$_5$ was also analyzed for these optimal conditions, and a value of 14.8 mg $O_2$ L$^{-1}$ was obtained, exceeding slightly the 10 mg L$^{-1}$ $O_2$ recommended by the USEPA for irrigation of raw food crops for human consumption; however, the treated cleaning water could be used for irrigation of processed food crops or non-food crops, reutilization in other processes and for industrial applications, once the iron has been removed by raising the pH and decanting. In order to comply with the EPA´s recommendations, the pH of the effluent from Fenton process was raised to 7 (final pH has to be between 6-8.5) and the iron was allowed to decant, remaining less than 2 mg L$^{-1}$ of total iron (the maximum according to the EPA is 5 mg L$^{-1}$). Stronger AOP's such as photo-Fenton and photocatalysis will be studied in the chapter 6 of the thesis.

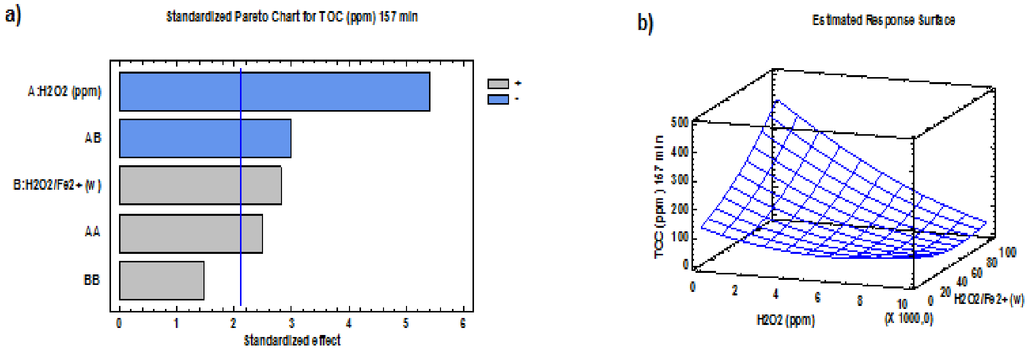


Figure 5.7. a) Pareto chart, and b) response surface for the TOC value after 157 min of Fenton reaction

## 5.4. CONCLUSIONS

Fenton process was studied for treating cleaning waters from RO membranes composed by 7.37 mg $L^{-1}$ starch, 200 mg $L^{-1}$ $Na_4$-EDTA and 150 mg $L^{-1}$ of SDS. The effluent TOC was evaluated at three reaction times.

Statistical analysis of the results showed that after 15 min of reaction, a decrease in TOC is favored by increasing doses of $H_2O_2$ and $Fe^{2+}$ until a maximum dose of $Fe^{2+}$. After 157 min of reaction, $Fe^{2+}$ dose does not have significant influence on the final TOC, however, $H_2O_2$ favors the reduction of TOC. Finally, at longer reaction times (after 300 min), for lowering the TOC, high doses of $H_2O_2$ and low doses of $Fe^{2+}$ are recommended.

That is, for rapid organic matter degradation is necessary the use of high doses of both reagents, being able to achieve within 15 min a maximum TOC removal of 53.3%; while if it is left for longer reaction times, only $H_2O_2$ has influence and 64.4% of TOC can be removed adding 8280 mg $L^{-1}$ $H_2O_2$ and 414 mg $L^{-1}$ $Fe^{2+}$ after 157 min. After 300 min a TOC removal of 67.5% can be achieved with the lowest dose of $Fe^{2+}$ (8280 mg $L^{-1}$ of $H_2O_2$ and 50 mg $L^{-1}$ of $Fe^{2+}$), according to the statistical model obtained.

Among the three reaction times tested, 157 min is the optimum time for the Fenton process and a minimum TOC value could be achieved with a $H_2O_2$ concentration above 4000 mg $L^{-1}$ and a $H_2O_2$ / $Fe^{2+}$ (w/w) ratio between 1 and 20, which could be fixed to 20 to reduce the amount of $Fe^{2+}$, corresponding to 200 mg $L^{-1}$ of $Fe^{2+}$. The maximum TOC removal obtained under these operating conditions was 67% and 14.8 mg $O_2$ $L^{-1}$ was the final $BOD_5$ value, that exceeds slightly the EPA recommendations for irrigation of raw food crops for human consumption. Nevertheless, the treated cleaning water could be used for irrigation of processed food crops or non-food crops, for reutilization in other processes and for industrial applications, once the iron has been removed by raising the pH and decanting.

## 5.5. REFERENCES

Ang, W.S., Ngai Yin Yip, Tiraferri, A., Elimelech, M., 2011. Chemical cleaning of RO membranes fouled by wastewater effluent: Achieving higher efficiency with dual-step cleaning. Journal of Membrane Science 382; 100–106.

Bandala, E.R., Peláez, M.A., Salgado, M.J., Torres, L., 2008. Degradation of sodium dodecyl sulphate in water using solar driven Fenton-like advanced oxidation processes. J Hazard Mater.;151:578–584.

Chesters, S.P., Pena, N., Gallego, S., Fazel, M., Armstrong, M.W., del Vigo, F., 2011. Results from 99 seawater RO membrane autopsies. IDA World Congress, Perth, Western Australia, September 2011.

Chitra, S., Paramasivan, K., Sinha, P. K., 2013. Sono-Photo Fenton Treatment of Liquid Waste Containing Ethylenediaminetetraacetic Acid (EDTA). International Journal of Nonferrous Metallurgy, 2; 89-94.

Chitra, S., Paramasivan, K., Shanmugamani, A.G., Rao, S.V.S., Biplob P., 2014. Advanced Oxidation Processes for the Treatment of Surfactant Wastes. J. Chem. Eng. Chem. Res. Vol. 1, No. 3, pp. 163-173.

Choukr-Allah, R., Ragab, R., Rodriguez-Clemente, R., eds., 2012. Integrated water resources management in the Mediterranean region: dialogue towards new strategy. Dordrecht, The Netherlands, Springer, 364 pp.

Directive 2013/39/UE of the European parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. Offi J Eur Commun L 226:1.

DOW FILMTEC™ Membranes. Cleaning Procedures for DOW FILMTEC FT30 Elements. Technical Manual.

Dow Water & Process Solutions, 2011. FILMTEC™ Reverse Osmosis Membranes. Technical Manual.

Engelmann, M.D., Bobier, R.T., Hiatt, T., Cheng, I.F., 2003. Variability of the Fenton reaction characteristics of the EDTA, DTPA, and citrate complexes of iron. BioMetals 16, 519–527.

Fritzmann, C., Löwenberg,J., Wintgens, T., Melin, T., 2007. State-of-the-art of reverse osmosis desalination. Desalination, 216; 1-76.

Ghiselli, G., Jardim, W. F., Litter, M. I. and Mansilla, H. D., 2004. Destruction of EDTA using Fenton and photo-Fenton-like reactions under UV-A irradiation. Journal of Photochemistry and Photobiology A: Chemistry, 167, 59–67.

Jiménez, S., 2016. Proceso Fenton aplicado a aguas de lavado de membranas. Closed Loop Project. Acciona Agua. Internal report.

Jones, C.W., 1999. Applications of hydrogen peroxide and derivatives. RSC Clean Technology Monographs, Series Editor James H Clark, Royal Society of Chemistry. ISBN 085404536-8.

Kim, S., Geissen, S., Vogelpohl, A., 1997. Landfill leachate treatment by a photoassisted Fenton reaction. Water Sci. Technol. 35, 239-248.

Kiran, I., Bektas, N., Yatmaz, H.C. and Tekbas. M., 2013. Photocatalytic Fenton oxidation of sodium dodecyl sulfate solution using iron-modified zeolite catalyst. Desalination and water treatment. 51 (28-30), pp. 5768-5775.

MAH7285/2007. Regional regulation on sea discharge.

Melián, N., 2015. Caracterización y evaluación del ensuciamiento en membranas de ósmosis inversa con combinación de agentes ensuciantes. Universidad de las Palmas de Gran Canaria. Dpto de ingeniería de procesos. Thesis doctoral.

Mitra, S.S., Thomas, A. J. , Gang, G. T., 2009. Evaluation and characterization of seawater RO membrane fouling. Desalination 247; 94-107.

Mohammadi, T., Moghadam, M. K., Madaeni, S.S., 2002. Hydrodynamic factors affecting flux and fouling during reverse osmosis of seawater. Desalination 151 (2002) 239-245.

Navea, S., Repollés, C., Romero, C., 2016. Escenarios oxidación avanzada aguas de limpieza en desalinizadoras. Closed Loop Project. Acciona Agua. Internal report.

Neyens, E., Baeyens, J., 2003. A review of classic Fenton's peroxidation as an advanced oxidation technique. Journal of Hazardous Materials 98 (1–3), 33–50.

Nguyen, T., Roddick, F. and Fan, L., 2012. Biofouling of Water Treatment Membranes: A Review of the Underlying Causes, Monitoring Techniques and Control Measures. Membranes. 2(4): p. 804.

Pignatello, J. J., Oliveros, E. and MacKay, A., 2006. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Crit. Rev. Env. Sci. Technol. 36(1), 1-84.

Pontié, M., Rapenne, S., Thekkedath, A., Duchesne, J., Jacquemet, V., Leparc, J., Suty, H., 2005. Tools for membrane autopsies and antifouling strategies in seawater feeds: a review. Desalination 181; 75-90.

Rekab, K., Lepeytre, C., Dunanda, M., Dappozze, F., Herrmann, J.M., Guillard, C., 2014. H2O2 and/or photocatalysis under UV-C irradiation for the removal of EDTA, a chelating agent present in nuclear waste waters. Applied Catalysis A: General 488; 103–110.

Royal Decree 1620/2007 of 7 December, that establish the legal status of the reutilization of depurated water. Boletín Oficial del Estado (BOE) 294, 08/12/2007, 50639-50661.

Shirazi, S., Lin, C., Chen, D., 2010. Inorganic fouling of pressure-driven membrane processes -A critical review. Desalination 250; 236-248.

Singh, V., Das A., Das, C., Pugazhenthi, G., Srinivas, M., 2015. Fouling and Cleaning Characteristics of Reverse Osmosis (RO) Membranes. J Chem Eng Process Technol 6:244. doi:10.4172/2157-7048.1000244.

Singh, S. and Hider, R. C.,1988. Colorimetric detection of the hydroxyl radical: Comparison of the hydroxyl-radical-generating ability of various iron complexes, Anal. Biochem. 171(1), 47-54.

Stuart, M.E., Lapworth, D.J., Crane, E., Hart, A., 2012. Review of risk from potential emerging contaminants in UK groundwater. Sci. Tot. Env. 416, 1-21.

Suárez, L., Diez, M.A., García, R., Riera, F.A., 2013. Recovery of Na4EDTA from aqueous solutions using nanofiltration, Sep. Purif. Technol., 118, 144-150.

United States Environmental Protection Agency (EPA), 2012. Guidelines for water reuse.

Walling, C.; Partch, R.E. and Weil, T., 1975. Kinetics of the decomposition of hydrogen peroxide catalyzed by ferric ethylenediaminetetraacetate complex, Proceedings of the National Academy of Sciences 72(1), 140-142.

World Health Organization, 2006. A compendium of standards for wastewater reuse in the Eastern Mediterranean Region. Document WHO-EM/CEH/142/E.

Young M. Kim, Seung J. Kim, Yong S. Kim, Sangho Lee, In S. Kim, Joon Ha Kim, 2009. Overview of systems engineering approaches for a large-scale seawater desalination plant with a reverse osmosis network, Desalination, 238, 312–332.

# Chapter 6. Reverse Osmosis Membranes Cleaning Waters Treatment for Reutilization Purposes. Part II: Application of Photo-Fenton and Photocatalysis Processes

**Content**

## 6.1. INTRODUCTION

This is the second part of the work focused on the treatment of seawater desalination reverse osmosis (RO) membranes cleaning waters for reutilization purposes. The first part (chapter 5) was dedicated to the application of the Fenton process for the organic load removal of this type of wastewaters (Jiménez et al. 2017, submitted for publication) and in the present part, photo-Fenton and photocatalysis processes are applied.

After studying the Fenton process for the treatment of simulated RO membranes cleaning waters composed of the organic matter that was adhered to the membrane, tetrasodium ethylenediaminetetraacetate ($Na_4$-EDTA) and sodium dodecyl sulfate (SDS), in which a maximum TOC removal of 67% was achieved with 4000 mg $L^{-1}$ $H_2O_2$ and 200 mg $L^{-1}$ $Fe^{2+}$ at pH 3, this study focuses on the application of photo-Fenton and photocatalysis processes, in order to choose the best treatment for the organic load removal of the RO membranes cleaning waters.

Among the Advanced Oxidation Processes (AOPs), the photo-Fenton process has been chosen due to the low cost of reagents, the ease of use of $H_2O_2$ and its harmless decomposition to the environment (Jones, 1999), and because sunlight can be used. Photo-Fenton reaction leads generally to higher velocities of degradation and mineralization, compared to the dark Fenton, due to the creation of an extra path for hydroxyl radical formation thanks to the photoreduction of $Fe^{3+}$ to $Fe^{2+}$, according to reaction 6.1.

$$Fe^{3+} + H_2O + h\upsilon \rightarrow Fe^{2+} + H^+ + \cdot OH \qquad (6.1)$$

In this way, ferrous cation is continuously recycled thanks to radiation, and there is always certain amount of $Fe^{2+}$ available in the media (Zepp et al. 1992). Additionally, according to Pignatello and collaborators also the formation and photodegradation of $Fe^{3+}$ aquocomplexes (predominant in acidic conditions) contribute to the generation of hydroxyl radicals (Pignatello et al. 2006) under 180-410 nm radiation.

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + {}^{\cdot}OH \quad (6.2)$$

$$Fe(OH)^{2+} + h\upsilon \rightarrow Fe^{2+} + {}^{\cdot}OH \quad (6.3)$$

Generally is accepted that optimum pH for Fenton and photo-Fenton reactions is 2.8 (Pignatello 1992). At this pH, $Fe^{3+}$ ion coexists with its complex $Fe(OH)^{2+}$ in a ratio of 1:1, and both are the most photoactive species of the system. At lower pH, the concentration of $Fe(OH)^{2+}$ decreases, favoring the generation of other complexes less photoactive. Over pH 2.8, $Fe^{3+}$ precipitates as $Fe(OH)_3$.

Photocatalysis processes based on the use of titanium dioxide ($TiO_2$) have emerged in the past two decades as a promising treatment option for micropollutants in wastewater effluents as in the case of photo-Fenton (Ahmed et al. 2011; Macounova et al. 2003; Zhang et al. 2007). $TiO_2$ is an n-type semiconductor. When its surface is hit by light radiation of greater energy than that of the band gap, an electron is promoted from the valence band (VB) to the CB conduction band (CB). This creates a positive hole ($h^+_{vb}$) in the VB, and an increase in one electron ($e^-_{cb}$) in the CB.

If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially, $h^+_{vb}$ may react with

surface-bound $H_2O$ or $OH^-$ to produce the hydroxyl radical (${}^{\cdot}OH$), while $e^-_{cb}$ is picked up by oxygen to generate superoxide radical anion ($O_2^{\cdot -}$), which are the primary oxidizing species in the photocatalytic oxidation processes (Colmenares et al. 2009).

The main advantage of this technique, by using $TiO_2$, among other physicochemical treatments lies firstly in the fact that $TiO_2$ is non-toxic, stable, does not undergo photocorrosion, is chemical-resistant and economical (Sobczyński and Dobosz, 2001). Nevertheless, it requires high retention times and an additional step for photocatalyst recovery when suspended and even reactivation (Ahmed et al. 2011).

Photo-Fenton process was applied by Chitra et al. (2014) for the degradation of SDS and revealed that the rate of degradation of surfactant using UV-C (15W) + $Fe^{2+}$ + $H_2O_2$ was 23 times faster than if the system uses $Fe^{2+}$ + $H_2O_2$ alone. Bandala et al. (2007) also observed the enhancement of SDS final degradation using solar radiation on the Fenton reaction. Fenton needs higher concentrations of reagents (10 times of metal and almost 17 times of oxidant) to reach ca. 63% of surfactant removal.

Fenton and photo-Fenton experiments at pH 3 were performed by Ghiselli et al. (2014) under similar conditions to study the degradation of EDTA. With Fenton process, TOC removal was very low at the end of 4 h in all the experiments, reaching a maximum of 31.9% removal in the case of 1:1 EDTA:$Fe^{2+}$. In addition, some by-products formed in this process, in particular oxalic acid, can accumulate in the reaction media due to its refractory nature to Fenton's reagent.

In relation to photocatalysis, Rekab et al. (2014) studied the removal of EDTA under UV-C radiation. The degradation efficiencies of the UV/$TiO_2$ and UV/$H_2O_2$ processes seemed to be similar in terms nitrogen and carbon mineralization, although photocatalysis seemed to be a better option as in the other case $H_2O_2$ was needed to be added continuously during the UV/$H_2O_2$ experiments. Baeza et al. (2003) removed EDTA at pH 3 under UV-C radiation in the presence of $H_2O_2$ and achieved 78% of TOC removal using 40:1 $H_2O_2$/EDTA (molar) after 540 min. $TiO_2$ addition (1 g $L^{-1}$) was detrimental in this case, it inhibited the oxidation reaction since $TiO_2$ particles produce scattering of light that hindered photocatalytic decomposition of $H_2O_2$.

However no references were found regarding the oxidation of these two components coexisting in the same matrix, (as they are present on the cleaning waters of this work) nor proposing the treatment of these effluents by neither photocatalysis nor photo-Fenton processes.

## 6.2. MATERIALS AND METHODS

### 6.2.1. Cleaning waters

Cleaning effluents used in this study were simulated in the same way as in the previous chapter (chapter 5). Table 6.1 shows the composition of the synthetic effluent prepared for this study.

Table 6.1. Composition of cleaning water including initial chemical oxygen demand (COD), total organic carbon (TOC) and biological oxygen demand ($BOD_5$).

| **Quality Parameter of the simulated cleaning water** | **Value** |
|---|---|
| $Na_4$-EDTA (Sigma-Aldrich, USA) (mg $L^{-1}$) | 200.0 |
| SDS (Sigma-Aldrich, USA) (mg $L^{-1}$) | 150.0 |
| Anionic modified potato starch from Cargill (C flake 35704) (mg $L^{-1}$) | 7.4 (1.65 mg C $L^{-1}$) |
| pH | 10.3 |
| COD (mg $L^{-1}$) | 414.0 |
| TOC (mg $L^{-1}$) | 134.5 |
| $BOD_5$ (mg $L^{-1}$) | 3.1 |

### 6.2.2. Photo-Fenton experiments

Photo-Fenton reactions were carried out at pH 3 and the reagents used were hydrogen peroxide solution (30% w/w in $H_2O$, with stabilizer) (Sigma-Aldrich, USA), iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) (Sigma-Aldrich, USA) and hydrochloric acid (HCl) (Panreac, Spain) to acidify. For each photo-Fenton experiment, 0.5 L of sample was used and carried out in a 1L container made of borosilicate glass of 86 mm high and 157 mm diameter (Duran, Germany) and with magnetic stirring.

The reaction took place inside a solar simulator (Solarbox 3000e, Cofomegra, Italy) (SB), shown in Figure 6.1, equipped at the top with a 2500 W Xenon lamp (Neurtek, Spain) and an outdoor light filter, which allows 290-800 nm wavelength to pass through. Irradiance was set to 250 W $m^{-2}$. The intensity of the radiation from the Xe lamp used in the SB reaching the solution was determined by actinometry, using the Parker method (Hatchard and Parker, 1956), based on the photochemical reduction of the ferrioxalate complex $[Fe(C_2O_4)_3]^{3-}$ to Fe (II) in acid medium. The reduction takes place with a quantum yield of 1-1.2 mol $Einstein^{-1}$ in the range of wavelengths between 250-450 nm (Goldstein and Rabani, 2008). The concentration of Fe (II) over time was followed by the o-phenanthroline method (Zuo, 1995), based on the formation of a colored complex between Fe (II) in solution and 1,10-phenanthroline in acid medium acetic acid / acetate at pH 3-4. The absorbance was measured at 510 nm. The intensity value resulted 6.5 $10^{-4}$ Einstein $min^{-1}$.

Figure 6.1. Solarbox 3000e (Cofomegra, Italy)

The optimal photo-Fenton experiment that resulted from this study was also carried out by using 4x 15 W UVA lamps (300-400 nm) (with a maximum at 360-365 nm) (Philips TL-D BLB), shown in Figure 6.2. The intensity of the total radiation from these UVA lamps, determined also by actinometry using the ferrioxalate method, was 1.3 $10^{-4}$ Einstein $min^{-1}$.

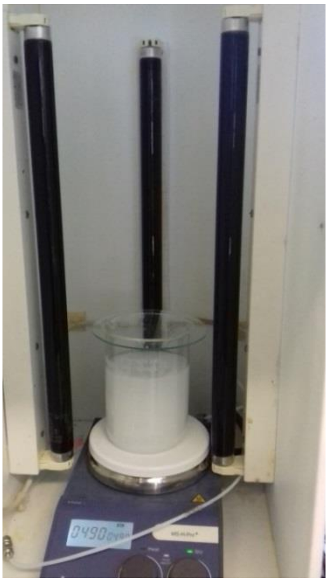


Figure 6.2. UVA lamps

TOC was analyzed at 15 min reaction, 60 min and 157 min reaction (to compare with the Fenton process studied in the previous chapter but using shorter times since photo-Fenton is a faster process). Samples were previously filtered through 0.20 µm Phenex Nylon filter membranes before TOC analysis.

### 6.2.3. Photocatalytic experiments

For each experiment, 0.5 L of cleaning water was used. The experiments were carried out with the solar simulator (Solarbox 3000e, Cofomegra, Italy) (SB), 4x 15 W UVA lamps (300-400 nm) (with a maximum at 360-365 nm) (Philips TL-D BLB) and 4x 15 W UV-C low pressure lamps (that emit mostly at 253.7 nm) (Philips G15 T8) (shown in Figure 6.3).

The intensity of the total radiation from the UV-C lamps, determined by actinometry using the ferrioxalate method, was 1.3 $10^{-4}$ Einstein $min^{-1}$.

The experiments were carried out in closed containers; those for the solar simulator and the UVA lamps were made of borosilicate glass, while those for the UV-C lamps were made of quartz.

In these experiments, basic pH (free pH of 10.3) and pH 3 were tested.

Figure 6.3. UV-C lamps

The study started with adsorption experiments. Those experiments were carried out in the dark at free pH (10.3) and pH 3 using 0.25 g $L^{-1}$ Aeroxide® P25 (Acros Organics, Belgium) as a commercially available $TiO_2$ photocatalyst for 300 min. These experiments were also performed by adding hydrogen peroxide ($H_2O_2$). Aeroxide® P25 was analyzed by X-ray diffraction and is composed of anatase (87.6%) and rutile (12.4%). The crystallites size analysis were: anatase 16.9 nm and rutile 30 nm.

For the photocatalysis experiments with P25 and radiation, the SB and UVA lamps were used. The effect of $H_2O_2$ over target parameters was tested for the SB and in the UV-C lamps with and without P25.

Finally, a comparison in the SB was made with the best result obtained from the study of the photo-Fenton process and the addition of P25 to this, to test its possible synergistic effect.

In each experiment, the TOC was monitored at different times after adding bisulfite to the samples where $H_2O_2$ remained. When P25 or $FeSO_4 \cdot 7H_2O$ were used, samples were previously filtered through 0.20 µm Phenex Nylon filter membranes before TOC analysis.

### 6.2.4. Analytical methods

The pH measurements were performed using a PH 25 CRISON pH-meter. COD was determined photometrically using Hach Lange kit LCK 414. $H_2O_2$ consumption in the Fenton reactions was monitored with QUANTOFIX Peroxide test strips (Macherey-Nagel). Residual $H_2O_2$ was neutralized at the end of the experiments with the addition of sodium bisulfite (Sigma-Aldrich) to avoid undesirable reactions. TOC concentrations were measured using a GE Total Organic Carbon Analyzer, Sievers Innovox model. Samples with $TiO_2$ or iron were previously filtered through 0.20 µm Phenex Nylon filter membranes before

TOC analysis. Sample for determining five days Biochemical Oxygen Demand ($BOD_5$) was measured according to the standard method [SM 5210-D] using an Oxitop system (VELP Scientifica, Italy). Some samples were analyzed with liquid chromatography-TOF mass spectrometry. The chromatographic system was an Agilent 1200 liquid chromatograph coupled to 6210 Time of Flight (TOF) mass spectrometer from Agilent Technologies (Waldbronn, Germany) with an ESI interface, using a Zorbax Eclipse XDB-C18 (4.6 × 150 mm, 5 µm) from Agilent Technologies (Waldbronn, Germany).

## 6.3. RESULTS AND DISCUSSION

### 6.3.1. Photo-Fenton experiments

Table 6.2 shows the photo-Fenton experiments set performed with the SB and the TOC results after 15 min, 60 min and 157 min, the effluent TOC value for comparing with the Fenton experiments performed in the first part of this study, and the TOC removal percentage as well as the residual $H_2O_2$ that remains after 60 and 157 min.

Stoichiometric $H_2O_2$ required for the oxidation of organic matter was calculated as reported by Kim and colleagues (1997) who considered that the stoichiometric ratio $H_2O_2$ / COD (w) should be 2.125. In this work, three $H_2O_2$ concentrations were tested, ranged between 800 mg $L^{-1}$ ($H_2O_2$/COD (w)=1.9, close to the stoichiometric quantity) and 2000 mg $L^{-1}$ ($H_2O_2$/COD (w)=4.8), and Fe concentrations to obtain $H_2O_2$ /Fe ratios of 2, 10 and 20.

Table 6.2. Photo-Fenton experiments in the SB for the RO membranes cleaning waters at pH 3 with the reagent doses used and results of effluent TOC value, %TOC removal and residual $H_2O_2$

| **Nº Exp.** | **$H_2O_2$/ COD (w/w)** | **$H_2O_2$, mg $L^{-1}$** | **$H_2O_2$/ Fe (w/w)** | **$Fe^{2+}$, mg $L^{-1}$** | **TOC 15 min, mg $L^{-1}$, (%TOC removal)** | **TOC 60 min, mg $L^{-1}$, (%TOC removal)** | **TOC 157 min, mg $L^{-1}$, (%TOC removal)** | **Resid $H_2O_2$ 60 min, mg $L^{-1}$** | **Resid $H_2O_2$ 157 min, mg $L^{-1}$** |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.93 | 800 | 2 | 400 | 112.2,<br>(16.9) | 50.8<br>(62.4) | 47.3<br>(65.0) | 0.0 | 0 |
| 2 | 1.93 | 800 | 10 | 80 | 125.9<br>(6.7) | 111.7<br>(17.3) | 33.7<br>(75.0) | 10.0 | 0 |
| 3 | 1.93 | 800 | 20 | 40 | 121.9<br>(9.7) | 121.3<br>(10.1) | 31.1<br>(77.0) | 25.0 | 0 |
| 4 | 2.90 | 1200 | 2 | 600 | 79.5<br>(41.1) | 42.4<br>(68.6) | 39.1<br>(71.0) | 0.0 | 0 |
| 5 | 2.90 | 1200 | 10 | 120 | 130.0<br>(3.7) | 33.6<br>(75.1) | 32.7<br>(75.8) | 0.5 | 0 |
| 6 | 2.90 | 1200 | 20 | 60 | 130.9<br>(3.0) | 30.2<br>(77.6) | 28.5<br>(78.9) | 10.0 | 0 |
| 7 | 4.83 | 2000 | 2 | 1000 | 74.0<br>(45.2) | 39.8<br>(70.5) | 34.5<br>(74.4) | 0.0 | 0 |
| 8 | 4.83 | 2000 | 10 | 200 | 130.3<br>(3.5) | 31.3<br>(76.8) | 30.2<br>(77.6) | 0.0 | 0 |
| 9 | 4.83 | 2000 | 20 | 100 | 131.0<br>(3.0) | 31.4<br>(76.7) | 26.8<br>(80.1) | >25 | 0 |
| 10 | 2.90 | 1200 | - | 0 | (0.2) | (0.7) | (6.4) | >100 | 100 |
| 11 | 0 | 0 | 0 | 60 | (0.2) | (0.5) | (2.8) | - | - |
| 12 | 0 | 0 | 0 | 0 | (0.2) | (0.3) | (1.1) | - | - |

In all these experiments, $H_2O_2$ remained in solution at 15 min. At 60 min, it was completely consumed for the experiments with $H_2O_2$/Fe (w)= 2 and in the reaction where a significant decrease in TOC occurred between 15 min and 60 min. These experiments also had in common that equal or higher Fe doses of 200 mg $L^{-1}$ were added. As it can be seen in Figure

6.4, high Fe doses enhance TOC removal during the first minutes. After 157 min no $H_2O_2$ remained in any experiment.

It is also observed that when $H_2O_2$ has been consumed, the value of TOC does not decrease significantly afterwards.

TOC values from experiments 10, 11 and 12, confirmed that only solar radiation by its own or combined just with one of the reagents ($H_2O_2$ or Fe) did not produce TOC removal, so the organic matter degradation is indeed due to the photo-Fenton process.

A statistical analysis of the presented data was carried out. The operational factors studied as playing a role were the $H_2O_2$ and $Fe^{2+}$ concentrations, and the response in order to optimize the process performance was effluent TOC at the three tested times. Figure 6.4 shows the Pareto chart for the TOC in the effluent after (a) 15 min (b) 60 min and (c) 157 min.

Figure 6.4 (a) indicates that in the first minutes of the reaction, Fe enhanced the photo-Fenton process, that is, during the first 15 min, a greater decrease in TOC occurs if high doses of iron were used, regardless of the initial dose of $H_2O_2$ added for the concentration interval studied. In those experiments which 600 mg $L^{-1}$ and 1000 mg $L^{-1}$ of $Fe^{2+}$ ($H_2O_2$ /Fe= 2) were added, a more significant decrease in TOC occurred after those 15 min, resulting in a TOC removal of 39% and 43%, respectively. This may be because although $H_2O_2$ is the oxidizing agent, $Fe^{2+}$ catalyzes the decomposition of $H_2O_2$. Fe can also be chelated with EDTA, forming Fe-EDTA complexes. In the presence of EDTA, oxidation of ferrous ion is accelerated. According to the literature, Fenton or photo-Fenton reactions can occur with Fe(III)-EDTA and $H_2O_2$ (with the subsequent hydroxyl radicals formation) if the ratio EDTA:Fe is lower than one (Engelmann et al. 2003). In our study, ratio EDTA:Fe was lower than one with concentrations of Fe higher than 153 mg $L^{-1}$ (assuming that all the initial $Fe^{2+}$ is oxidized to $Fe^{3+}$). Therefore, high concentrations of iron are needed to favor the (photo) Fenton reaction in presence of EDTA.

Figure 6.4 (b) shows Pareto chart for the TOC in the effluent after 60 min and Figure 6.5 (a) its corresponding response surface, where it can be seen that after 60 min, iron doses did not influence in TOC removal but the $H_2O_2$ was significant and favored that TOC decreases, although there is little difference between the addition of 1400 mg $L^{-1}$ and 2000 mg $L^{-1}$ of $H_2O_2$, so the optimum dose would be equal to or less than 1400 mg $L^{-1}$.

Finally, Figure 6.4 (c) shows the Pareto chart after 157 min and Figure 6.5 (b) its corresponding response surface. After 157 min, the decrease in TOC was favored by the $H_2O_2$ dose and, instead, the iron dose influenced negatively. When $H_2O_2$ concentration is low, iron can participate in other secondary reactions.

On the other hand, at 157 min, there was no significant differences between the TOC of the effluent in most of the experiments performed. Starting from an initial TOC of 135 mg $L^{-1}$, the optimal dose of reagents to achieve a TOC removal of 79% after 157 min are 1200 mg $L^{-1}$ of $H_2O_2$ and 60 mg $L^{-1}$ of $Fe^{2+}$. It was additionally verified in random samples (experiments 5 and 9) that although longer reaction time was left, the TOC did not drop more than the value of 28.3 mg $L^{-1}$, possibly because the remained organic matter is recalcitrant to $\cdot OH$ .

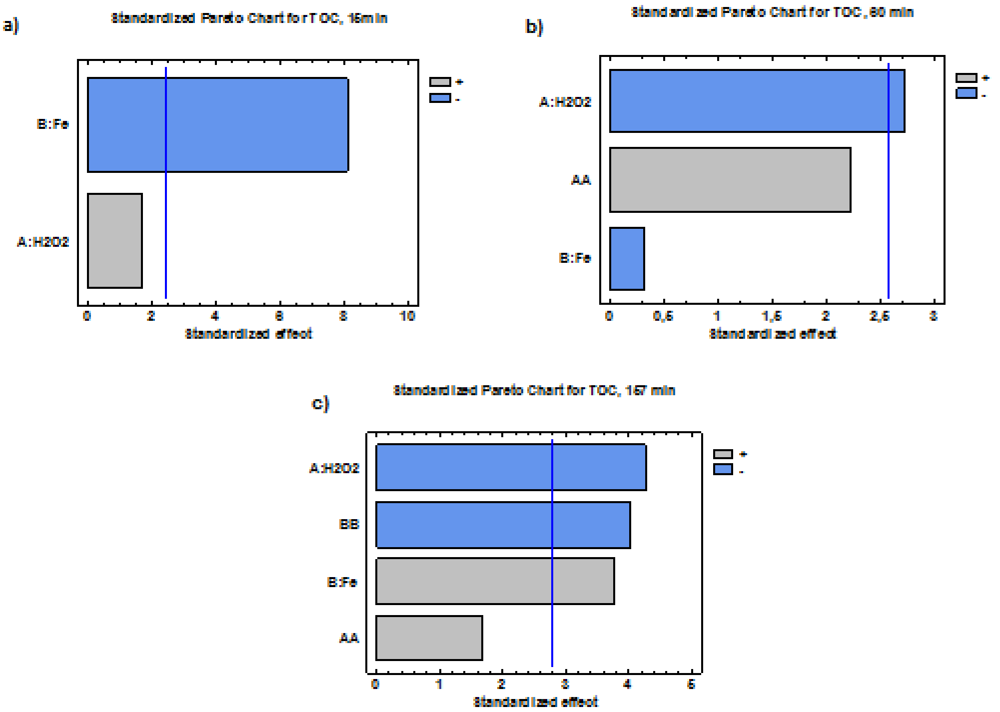


Figure 6.4. Pareto charts for TOC value at a) 15 min, b) 60 min and c) 157 min, in the photo-Fenton process

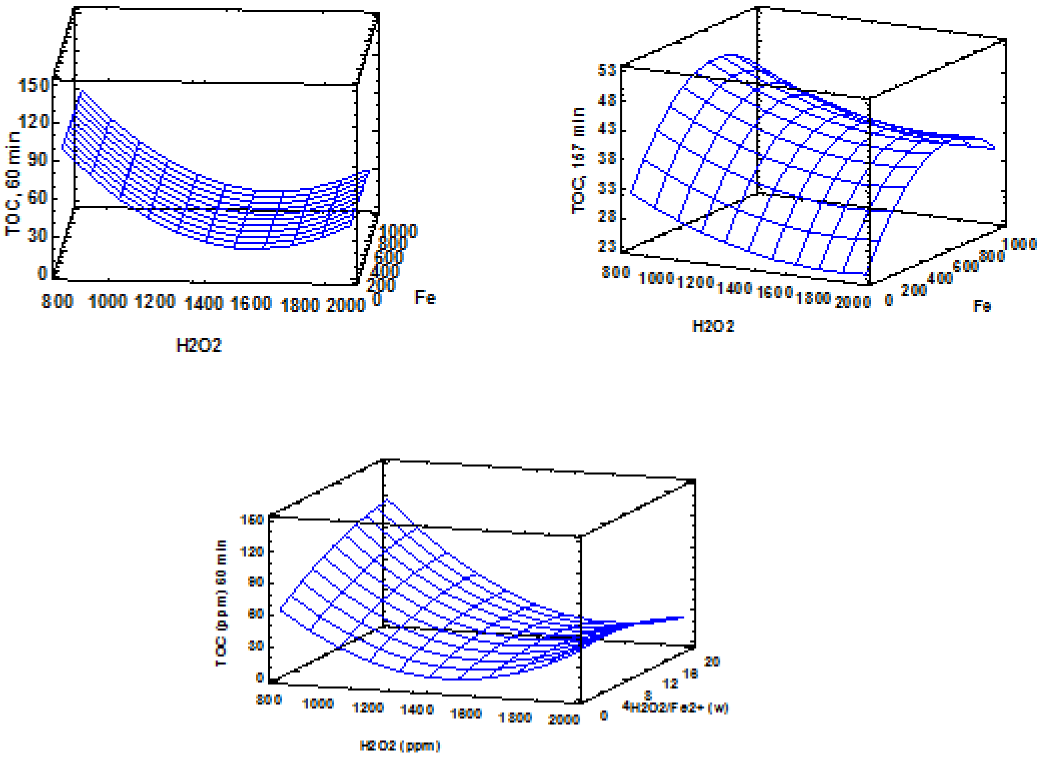


Figure 6.5. Response surfaces for the TOC value at a) 60 min, b) 157 min and c) 60 min considering as operational factors $H_2O_2$ concentration and the ratio $H_2O_2$ / $Fe^{2+}$ (w)

There was hardly any difference between the effluent TOC after 60 min and 157 min, except in experiments where 800 mg $L^{-1}$ of $H_2O_2$ and 80 of $Fe^{2+}$ (2) and 800 mg $L^{-1}$ of $H_2O_2$ and 40 mg $L^{-1}$ of $Fe^{2+}$ (3) were added, so 60 min for the photo-Fenton reaction could be considered as an optimal operation time. This conclusion can be withdrawn also from Figure 6.6, where TOC is represented at different reaction times.

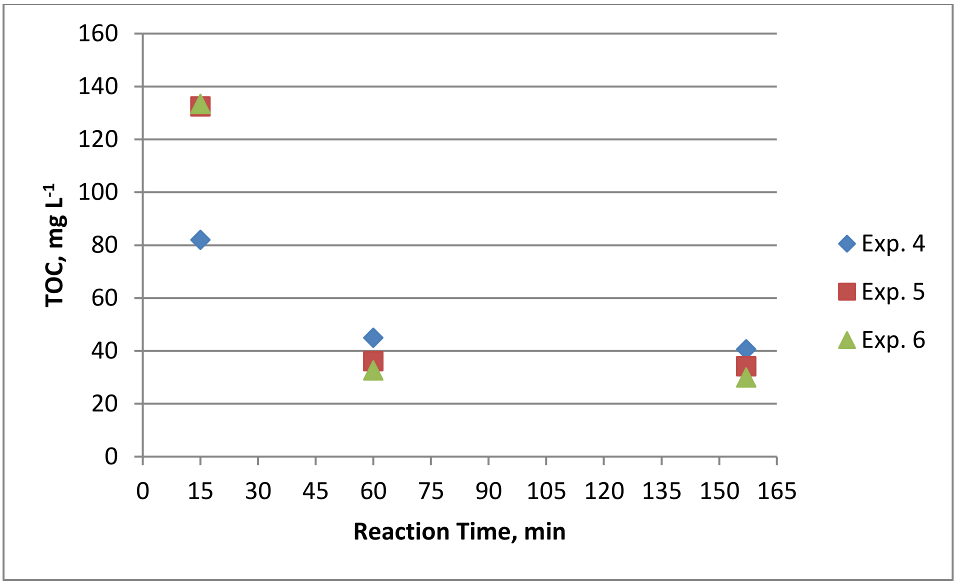


Figure 6.6. TOC evaluation at different reaction times

Thus, the optimal time for the photo-Fenton process was 60 min. From Figure 6.5 (a) that shows the TOC response surface at 60 min and Figure 6.5 (c) that shows this response surface but considering as operational factors $H_2O_2$ concentration and $H_2O_2$ / $Fe^{2+}$ (w) ratio, it is observed that in order to minimize the TOC value of the effluent, the optimum $H_2O_2$ dose according to the statistical model was 1400 mg $L^{-1}$, with an optimal $H_2O_2$ / $Fe^{2+}$ ratio of 20 (minimizing the dose of added iron), which corresponds to 70 mg $L^{-1}$ $Fe^{2+}$. With these conditions 79.7% of TOC removal at 60 min was achieved, according to the equation 6.4.

The process yield adjustment equation to obtain this operational optimum is (TOC, [$H_2O_2$] and [$Fe^{2+}$] in mg $L^{-1}$):

$$\text{TOC 60 min} = 274.347 - 0.360199\times[H_2O_2] + 6.87754\times\frac{[H_2O_2]}{[Fe^{2+}]} + 0.000122056\times[H_2O_2]^2 - 0.00299172\times[H_2O_2]\times\frac{[H_2O_2]}{[Fe^{2+}]} - 0.0894306\times\left(\frac{[H_2O_2]}{[Fe^{2+}]}\right)^2$$

(Equation 6.4)

This mathematically optimal experiment was also carried out experimentally, and it was demonstrated that 19%, 78.8% and 85.6% of TOC removal were achieved after 15, 60 and 157 min, respectively. COD and $BOD_5$ were analyzed at 60 min, and 57 mg $L^{-1}$ and 1 mg $L^{-1}$ were obtained, respectively; therefore this treated water could be reused for irrigation according to USEPA recommendations, once the iron has been removed by raising the pH and decanting.

The experiment from Table 6.2 closest to these optimal conditions was the one made with 1200 mg $L^{-1}$ $H_2O_2$ and 60 mg $L^{-1}$ $Fe^{2+}$, where a removal of 77.6% was achieved after 60 min (78.9% after 157 min). This experiment was also performed with the UVA lamps and resulted a TOC removal after 60 min of only 10.2% (at 15 min was also 10.2% and at 157 min the TOC removal was 75.6%).

These two optimal conditions were tested and discussed in section 6.3.3, where $TiO_2$ catalyst was also added to test its possible synergistic effect.

### 6.3.2. Photocatalytic experiments

Table 6.3 shows the experiments carried out using the SB, UVA and UV-C lamps, the initial pH (3 and free pH or 10.3) of the sample, the reagents concentrations, if residual $H_2O_2$ remained and the most significant TOC removals, both for the photocatalytic experiments.

Table 6.3. Photocatalytic experiments and results of TOC and residual $H_2O_2$

| **PHOTOCATALYSIS** | | | | | |
|---|---|---|---|---|---|
| **Light source** | **pH** | **P25, mg $L^{-1}$** | **$H_2O_2$, mg $L^{-1}$** | **Residual $H_2O_2$** | **TOC Removal, %** |
| UVA | free | 250 | 0 | - | 270 min:11.0% |
| SB | free | 250 | 0 | - | 240 min: 29.6% |
| UVA | 3 | 250 | 0 | - | 240 min:18.8% |
| SB | 3 | 250 | 0 | - | 157 min: 33.3% |
| SB | free | 250 | 500 | No (at 90 min) | 15 min: 18.7%<br>60 min:12.8%<br>157 min: 20.6% |
| SB | free | 250 | 1200 | Yes (157 min) | 15 min: 22.4%<br>157 min: 9.0% |
| SB | free | 0 | 500 | Yes (180 min) | 0% |
| SB | free | 0 | 1200 | Yes (157 min) | 15 min: 0%<br>60 min:0.7%<br>157 min: 6.4% |
| SB | 3 | 0 | 1200 | Yes (180 min) | 15 min: 3.8%<br>60 min: 5.5%<br>157 min: 5.5% |
| SB | 3 | 250 | 500 | Yes (157 min) | 15 min: 21.8%<br>60 min: 21.6%<br>157 min: 32.7% |
| SB | 3 | 250 | 1200 | Yes at 157 min (No at 180 min) | 15 min: 23.2%<br>60 min: 27.9%<br>157 min: 71.2%<br>180 min: 76.9% |
| UV-C | 3 | 0 | 1200 | Yes | 157 min: 50.1% |
| UV-C | 3 | 250 | 1200 | Yes | 157 min: 38.7% |

| | | | | | |
|---|---|---|---|---|---|
| UV-C | free | 0 | 1200 | Yes | 157 min: 60.7% |
| UV-C | free | 250 | 1200 | Yes | 157 min: 20.8% |

Adsorption tests in the dark were performed firstly, with 250 mg $L^{-1}$ P25 (the catalyst concentration used in the photocatalysis experiments) at pH 3 and basic pH (free or 10.3) with and without the addition of 1200 mg $L^{-1}$ $H_2O_2$. The results showed that until 2 hours, there was between 4-13% of TOC removal because of the adsorption of the organic matter to the titania and this percentage increased at longer times. The adsorption was slightly higher at acidic than basic pH because at low pH, $TiO_2$ surface is positively charged and the EDTA that possess negative charge is better adsorbed. Adsorption tests in presence of $H_2O_2$ did not show any effect.

The combination of P25 and radiation was tested with solar radiation (SB) and UVA radiation. Figure 6.7 shows the evolution of the TOC removal percentage over time in these experiments. It can be seen that the photocatalysis with only P25 was not very effective for the removal of organic matter and that most of the elimination was due to the phenomenon of adsorption. However, concerning the effect of pH, the process performed better at pH 3 than at basic pH due to the above mentioned presence of positive surface charges on the catalyst. Comparing the light source and the equipment, higher removals were achieved with the SB. The intensity of the radiation from the Xe lamp used in the SB is higher according to the actinometrical tests, and the configuration of the lamp on the top in the SB allows sample to take better profit of the light better. At pH 3, a 33.3% of removal was achieved at 157 min with the SB.

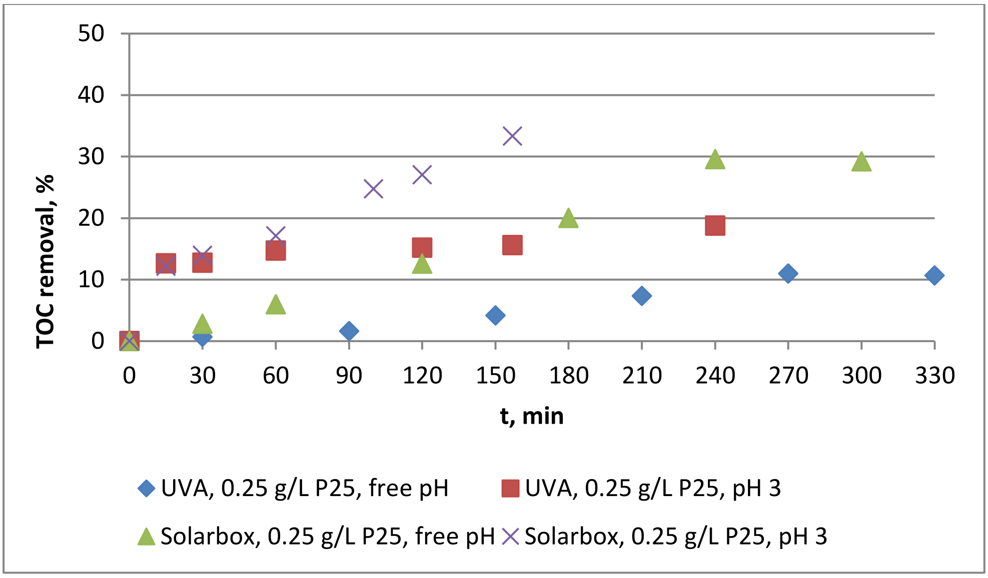
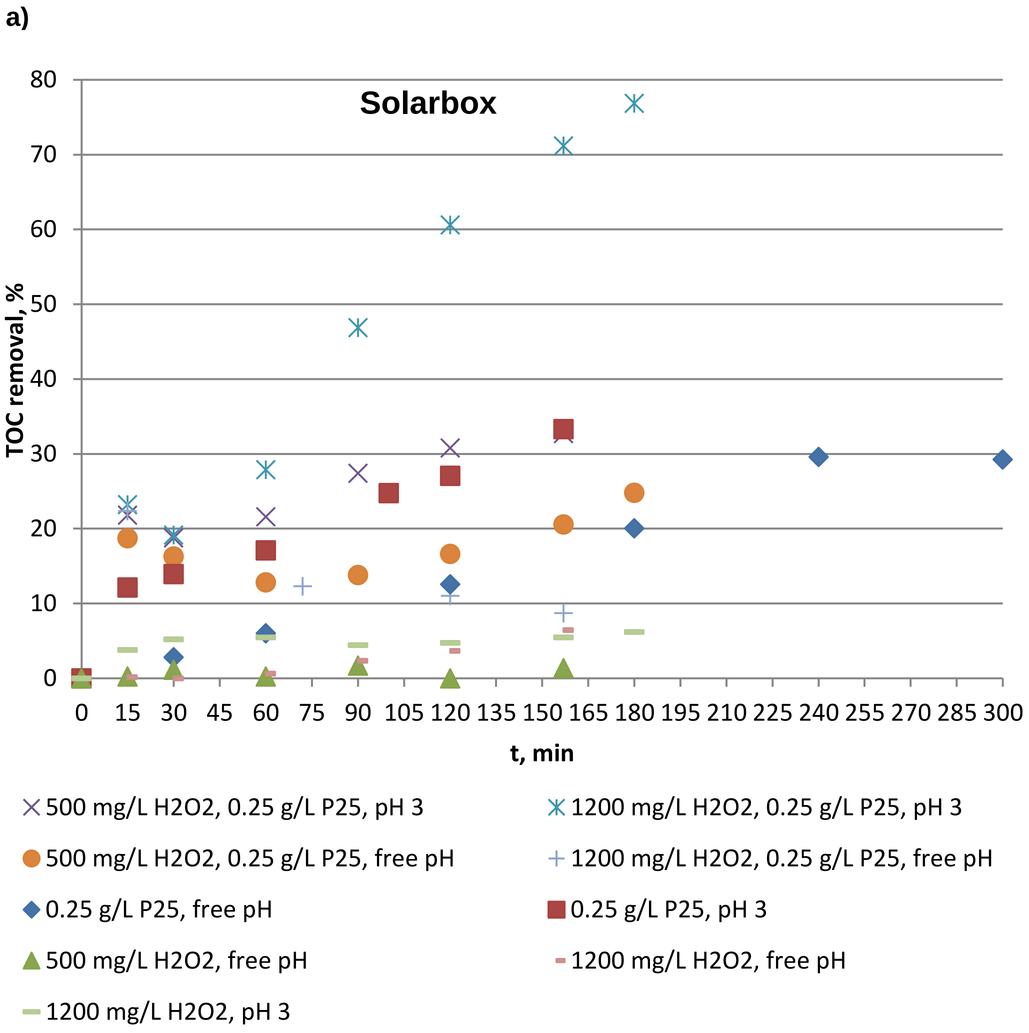


Figure 6.7. TOC removal in photocatalysis experiments with UVA and SB at free pH (10.3) and at pH 3 using 0.25 g $L^{-1}$ of P25.

The effect of $H_2O_2$ addition was therefore studied. As it can be seen in Figure 6.8 (a), if only $H_2O_2$ was added with solar radiation, elimination did not take place, since the $H_2O_2$ absorbs up to 300 nm and the SB emits at wavelengths outside this range.

Figure 6.8 (a) also shows that the combination of $H_2O_2$ and P25 produced a greater elimination of organic matter, compared when only adding P25, if the process starts at pH 3 and an amount higher than 500 mg $L^{-1}$ of $H_2O_2$ was used, (since with 500 mg $L^{-1}$ there was hardly any difference in the effluent TOC compared to the experiment performed with only 250 mg $L^{-1}$ of P25). At acidic pH with 1200 mg $L^{-1}$ $H_2O_2$ and 250 mg $L^{-1}$ P25, rapid elimination of TOC over time was achieved, reaching a mineralization degree of 71.2% (there was remaining $H_2O_2$) at 157 min and 76.9% at 180 min ($H_2O_2$ was consumed).

In Figure 6.8 (b), experiments with $H_2O_2$ and UV-C radiation were performed and a significant TOC removal was achieved. Similar results were obtained by Baeza et al. (2003), who studied the EDTA mineralization and achieved a high percentage of TOC removal at pH 3 using $H_2O_2$ (40:1 $H_2O_2$ / EDTA molar ratio or 20:1 with slightly lower results) and UV-C radiation after 540 min. It was observed that the pH did not affect the elimination when only $H_2O_2$ was used but if 250 mg $L^{-1}$ P25 was also added, the pH 3 was more favorable than the basic one, due to the surface charge that the catalyst acquires at acidic pH. However, it is also observed in the Figure 6.8 (b) that greater eliminations were achieved without the addition of P25. As it was obtained by Baeza et al. (2003), $TiO_2$ particles produce scattering of light that inhibits the photocatalytic decomposition of $H_2O_2$. 61% of TOC removal was achieved at basic pH (free pH) with 1200 mg $L^{-1}$ $H_2O_2$ under UV-C radiation at 157 min.


a)
Solarbox
TOC removal, %
0
10
20
30
40
50
60
70
80
t, min
0 15 30 45 60 75 90 105 120 135 150 165 180 195 210 225 240 255 270 285 300
500 mg/L H2O2, 0.25 g/L P25, pH 3
1200 mg/L H2O2, 0.25 g/L P25, pH 3
500 mg/L H2O2, 0.25 g/L P25, free pH
1200 mg/L H2O2, 0.25 g/L P25, free pH
0.25 g/L P25, free pH
0.25 g/L P25, pH 3
500 mg/L H2O2, free pH
1200 mg/L H2O2, free pH
1200 mg/L H2O2, pH 3

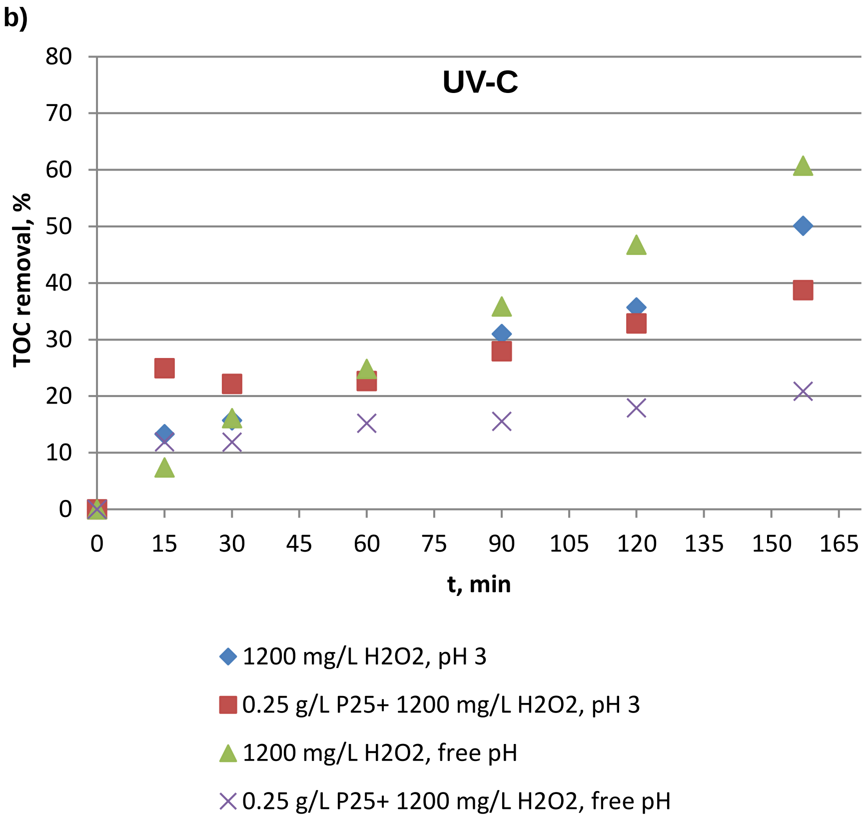


Figure 6.8. TOC removal in experiments a) with $H_2O_2$ and $H_2O_2$ + P25 in the SB, b) with $H_2O_2$ and $H_2O_2$ +P25 under UV-C radiation

### 6.3.3. Comparison between photocatalysis and photo-Fenton

As better removals were obtained with the photo-Fenton process (section 6.3.1) than with photocatalysis (section 6.3.2), it was studied if the addition of P25 would improve the photo-Fenton reaction itself. To essay this, two experiments were carried out in parallel at initial pH 3, adding in both 1400 mg $L^{-1}$ of $H_2O_2$ and 70 mg $L^{-1}$ of Fe (optimum amounts obtained for the photo-Fenton process according to the statistical model), but in one of them 0.25 g $L^{-1}$ of P25 was added too. These results are shown in Table

6.4 and Figure 6.9. As can be seen, TOC eliminations were similar, except at 30 min where a 19% of TOC removal was obtained in the experiment without P25 and a 71.5% if P25 was added. That is, the difference between adding or no adding P25 to the photo-Fenton process was the higher organic matter degradation rate in the first 30 min, but after one hour similar elimination was obtained. The maximum degradation achieved was 78.8% at 60 min (85.6% at 157 min) using 1400 mg $L^{-1}$ of $H_2O_2$ and 70 mg $L^{-1}$ of Fe, and 84% at 60 min (86.6% at 157 min) if 0.25 g $L^{-1}$ of P25 was also added.

As Figure 6.9 shows, these photo-Fenton experiments were also performed at neutral pH, instead of acidifying down to pH 3. It was obtained that at acidic pH, a noticeable higher TOC removal was achieved at 60 and 90 min than at pH 7, although at 157 min, the same elimination was finally reached. The low efficiency affecting photo-Fenton processes at neutral pH is mainly due to iron precipitation, and could be therefore prevented by properly adding iron complexing agents such as EDTA. In this case, neutral pH would not affect TOC removal probably because among the complexes formed between EDTA and metals, $Fe^{3+}$ - EDTA is the most photosensitive one (Natarajan and Endicott, 1973) and $Fe^{3+}$-EDTA complex can enhance the production of reactive radicals in aqueous solutions, especially at neutral pH (Graf et al. 1984).

The photolysis of $Fe^{3+}$-EDTA is initiated according to reaction 6.5, which is followed by the reaction 6.6 where $Fe^{2+}$ species or $O_2^{\bullet-}$ are formed (Kocot et al. 2006) and the reaction sequence between $Fe^{3+}$/ $Fe^{2+}$ and $O_2^{\bullet-}$/$HO_2^{\bullet}$ leads to more reactive species generation (Bielski et al. 1985).

$$Fe^{3+}\text{-}L + h\upsilon \rightarrow [Fe^{3+}\text{-}L]^* \rightarrow Fe^{2+} + L^{\bullet} \qquad (6.5)$$

$$L^{\bullet} + O_2 \rightarrow O_2^{\bullet-} + L' \qquad (6.6)$$

Therefore, photochemical system using $Fe^{3+}$-EDTA is available in a wider pH range than traditional Fenton reagent (Zhou et al. 2008). However, quantum yields for Fe(III)-EDTA photolysis depend on pH, being higher at acidic pH than at neutral or basic pH (Kocot et al. 2006). This fact could explain that at shorter reaction times, it is more noticeable the effect of the reaction on TOC removal when pH is lower.

By contrast, photo-Fenton combined with P25 (except in the 30 min in which an acidic initial pH is better), the eliminations were similar at both pHs.

Table 6.4. Photo-Fenton and photo-Fenton + P25 experiments and results of TOC and residual $H_2O_2$

| **PHOTO-FENTON AND PHOTO-FENTON + P25** | | | | | | |
|---|---|---|---|---|---|---|
| **Light source** | **pH** | **P25, mg $L^{-1}$** | **$H_2O_2$, mg $L^{-1}$** | **Fe, mg $L^{-1}$** | **Residual $H_2O_2$** | **TOC Removal, %** |
| SB | 3 | No | 1200 | 60 | Yes at 60 min, no at 157 min. | 15 min: 3.0%<br>60 min: 75.9%<br>157 min: 78.9% |
| SB | 3 | 250 | 1200 | 60 | Yes (157 min) | 15 min: 10.2%<br>72-157 min: 82.3 % |
| SB | 3 | No | 1400 | 70 | No (157 min) | 15 min: 10.2%<br>30 min: 19.0%<br>60 min: 78.8%<br>157 min: 85.6% |
| SB | 3 | 250 | 1400 | 70 | No (90 min) | 15 min: 10.5%<br>30 min: 71.5%<br>60 min: 84.0%<br>157 min: 86.6% |
| SB | 7 | No | 1400 | 70 | Yes (157 min) | 15 min: 17.2%<br>60 min: 15.7%<br>157 min: 80.9% |

| | | | | | | |
|---|---|---|---|---|---|---|
| SB | 7 | 250 | 1400 | 70 | No<br>(90 min) | 15 min: 12.2%<br>30 min: 44.9%<br>60 min: 79.8%<br>157 min: 84.0% |

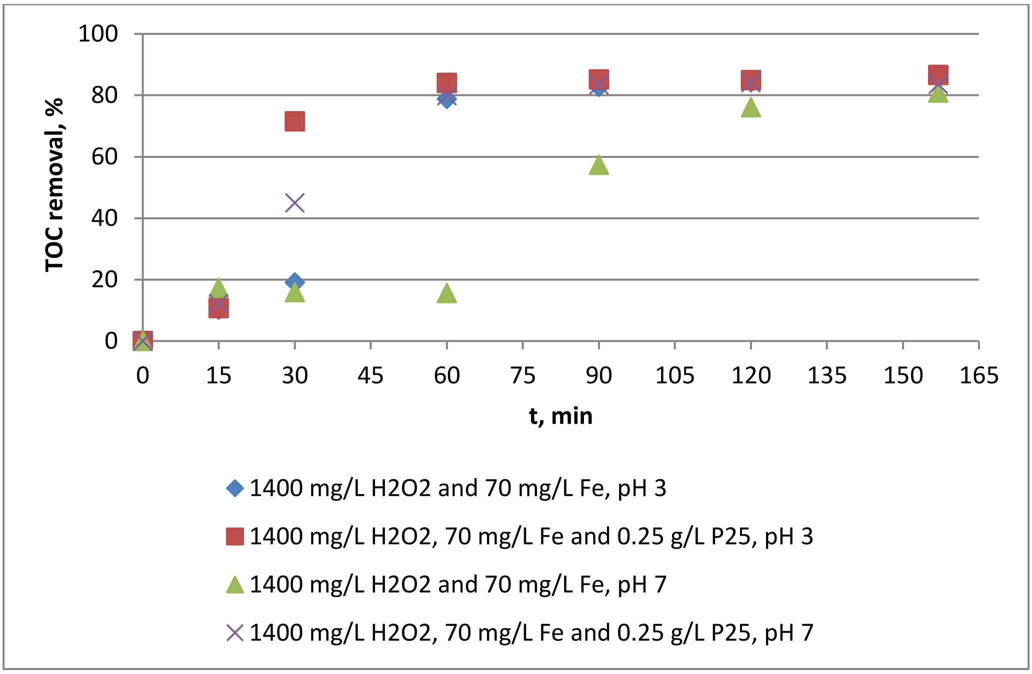


Figure 6.9. TOC removal in the photo-Fenton experiments in the SB with 1400 mg $L^{-1}$ of $H_2O_2$ and 70 mg $L^{-1}$ of Fe at pH 3 and 7, with and without 0.25 g $L^{-1}$ P25

To sum up, these experiments show that most suitable process for the organic load mineralization in the RO membranes cleaning waters from those essayed in this work was the photo-Fenton at pH 3, with 1400 mg $L^{-1}$ of $H_2O_2$ and 70 mg $L^{-1}$ of Fe in the SB, which lead to a TOC removal of

78.8% at 60 min, and 85.6% after 157 min with total $H_2O_2$ consumption. However, with 1200 mg $L^{-1}$ of $H_2O_2$ and 60 mg $L^{-1}$ of Fe, a 75.9% is achieved at 60 min. This conditions could be considered economically more attractive. The photo-Fenton reaction could also be performed at pH 7 because, although until 60 min the reaction was slower, at 157 min, the same elimination was reached. By contrast, the addition of P25 increased the speed of the process both at pH 3 and at 7, especially at 30 min of reaction, but at 157 min the same elimination was reached, so there would be no need to add P25, besides it would have to be removed from the effluent afterwards.

COD and $BOD_5$ were analyzed after 60 min in the photo-Fenton experiment at pH 3 using 1400 mg $L^{-1}$ of $H_2O_2$ and 70 mg $L^{-1}$ of Fe in the SB, and 57 mg $L^{-1}$ and 1 mg $L^{-1}$, respectively were obtained, complying with the USEPA recommendations for irrigation of raw food crops for human consumption (that sets a maximum limit of 10 mg $L^{-1}$ $BOD_5$).

To check if SDS remained, the samples obtained after these photo-Fenton reactions (at pH 3 and using 1400 mg $L^{-1}$ $H_2O_2$ and 70 mg $L^{-1}$ Fe, and 1200 mg $L^{-1}$ $H_2O_2$ and 60 mg $L^{-1}$ Fe with and without P25) were also analyzed by HPLC-TOF. SDS standards of 1.5 and 15 mg $L^{-1}$ were analyzed (retention time 3.3 min, peak identification M-*=265.1478). The samples were analyzed in two different ways (at actual pH of 3.3 and adjusted to 6.5), and in both cases the ion M-*=265.1478 was searched at 3.3 min and it did not appear. This means that no SDS is detected, either because it is not present or because its concentration is smaller than the detection limit (< 0.5 mg $L^{-1}$).

## 6.4. CONCLUSIONS

After the study of the photo-Fenton process at pH 3 under simulated solar radiation in cleaning waters from seawater desalination reverse osmosis membranes, the evaluated effluent TOC at three reaction times, indicated that 60 min of reaction were sufficient for the removal of a high TOC percentage.

After a statistical analysis of the results, for the range of reagent concentrations studied, the optimal dose of reagents for optimal time of 60 min were 1400 mg $L^{-1}$ of $H_2O_2$ and 70 mg $L^{-1}$ of $Fe^{2+}$ (3 times lower that the optimum concentrations determined in the first part of the study), achieving a 79.70% of TOC removal. An empirical equation was proposed to estimate the percentage of TOC removal after 60 min of reaction. Experimentally, the TOC removal at 60 min was 78.8% and with longer time (157 min) a 85.6% and all the $H_2O_2$ was consumed. This photo-Fenton reaction could also be performed at pH 7 because, although the reaction was slower than for pH 3, at 157 min, the same elimination was reached. The photoactivity of the $Fe^{3+}$-EDTA complex could help to explain this behavior. By contrast, the addition of P25 accelerated this process both at pH 3 and at 7 in the first 30 min but after one hour, similar elimination was obtained. Therefore it was concluded that there would be no need to add P25 that afterwards would have to be removed from the effluent.

SDS was analyzed in the water obtained after this treatment and this component was not found. Thanks to this and to the fact that final $BOD_5$ was 1 mg $L^{-1}$, this water could be reused for irrigation according to EPA recommendations.

A high mineralization was also obtained under simulated solar radiation at pH 3 by adding 1200 mg $L^{-1}$ of $H_2O_2$ with 0.25 g $L^{-1}$ of P25 instead of Fe, where 76.9% of TOC removal was achieved at 180 min.

Under UV-C radiation and by adding 1200 mg $L^{-1}$ of $H_2O_2$ at free pH, 61% of TOC removal was achieved at 157 min.

## 6.5. REFERENCES

Ahmed, S., Rasul, M.G., Brown, R. and Hashib, M. 2011. Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: A short review J. Environ. Manage. 92 311–30.

Baeza, C., Rossner, A., Jardim, W., Litter, M. and Mansilla, H., 2003. Removal of EDTA by UV-C/ hydrogen peroxide. Environ. Technol. 24: 1277-1281.

Bandala, E.R., Peláez, M.A., Salgado, M.J., Torres, L., 2008. Degradation of sodium dodecyl sulphate in water using solar driven Fenton-like advanced oxidation processes. J Hazard Mater.;151:578–584.

Bielski, B.H.J., Cabelli, D.E., Arudi, L.R., Ross, A.B., 1985. Reactivity of HO2/O2- radicals in aqueous solution. J. Phys. Chem. Ref. Data, 14, 1041-1100.

Chitra, S., Paramasivan, K., Sinha, P. K., 2013. Sono-Photo Fenton Treatment of Liquid Waste Containing Ethylenediaminetetraacetic Acid (EDTA). International Journal of Nonferrous Metallurgy, 2; 89-94.

Chitra, S., Paramasivan, K., Shanmugamani, A.G., Rao, S.V.S. and Biplob Paul. Advanced Oxidation Processes for the Treatment of Surfactant Wastes. J. Chem. Eng. Chem. Res. Vol. 1, No. 3, 2014, pp. 163-173.

Colmenares, J.C., Luque, R., Campelo, J.M., Colmenares, F., Karpiński, Z. and Romero, A.A. 2009. Nanostructured photocatalysts and their applications in the photocatalytic transformation of lignocellulosic biomass: An overview Materials (Basel). 2 2228–58

Dow Filmtec™ Membranes. Cleaning Procedures for DOW FILMTEC FT30 Elements. Technical Manual.

Engelmann, M.D., Bobier, R.T., Hiatt, T., Cheng, I.F., 2003. Variability of the Fenton reaction characteristics of the EDTA, DTPA, and citrate complexes of iron. BioMetals 16, 519–527.

Ghiselli, G., Jardim, W. F., Litter, M. I. and Mansilla, H. D., 2004. Destruction of EDTA using Fenton and photo-Fenton-like reactions under UV-A irradiation. Journal of Photochemistry and Photobiology A: Chemistry, 167, 59–67.

Goldstein, S., Rabani, J., 2008. The ferrioxalate and iodide-iodate actinometers in the UV region. Journal of Photochemistry and Photobiology A: Chemistry, 193, 50-55.

Graf, E., Mahoney, J.R., Bryan, R.G., Eaton, J.W., 1984. Iron-catalyzed hydroxyl radical formation. Stringent requirement for free iron coordination site. J. Biol. Chem., 259, 3620-3624.

Hatchard, C.-G., Parker, C.A., 1956. A new sensitive chemical actinometer. II. Potassiumferrioxalate as a standard actinometer". Proceedings of the Royal Society London Service A, 235, 518-536.

Jiménez, S., Micó, M.M., Contreras, S., 2017. Treatment of Reverse Osmosis Membranes Cleaning Waters for Reutilization Purposes. Part I:

Application of Fenton Process (submitted for publication in Water Research Journal).

Jones, C.W., 1999, Applications of hydrogen peroxide and derivates. Royal Society of Chemistry.

Kim, S., Geissen, S., Vogelpohl, A., 1997. Landfill leachate treatment by a photoassisted Fenton reaction. Water Sci. Technol. 35, 239-248.

Kiran, I., Bektas, N., Yatmaz, H.C. and Tekbas. M., 2013. Photocatalytic Fenton oxidation of sodium dodecyl sulfate solution using iron-modified zeolite catalyst. Desalination and water treatment. 51 (28-30), pp. 5768-5775.

Kocot, P., Karocki, A., Stasicka, Z., 2006. Photochemistry of the Fe(III)–EDTA complexes A mechanistic study. J. Photochem.Photobiol. A, 179, 176-183.

Macounova, K., Krysova, H., Ludvik, J. and Jirkovsky, J. 2003. Kinetics of photocatalytic degradation of diuron in aqueous colloidal solutions of Q-TiO 2 particles J. Photochem. Photobiol. A Chem. 156 273–82

Navea, S., Repollés, C., Romero, C., 2016. Escenarios oxidación avanzada aguas de limpieza en desalinizadoras. Closed Loop Project. Acciona Agua. Internal report.

Natarajan, P., Endicott, J.F., 1973. Photoredox behavior of transition metalethylenediaminetetraacetate complexes. A comparison of some group VIII metals. J. Phys. Chem., 77, 2049-2054.

Neyens, E., Baeyens, J., 2003. A review of classic Fenton's peroxidation as an advanced oxidation technique. Journal of Hazardous Materials 98 (1–3), 33–50.

Nguyen, T., Roddick, F. and Fan, L., 2012. Biofouling of Water Treatment Membranes: A Review of the Underlying Causes, Monitoring Techniques and Control Measures. Membranes. 2(4): p. 804.

Pignatello, J.J., Oliveros, E., MacKay, A., 2006. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. Crit. Rev. Environ. Sci. Technol. 36, 1–84.

Rekab, K., Lepeytre, C., Dunanda, M., Dappozze, F., Herrmann, J.M., Guillard, C., 2014. H2O2 and/or photocatalysis under UV-C irradiation for the removal of EDTA, a chelating agent present in nuclear waste waters. Applied Catalysis A: General 488; 103–110.

Royal Decree 1620/2007 of 7 December, that establish the legal status of the reutilization of depurated water. Boletín Oficial del Estado (BOE) 294, 08/12/2007, 50639-50661.

Sobczyński, A. and Dobosz, A. 2001. Water Purification by Photocatalysis on Semiconductors Polish J. Environ. Stud. 10 195–205.

Zepp, R.G., Faust, C., Hoigne, J., 1992. Hydroxyl radical formation in aqueous reactions (pH 3-8) of iron (III) with hydrogen peroxide : the photo-Fenton reaction, Environ. Sci Technol., 26(2), 313-319.

Zhang, Y., Zhou, J. L., Ning, B., 2007. Photodegradation of estrone and 17β-estradiol in water Water Res. 41 19–26.

Zhou, T., Li, Y., Wong, F., Lu, X., 2008. Enhanced degradation of 2, 4-dichlorophenol by ultrasound in a new Fenton like system (Fe/EDTA) at ambient circumstance. Ultrason. Sonochem., 15, 782-790.

Zuo, Y., 1995. Kinetics of photochemical/chemical cycling of iron coupled with organic substances in cloud and fog droplets. Geochimica et Cosmochimica Acta, 59, 3123-3130.

# Chapter 7. Life Cycle Assessment applied to the Produced Water and Reverse Osmosis Membranes Cleaning Water Treatments

**Content**

## 7.1. INTRODUCTION

Life Cycle Assessment (LCA) is an environmental management tool that enables quantification of environmental burdens and their potential impacts over the whole life cycle of a product, process or activity. LCA is defined by the Society for Environmental Toxicology and Chemistry (SETAC) as “a process to evaluate the environmental burdens associated with a product, process, or activity by identifying and quantifying energy and materials used and wastes released to the environment; to assess the impact of those energy and material uses and releases to the environment; and to identify and evaluate opportunities to affect environmental improvements" (Consoli et al. 1993; Fava et al. 1991).

The methodological framework for conducting LCA, as defined by both SETAC and the International Organization for Standardization (ISO) within the series ISO 14040 and 14044 (ISO/DIS 14040, 1997) comprises four main phases:

- Goal and Scope
- Inventory Analysis
- Impact Assessment
- Interpretation

**Goal and scope** is the first stage. This is an interactive and continuously revisable stage, so if during the development of the study new information or data is found, it may be advisable to make changes in this stage.

In the first place, the goal of the study is defined, as well as the reasons that have led to its realization, the kind of decisions that will be made from the results obtained (technical, governance, etc.), and if these will be of internal use (for a company, for instance) or external (to inform the general public or an institution).

Secondly, the scope of the study is defined. Usually this implies defining the system, its boundaries (conceptual, geographical and temporal), the quality of the data used, the main hypothesis and a priori limitations. A key issue in the scope is the definition of the 'functional unit'. This is the unit of the product or service whose environmental impacts will be assessed or compared. It is often expressed in terms of amount of product, but should really be related to the amount of product needed to perform a given function.

The objective is the definition of the reasons why the study is done and it has also to be stated in this stage. Some plausible objectives could be:

- To compare different products / processes / services
- To detect stages of life with more impact
- To identify options for improvement
- To evaluate alternatives for the same product / process / service
- To design a new product.

The **inventory analysis**, the second stage of LCA, includes information of all the environmental inputs and outputs associated with the process, taking into account the material and energy requirements, as well as emissions and wastes.

Regarding the **impact assessment**, the inventory result is usually a very long list of emissions, consumed resources and sometimes other items. The interpretation of this list is difficult. A Life Cycle Inventory Assessment (LCIA) procedure, such as the ReCiPe methodology is designed to help with this interpretation.

The primary objective of the ReCiPe method is to transform the long list of Life Cycle Inventory results, into a limited number of indicator scores. These indicator scores express the relative severity of the studied effect on an environmental impact category. In ReCiPe indicators are determined at two levels: eighteen midpoint indicators and three endpoint indicators.

Midpoint impact category, or problem-oriented approach, translates impacts into environmental themes such as climate change, water bodies' acidification, human toxicity, etc.

Endpoint impact category, also known as the damage-oriented approach, translates environmental impacts into issues of concern such as human health, natural environment, and natural resources. Endpoint results have a higher level of uncertainty compared to midpoint results but are easier to understand by decision makers.

In the **interpretation** step, the results are examined in terms of critical sources of impact and the ways or opportunities for reducing these impacts.

In our case, LCA was carried out to detect the stages of the effluent treatment that contribute the most to the environmental impact, and to compare the different processes that have been studied in this thesis for the treatment of PW and RO membranes cleaning water.

The functional unit to which all system data (both inputs and outputs) were referenced was 1 L of treated water (for PW and RO membranes cleaning water).

In this chapter LCA is applied for each PW treatment and RO membranes cleaning water treatment that have been studied in this thesis, with the optimal condition obtained for each of these processes.

For the PW treatment, LCA is applied to the best conditions obtained in the DAF, E-DAF and settling processes (studied as PW pretreatments in chapter 3), as well as to the photocatalysis, photo-Fenton, temperature-enhanced Fenton and ozonation (studied in chapter 4).

In the treatment of RO membranes cleaning water, LCA is applied to the best conditions obtained for the Fenton, photo-Fenton and photocatalysis processes (studied in chapter 5 and 6).

## 7.2. MATERIALS AND METHODS

### 7.2.1. Ecoinvent Database

The *Ecoinvent* Database offers LCI and LCIA results. Among all the LCIA methods implemented in the *Ecoinvent*, ReCiPe Midpoint will be applied in this case.

For each process, all the inputs and outputs must be identified and quantified. For this a flow chart for each process that has been studied can be helpful.

Each type of reagent, material and energy consumption for the inputs, and each product generated for the output, has to be searched in the *Ecoinvent* Database, where the LCIA is obtained for the production/treatment of these reagents, materials, energy or compounds, i.e. a series of values (related to its emission factor and characterization factor) for each impact category of the ReCiPe Midpoint method. These impact categories are: agricultural land occupation, climate change, fossil depletion, freshwater ecotoxicity, freshwater eutrophication, human toxicity, ionizing radiation, marine ecotoxicity, marine eutrophication, metal depletion, natural land transformation, ozone depletion, particulate matter formation, photochemical oxidant formation, terrestrial acidification, terrestrial ecotoxicity, urban land occupation and water depletion with their correspondent units. Each LCIA value found in the Database must be multiplied by the quantity of reagent, material or energy consumption, etc., used/generated in the process and the impact will be obtained, i.e. the LCIA for the concrete process.

For each process, 1 L of treated wastewater (PW or RO membrane cleaning waters) will be considered as product unit.

## 7.3. RESULTS

### 7.3.1. Produced water

Figure 7.1 shows the flowcharts for the best conditions that were obtained for each PW pretreatment: a) DAF, b) E-DAF and c) Settling. This inventory analysis includes the inputs and outputs associated with each process. For the inputs, all the reagents, materials electricity consumed by the process are taken into account.

Considering that initial PW that enters in each pretreatment a), b) or c) was composed of its complete recipe (O&G and all the components added, as it was shown in chapter 4), in chapter 3 was obtained that only the oil and grease (O&G) fraction was removed with these pretreatments, so in addition to phenol, the rest of the soluble components constituted the effluent of the pretreatment that will be later treated by an AOP. For this reason, considered pretreatment outputs were only those compounds that have been volatilized during the processes to the air (toluene and xylene that disappear by striping due to the agitation, and as it was seen in chapter 3, 0.5 mg $L^{-1}$ of phenol, since the rest of this component was not eliminated and remained in the effluent) and also the iron sludge generated that contained the O&G adhered onto it.

As an AOP is carried out (photocatalysis, photo-Fenton, Fenton with temperature or ozonation) after the pretreatment, the input for this AOP considered for the LCA was the liquid effluent from the pretreatment, (together with the reagents, materials and electricity consumed by this AOP).

For the AOPs outputs, the compounds that remain in the treated water, possible emissions to air and their impact in ocean water will be taken into account.

Figure 7.2 shows the flowcharts of the different AOPs that were studied with the inventory analysis for PW.

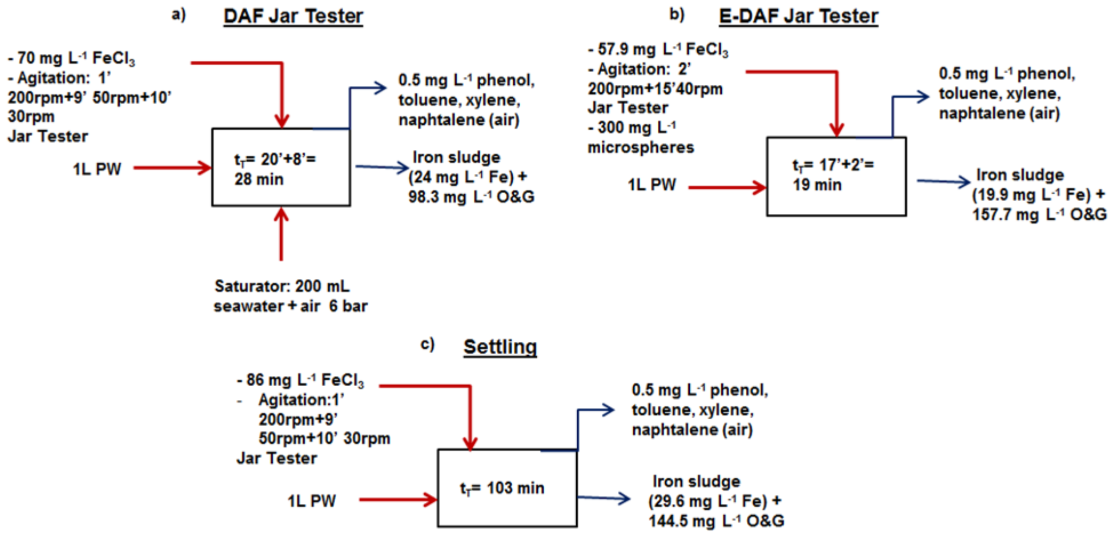


Figure 7.1. Flowcharts of the optimum conditions obtained of the PW pretreatments: a) DAF, b) E-DAF and c) Settling processes for applying the LCA that are the basis for the inventory analysis

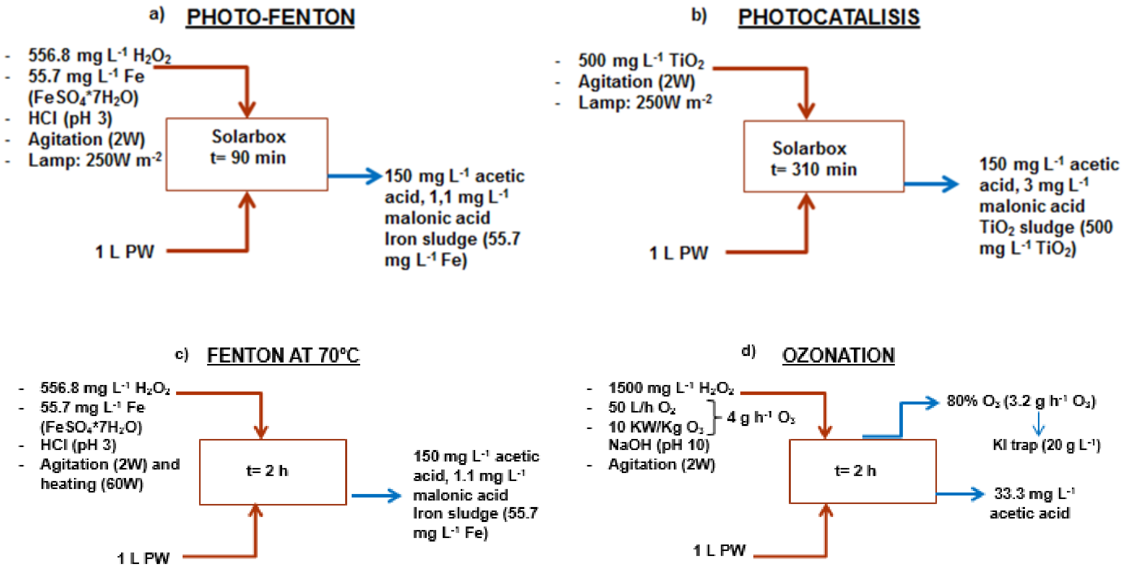


Figure 7.2. Flowcharts of the optimum conditions obtained of the AOPs for the PW polishing: a) Photo-Fenton, b) Photocatalysis c) Fenton at

70ºC and c) Ozonation for applying the LCA that are the basis for the inventory analysis

#### 7.3.1.1. Pretreatment of produced water

Table 7.1 (a) shows the inventory analysis and the impact for the DAF process inputs. For 1 L PW and applying this pretreatment, ferric chloride, compressed air at 6 bar (contained in 200 mL of saturated seawater) and electricity consumed by the Jar test during 20 min of agitation (considering the powerpack and drive motors) were required. For each one of these inputs in the Table 7.1 (a), in the column on the left (in black color) is shown the value of the emission factor multiplied by the characterization factor, and in the column on the right (in red color) its multiplication by the concrete consumption in the process. The last column shows the inputs sum for each impact category.

Table 7.1 (b) shows the DAF process outputs. The iron sludge and O&G generated after DAF are incinerated, so in the database the option of '*treatment of refinery sludge, hazardous waste incineration*' is chosen. After the DAF process, 24 mg $L^{-1}$ of iron sludge and 98.3 mg $L^{-1}$ O&G are generated, so the sum for the incineration score is 122.3 mg $L^{-1}$. In addition, components emitted into the atmosphere are taken into account. As can be seen, phenol, toluene, xylene and naphthalene have toxic impacts and toluene also contributes to photochemical oxidant formation.

Table 7.2 (a) and (b) shows the inventory analysis and the impact of the E-DAF process (for the inputs and outputs, respectively). In this case, the inputs are the ferric chloride, the microspheres (in the database found as "glass fibres") and electricity consumed by the Jar tester during 17 min of agitation (considering the powerpack and drive motors). The outputs are the same as those in the DAF process but with different concentrations of iron sludge and O&G.

Table 7.3 (a) and (b) shows the inventory analysis and the impact of the settling process (for the inputs and outputs, respectively). The inputs are the ferric chloride and electricity consumed during 20 min of agitation. The outputs are the same as those in the other pretreatments but with different concentrations of iron sludge and O&G.

Finally, in Table 7.4, for each of the treatments, the total impact on each category in the ReCiPe Midpoint method is shown. These impacts have been calculated for each of the PW pre-treatments adding the inputs and outputs of each of the categories.

As it can be seen in Table 7.4, when DAF, E-DAF and settling are compared, since the reference unit is a small volume (1 L), the consumptions of reagents, etc. are low, and therefore there are no significant differences between the three scenarios. The quantity of $FeCl_3$ and KW h of electricity in the inputs were similar for the three treatments with the difference in the microsphere addition for the E-DAF process, and the compressed air in DAF, although these consumptions were low. In this last one, the compressed air expense that was required is compensated with the lowest generation of oil and grease sludge (and therefore the impact corresponding to its incineration) because this treatment was not effective for the O&G removal of PW.

In general, impacts were slighter minor in DAF process followed by settling process.

Table 7.1. Inventory analysis and impacts of DAF process in PW taking into account a) the inputs, and b) the outputs

a)

| ReCiPe Midpoint (H) | FeCl$_3$: 70 E-06 Kg | | Compressed air 6 bar: 2,4E-05 m3 | | Electricity JarTester + agitation: 0,063 KW h | | INPUTS SUM |
|---|---|---|---|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 0,11436297 | 8,01E-06 | 0,01396091 | 3,35E-07 | 0,03970402 | 2,50E-04 | 2,58E-04 |
| climate change:GWP100 (kg CO2-Eq) | 0,72205366 | 5,05E-05 | 0,099201111 | 2,38E-06 | 0,46997944 | 2,96E-03 | 3,01E-03 |
| fossil depletion:FDP (kg oil-Eq) | 0,19880927 | 1,39E-05 | 0,028132584 | 6,75E-07 | 0,14099153 | 8,88E-04 | 9,03E-04 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 0,038777457 | 2,71E-06 | 0,005086018 | 1,22E-07 | 0,021929677 | 1,38E-04 | 1,41E-04 |
| freshwater eutrophication:FEP (kg P-Eq) | 0,000683085 | 4,78E-08 | 9,18699E-05 | 2,20E-09 | 0,000148001 | 9,32E-07 | 9,82E-07 |
| human toxicity:HTPinf (kg 1,4-DC.) | 0,95332167 | 6,67E-05 | 0,072257643 | 1,73E-06 | 0,1556088 | 9,80E-04 | 1,05E-03 |
| ionising radiation:IRP_HE (kg U235-Eq) | 0,2344345 | 1,64E-05 | 0,048056753 | 1,15E-06 | 0,20320668 | 1,28E-03 | 1,30E-03 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 0,036092783 | 2,53E-06 | 0,00456612 | 1,10E-07 | 0,019239411 | 1,21E-04 | 1,24E-04 |
| marine eutrophication:MEP (kg N-Eq) | 0,00083788 | 5,87E-08 | 8,92181E-05 | 2,14E-09 | 0,000530836 | 3,34E-06 | 3,41E-06 |
| metal depletion:MDP (kg Fe-Eq) | 0,1840683 | 1,29E-05 | 0,0057471 | 1,38E-07 | 0,016650484 | 1,05E-04 | 1,18E-04 |
| natural land transformation:NLTP (m2) | 0,000124644 | 8,73E-09 | 9,80353E-06 | 2,35E-10 | 5,88219E-05 | 3,71E-07 | 3,80E-07 |
| ozone depletion:ODPinf (kg CFC-11.) | 4,73487E-07 | 3,31E-11 | 1,18388E-08 | 2,84E-13 | 6,41326E-08 | 4,04E-10 | 4,37E-10 |
| particulate matter formation:PMFP (kg PM10-Eq) | 0,001714527 | 1,20E-07 | 0,000152151 | 3,65E-09 | 0,001026994 | 6,47E-06 | 6,59E-06 |
| photochemical oxidant formation:POFP (kg NMVOC) | 0,002169576 | 1,52E-07 | 0,000216377 | 5,19E-09 | 0,001527486 | 9,62E-06 | 9,78E-06 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 0,003900423 | 2,73E-07 | 0,000441955 | 1,06E-08 | 0,002915916 | 1,84E-05 | 1,87E-05 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 0,000118687 | 8,31E-09 | 9,42486E-06 | 2,26E-10 | 3,09778E-05 | 1,95E-07 | 2,04E-07 |
| urban land occupation:ULOP (m2a) | 0,012916914 | 9,04E-07 | 0,000635667 | 1,53E-08 | 0,003393926 | 2,14E-05 | 2,23E-05 |
| water depletion:WDP (m3) | 0,005188625 | 3,63E-07 | 0,000632947 | 1,52E-08 | 0,002089115 | 1,32E-05 | 1,35E-05 |

| b) | Incineration Iron sludge+ O&G: 122,3 E-06 Kg | | Phenol 0,5 E-06 Kg | | Toluene 10 E-06 Kg | | Xylene 10 E-06 Kg | | Naphthalene 3 E-06 Kg | | OUTPUTS SUM |
|---|---|---|---|---|---|---|---|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 0,24075018 | 2,94E-05 | | | | | | | | | 2,94E-05 |
| climate change:GWP100 (kg CO2-Eq) | 2,8889828 | 3,53E-04 | | | | | | | | | 3,53E-04 |
| fossil depletion:FDP (kg oil-Eq) | 0,53354981 | 6,53E-05 | | | | | | | | | 6,53E-05 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 0,02533157 | 3,10E-06 | 2,1E-03 | 1,03E-08 | 1,2E-05 | 1,18E-10 | 2,7E-05 | 2,75E-10 | 6,0E-04 | 1,80E-09 | 3,11E-06 |
| freshwater eutrophication:FEP (kg P-Eq) | 0,0009831 | 1,20E-07 | | | | | | | | | 1,20E-07 |
| human toxicity:HTPinf (kg 1,4-DC.) | 0,85556333 | 1,05E-04 | 9,3E-01 | 4,63E-06 | 8,2E-01 | 8,20E-06 | | | 8,2E+00 | 2,45E-05 | 1,42E-04 |
| ionising radiation:IRP_HE (kg U235-Eq) | 0,02956685 | 3,62E-06 | | | | | | | | | 3,62E-06 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 0,02487669 | 3,04E-06 | 2,7E-04 | 1,35E-09 | 9,1E-05 | 9,07E-10 | 4,0E-04 | 4,04E-09 | 3,0E-03 | 8,89E-09 | 3,06E-06 |
| marine eutrophication:MEP (kg N-Eq) | 0,0011326 | 1,39E-07 | | | | | | | | | 1,39E-07 |
| metal depletion:MDP (kg Fe-Eq) | 0,01956331 | 2,39E-06 | | | | | | | | | 2,39E-06 |
| natural land transformation:NLTP (m2) | 0,00027883 | 3,41E-08 | | | | | | | | | 3,41E-08 |
| ozone depletion:ODPinf (kg CFC-11.) | 5,5918E-08 | 6,84E-12 | | | | | | | | | 6,84E-12 |
| particulate matter formation:PMFP (kg PM10-Eq) | 0,00360465 | 4,41E-07 | | | | | | | | | 4,41E-07 |
| photochemical oxidant formation:POFP (kg NMVOC | 0,01198468 | 1,47E-06 | | | 1,076 | 1,08E-05 | 1,779 | 1,78E-05 | | | 3,00E-05 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 0,011294 | 1,38E-06 | | | | | | | | | 1,38E-06 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 0,00011478 | 1,40E-08 | 7,4E-03 | 3,68E-08 | 1,4E-05 | 1,35E-10 | 2,9E-05 | 2,88E-10 | 3,8E-04 | 1,14E-09 | 5,24E-08 |
| urban land occupation:ULOP (m2a) | 0,02598317 | 3,18E-06 | | | | | | | | | 3,18E-06 |
| water depletion:WDP (m3) | 0,00690007 | 8,44E-07 | | | | | | | | | 8,44E-07 |

Table 7.2. Inventory analysis and impacts of E-DAF process in PW taking into account a) the inputs, and b) the outputs

a)

| ReCiPe Midpoint (H) | $FeCl_3$: 57,9 E-06 Kg | | Microsph.:300 E-06 Kg (glass fibres) | | Electricity JarTester + agitation: 0,0054 KW h | | INPUTS SUM |
|---|---|---|---|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 0,11436297 | 6,62E-06 | 0,096712321 | 2,90E-05 | 0,03970402 | 2,13E-04 | 2,48E-04 |
| climate change:GWP100 (kg CO2-Eq) | 0,72205366 | 4,18E-05 | 2,3230982 | 6,97E-04 | 0,46997944 | 2,52E-03 | 3,26E-03 |
| fossil depletion:FDP (kg oil-Eq) | 0,19880927 | 1,15E-05 | 0,69985402 | 2,10E-04 | 0,14099153 | 7,55E-04 | 9,76E-04 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 0,038777457 | 2,25E-06 | 0,027115198 | 8,13E-06 | 0,021929677 | 1,17E-04 | 1,28E-04 |
| freshwater eutrophication:FEP (kg P-Eq) | 0,000683085 | 3,96E-08 | 0,000849866 | 2,55E-07 | 0,000148001 | 7,93E-07 | 1,09E-06 |
| human toxicity:HTPinf (kg 1,4-DC.) | 0,95332167 | 5,52E-05 | 2,3559994 | 7,07E-04 | 0,1556088 | 8,33E-04 | 1,60E-03 |
| ionising radiation:IRP_HE (kg U235-Eq) | 0,2344345 | 1,36E-05 | 0,29329396 | 8,80E-05 | 0,20320668 | 1,09E-03 | 1,19E-03 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 0,036092783 | 2,09E-06 | 0,025466687 | 7,64E-06 | 0,019239411 | 1,03E-04 | 1,13E-04 |
| marine eutrophication:MEP (kg N-Eq) | 0,00083788 | 4,85E-08 | 0,003792168 | 1,14E-06 | 0,000530836 | 2,84E-06 | 4,03E-06 |
| metal depletion:MDP (kg Fe-Eq) | 0,1840683 | 1,07E-05 | 0,18305457 | 5,49E-05 | 0,016650484 | 8,92E-05 | 1,55E-04 |
| natural land transformation:NLTP (m2) | 0,000124644 | 7,22E-09 | 0,000346466 | 1,04E-07 | 5,88219E-05 | 3,15E-07 | 4,26E-07 |
| ozone depletion:ODPinf (kg CFC-11.) | 4,73487E-07 | 2,74E-11 | 1,80987E-07 | 5,43E-11 | 6,41326E-08 | 3,43E-10 | 4,25E-10 |
| particulate matter formation:PMFP (kg PM10-Eq) | 0,001714527 | 9,93E-08 | 0,007109178 | 2,13E-06 | 0,001026994 | 5,50E-06 | 7,73E-06 |
| photochemical oxidant formation:POFP (kg NMVOC) | 0,002169576 | 1,26E-07 | 0,011010132 | 3,30E-06 | 0,001527486 | 8,18E-06 | 1,16E-05 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 0,003900423 | 2,26E-07 | 0,01544362 | 4,63E-06 | 0,002915916 | 1,56E-05 | 2,05E-05 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 0,000118687 | 6,87E-09 | 0,000309236 | 9,28E-08 | 3,09778E-05 | 1,66E-07 | 2,66E-07 |
| urban land occupation:ULOP (m2a) | 0,012916914 | 7,48E-07 | 0,020892981 | 6,27E-06 | 0,003393926 | 1,82E-05 | 2,52E-05 |
| water depletion:WDP (m3) | 0,005188625 | 3,00E-07 | 0,017878049 | 5,36E-06 | 0,002089115 | 1,12E-05 | 1,69E-05 |

b)

| | Incineration Iron sludge+ O&G: 177,7 E-06 Kg | | Phenol 0,5 E-06 Kg | | Toluene 10 E-06 Kg | | Xylene 10 E-06 Kg | | Naphthalene 3 E-06 Kg | | OUTPUTS SUM |
|---|---|---|---|---|---|---|---|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 0,24075018 | 4,28E-05 | | | | | | | | | 4,28E-05 |
| climate change:GWP100 (kg CO2-Eq) | 2,8889828 | 5,13E-04 | | | | | | | | | 5,13E-04 |
| fossil depletion:FDP (kg oil-Eq) | 0,53354981 | 9,48E-05 | | | | | | | | | 9,48E-05 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 0,02533157 | 4,50E-06 | 2,1E-03 | 1,03E-08 | 1,2E-05 | 1,18E-10 | 2,7E-05 | 2,75E-10 | 6,0E-04 | 1,80E-09 | 4,51E-06 |
| freshwater eutrophication:FEP (kg P-Eq) | 0,0009831 | 1,75E-07 | | | | | | | | | 1,75E-07 |
| human toxicity:HTPinf (kg 1,4-DC.) | 0,85556333 | 1,52E-04 | 9,3E-01 | 4,63E-06 | 8,2E-01 | 8,20E-06 | | | 8,2E+00 | 2,45E-05 | 1,89E-04 |
| ionising radiation:IRP_HE (kg U235-Eq) | 0,02956685 | 5,25E-06 | | | | | | | | | 5,25E-06 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 0,02487669 | 4,42E-06 | 2,7E-04 | 1,35E-09 | 9,1E-05 | 9,07E-10 | 4,0E-04 | 4,04E-09 | 3,0E-03 | 8,89E-09 | 4,44E-06 |
| marine eutrophication:MEP (kg N-Eq) | 0,0011326 | 2,01E-07 | | | | | | | | | 2,01E-07 |
| metal depletion:MDP (kg Fe-Eq) | 0,01956331 | 3,48E-06 | | | | | | | | | 3,48E-06 |
| natural land transformation:NLTP (m2) | 0,00027883 | 4,95E-08 | | | | | | | | | 4,95E-08 |
| ozone depletion:ODPinf (kg CFC-11.) | 5,5918E-08 | 9,94E-12 | | | | | | | | | 9,94E-12 |
| particulate matter formation:PMFP (kg PM10-Eq) | 0,00360465 | 6,41E-07 | | | | | | | | | 6,41E-07 |
| photochemical oxidant formation:POFP (kg NMVOC | 0,01198468 | 2,13E-06 | | | 1,076 | 1,08E-05 | 1,779 | 1,78E-05 | | | 3,07E-05 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 0,011294 | 2,01E-06 | | | | | | | | | 2,01E-06 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 0,00011478 | 2,04E-08 | 7,4E-03 | 3,68E-08 | 1,4E-05 | 1,35E-10 | 2,9E-05 | 2,88E-10 | 3,8E-04 | 1,14E-09 | 5,87E-08 |
| urban land occupation:ULOP (m2a) | 0,02598317 | 4,62E-06 | | | | | | | | | 4,62E-06 |
| water depletion:WDP (m3) | 0,00690007 | 1,23E-06 | | | | | | | | | 1,23E-06 |

Table 7.3. Inventory analysis and impacts of settling process in PW taking into account a) the inputs, and b) the outputs

a)

| ReCiPe Midpoint (H) | $FeCl_3$: 86 E-06 Kg | | Electricity JarTester + agitation: 0,0063 KW h | | INPUTS SUM |
|---|---|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 0,11436297 | 9,84E-06 | 0,03970402 | 2,50E-04 | 2,60E-04 |
| climate change:GWP100 (kg CO2-Eq) | 0,72205366 | 6,21E-05 | 0,46997944 | 2,96E-03 | 3,02E-03 |
| fossil depletion:FDP (kg oil-Eq) | 0,19880927 | 1,71E-05 | 0,14099153 | 8,88E-04 | 9,05E-04 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 0,038777457 | 3,33E-06 | 0,021929677 | 1,38E-04 | 1,41E-04 |
| freshwater eutrophication:FEP (kg P-Eq) | 0,000683085 | 5,87E-08 | 0,000148001 | 9,32E-07 | 9,91E-07 |
| human toxicity:HTPinf (kg 1,4-DC.) | 0,95332167 | 8,20E-05 | 0,1556088 | 9,80E-04 | 1,06E-03 |
| ionising radiation:IRP_HE (kg U235-Eq) | 0,2344345 | 2,02E-05 | 0,20320668 | 1,28E-03 | 1,30E-03 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 0,036092783 | 3,10E-06 | 0,019239411 | 1,21E-04 | 1,24E-04 |
| marine eutrophication:MEP (kg N-Eq) | 0,00083788 | 7,21E-08 | 0,000530836 | 3,34E-06 | 3,42E-06 |
| metal depletion:MDP (kg Fe-Eq) | 0,1840683 | 1,58E-05 | 0,016650484 | 1,05E-04 | 1,21E-04 |
| natural land transformation:NLTP (m2) | 0,000124644 | 1,07E-08 | 5,88219E-05 | 3,71E-07 | 3,81E-07 |
| ozone depletion:ODPinf (kg CFC-11.) | 4,73487E-07 | 4,07E-11 | 6,41326E-08 | 4,04E-10 | 4,45E-10 |
| particulate matter formation:PMFP (kg PM10-Eq) | 0,001714527 | 1,47E-07 | 0,001026994 | 6,47E-06 | 6,62E-06 |
| photochemical oxidant formation:POFP (kg NMVOC) | 0,002169576 | 1,87E-07 | 0,001527486 | 9,62E-06 | 9,81E-06 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 0,003900423 | 3,35E-07 | 0,002915916 | 1,84E-05 | 1,87E-05 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 0,000118687 | 1,02E-08 | 3,09778E-05 | 1,95E-07 | 2,05E-07 |
| urban land occupation:ULOP (m2a) | 0,012916914 | 1,11E-06 | 0,003393926 | 2,14E-05 | 2,25E-05 |
| water depletion:WDP (m3) | 0,005188625 | 4,46E-07 | 0,002089115 | 1,32E-05 | 1,36E-05 |

| b) | Incineration Iron sludge+ O&G: 174,1 E-06 Kg | | Phenol 0,5 E-06 Kg | | Toluene 10 E-06 Kg | | Xylene 10 E-06 Kg | | Naphthalene 3 E-06 Kg | | OUTPUTS SUM |
|---|---|---|---|---|---|---|---|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 0,24075018 | 4,19E-05 | | | | | | | | | 4,19E-05 |
| climate change:GWP100 (kg CO2-Eq) | 2,8889828 | 5,03E-04 | | | | | | | | | 5,03E-04 |
| fossil depletion:FDP (kg oil-Eq) | 0,53354981 | 9,29E-05 | | | | | | | | | 9,29E-05 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 0,02533157 | 4,41E-06 | 2,1E-03 | 1,03E-08 | 1,2E-05 | 1,18E-10 | 2,7E-05 | 2,75E-10 | 6,0E-04 | 1,80E-09 | 4,42E-06 |
| freshwater eutrophication:FEP (kg P-Eq) | 0,0009831 | 1,71E-07 | | | | | | | | | 1,71E-07 |
| human toxicity:HTPinf (kg 1,4-DC.) | 0,85556333 | 1,49E-04 | 9,3E-01 | 4,63E-06 | 8,2E-01 | 8,20E-06 | | | 8,2E+00 | 2,45E-05 | 1,86E-04 |
| ionising radiation:IRP_HE (kg U235-Eq) | 0,02956685 | 5,15E-06 | | | | | | | | | 5,15E-06 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 0,02487669 | 4,33E-06 | 2,7E-04 | 1,35E-09 | 9,1E-05 | 9,07E-10 | 4,0E-04 | 4,04E-09 | 3,0E-03 | 8,89E-09 | 4,35E-06 |
| marine eutrophication:MEP (kg N-Eq) | 0,0011326 | 1,97E-07 | | | | | | | | | 1,97E-07 |
| metal depletion:MDP (kg Fe-Eq) | 0,01956331 | 3,41E-06 | | | | | | | | | 3,41E-06 |
| natural land transformation:NLTP (m2) | 0,00027883 | 4,85E-08 | | | | | | | | | 4,85E-08 |
| ozone depletion:ODPinf (kg CFC-11.) | 5,5918E-08 | 9,74E-12 | | | | | | | | | 9,74E-12 |
| particulate matter formation:PMFP (kg PM10-Eq) | 0,00360465 | 6,28E-07 | | | | | | | | | 6,28E-07 |
| photochemical oxidant formation:POFP (kg NMVOC | 0,01198468 | 2,09E-06 | | | 1,076 | 1,08E-05 | 1,779 | 1,78E-05 | | | 3,06E-05 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 0,011294 | 1,97E-06 | | | | | | | | | 1,97E-06 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 0,00011478 | 2,00E-08 | 7,4E-03 | 3,68E-08 | 1,4E-05 | 1,35E-10 | 2,9E-05 | 2,88E-10 | 3,8E-04 | 1,14E-09 | 5,83E-08 |
| urban land occupation:ULOP (m2a) | 0,02598317 | 4,52E-06 | | | | | | | | | 4,52E-06 |
| water depletion:WDP (m3) | 0,00690007 | 1,20E-06 | | | | | | | | | 1,20E-06 |

Table 7.4. Total impact for each pretreatment of PW and category

| | DAF | E-DAF | SETTLING |
|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 2,88E-04 | 2,91E-04 | 3,02E-04 |
| climate change:GWP100 (kg CO2-Eq) | 3,37E-03 | 3,77E-03 | 3,53E-03 |
| fossil depletion:FDP (kg oil-Eq) | 9,68E-04 | 1,07E-03 | 9,98E-04 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 1,44E-04 | 1,32E-04 | 1,46E-04 |
| freshwater eutrophication:FEP (kg P-Eq) | 1,10E-06 | 1,26E-06 | 1,16E-06 |
| human toxicity:HTPinf (kg 1,4-DC.) | 1,19E-03 | 1,78E-03 | 1,25E-03 |
| ionising radiation:IRP_HE (kg U235-Eq) | 1,30E-03 | 1,19E-03 | 1,31E-03 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 1,27E-04 | 1,17E-04 | 1,29E-04 |
| marine eutrophication:MEP (kg N-Eq) | 3,54E-06 | 4,23E-06 | 3,61E-06 |
| metal depletion:MDP (kg Fe-Eq) | 1,20E-04 | 1,58E-04 | 1,24E-04 |
| natural land transformation:NLTP (m2) | 4,14E-07 | 4,76E-07 | 4,30E-07 |
| ozone depletion:ODPinf (kg CFC-11.) | 4,44E-10 | 4,35E-10 | 4,54E-10 |
| particulate matter formation:PMFP (kg PM10-Eq) | 7,03E-06 | 8,37E-06 | 7,25E-06 |
| photochemical oxidant formation:POFP (kg NMVOC) | 3,98E-05 | 4,23E-05 | 4,04E-05 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 2,00E-05 | 2,25E-05 | 2,07E-05 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 2,56E-07 | 3,24E-07 | 2,64E-07 |
| urban land occupation:ULOP (m2a) | 2,55E-05 | 2,98E-05 | 2,70E-05 |
| water depletion:WDP (m3) | 1,44E-05 | 1,81E-05 | 1,48E-05 |

#### 7.3.1.2. Produced water treatment by advanced oxidation processes

Regarding AOPs that would be carried out after the pretreatment, Table 7.5 (a) shows the inventory analysis and the impact of the photo-Fenton process where the reagents added were 556.75 mg $L^{-1}$ $H_2O_2$, 276.41 mg $L^{-1}$ $FeSO_4 \cdot 7H_2O$ and HCl to acidify until pH 3. In addition, as in previous processes, one of the inputs is the energy consumption, expressed as KW h, corresponding in this case to the 2W agitation plate and the 250 W $m^{-2}$ Solarbox Xenon lamp irradiance that was used in the photo-Fenton process during 90 min. It has been taken into account for the energy consumption of this lamp, that 2 experiments can be performed at a time in the Solarbox. So, for 1 L of PW, the energy consumption corresponding to the agitation is 0.002 KW x 1.5 h= 0.003 KW h, and for the lamp: 0.250

KW $m^{-2}$ x 0.086 $m^2$ x 1.5 h/ 2 experiments= 0.0161 KW h. The total energy consumption is 0.0191 KW h.

For the outputs, 55.7 mg $L^{-1}$ Fe (as iron sludge) and the malonic and acetic acids not eliminated are taken into account (Table 7.5 (b)).

Table 7.6 (a) shows the inventory analysis and the impact of the inputs to carry out 2 photocatalysis experiments in the Solarbox during 310 min, and Table 7.6 (b) the corresponding outputs where $TiO_2$ sludge is generated (which is managed the same as the iron sludge), and malonic and acetic acids remain.

Table 7.7 (a) shows the inventory analysis and the impact of the inputs to carry out the Fenton reaction at 70ºC where the reagents added were 556.75 mg $L^{-1}$ $H_2O_2$, 276.41 mg $L^{-1}$ $FeSO_4{\cdot}7H_2O$ and HCl to acidify to pH 3, and the energy corresponds to the plate that consumes 2W for the agitation and 60W for heating during 2 h. In this process, the outputs obtained were the same than in the photo-Fenton process (Table 7.7 (b)).

Finally, Table 7.8 (a) shows the inventory analysis and the impact of the inputs to carry out the ozonation process with $H_2O_2$ at pH 10. 1500 mg $L^{-1}$ $H_2O_2$, 200 mg NaOH to basify at pH 10 and electricity for the agitation were needed (0.004 KW h for the agitation). The generation of 4 g $h^{-1}$ $O_3$ was produced from 50 L $h^{-1}$ $O_2$ (0.143 Kg $O_2$ required for the 2 h of process) and electricity by the ozone generator (ANSEROS COM-AD-02), that consumed around 10 kW/kg $O_3$ according this manufacturer (10 kW/Kg $O_3$ x 0.004 Kg $O_3$ x 2 h= 0.08 KW h consumed by the ozone generator). There is also a consumption of 5 g potassium iodide (KI) in each experiment, i.e. 3.8 g I, (the trap has a volume of 0.5 L, a concentration of 20 g $L^{-1}$ KI but 2 ozonation experiments can be performed using the same trap) to collect the $O_3$ gas passing through the reactor unreacted (80% of the incoming $O_3$, i.e. 3.2 g $h^{-1}$ $O_3$, since only about a 20% $O_3$ was dissolved in the water). Table 7.8 (b) shows the outputs of the process that were 33.3 mg $L^{-1}$ acetic acid that remained in the treated water.

Table 7.9 shows the total impacts for each AOP which result from adding the inputs and outputs.

As it can be seen, photo-Fenton was the AOP studied that caused less environmental impacts and the AOP that generated the most impacts was Fenton with temperature. Comparing the photo-Fenton process and Fenton at 70ºC where the same doses of reagents were added, the difference was mainly related to the electric consumption, since for the photo-Fenton 0.019 KW h were required, while 1.20 KW h were required for Fenton process, due to the consumption of the heating plate for 2 h. For the photo-Fenton process, the lamp consumption was not very high with the advantage that two experiments can be performed at a time inside the solarbox and that the reaction time was 1.5 h.

After photo-Fenton, the treatment that generated the least impact was photocatalysis (although was not completely effective for the PW treatment). The electric consumption was 0.055 KW h because although the solarbox was used as in the photo-Fenton process, photocatalysis required more time (310 min instead of 90 min in photo-Fenton). Comparing Fenton at 70ºC and ozonation, the environmental impacts were higher in all categories in Fenton than in the treatment with ozone/$H_2O_2$, with more differences in the following categories: fossil depletion, freshwater ecotoxicity, human toxicity, ionizing radiation, marine ecotoxicity, metal depletion, particulate matter formation, photochemical oxidant formation, terrestrial acidification and water depletion. In the ozonation, total electric consumption was 0.084 KW h and the consumption of $O_2$ was what generated the highest impacts (50 L $h^{-1}$).

Table 7.5. Inventory analysis and impacts of photo-Fenton process in PW taking into account a) the inputs, and b) the outputs

a) **PHOTO-FENTON**

| **ReCiPe Midpoint (H)** | **$H_2O_2$: 556,75 E-06 Kg** | | **$FeSO_4$*$7H_2O$: 276,41 E-06 Kg (FeSO4: 151,1 E-06 Kg)** | | **HCl: 20 µL** | | **Electricity: Agitation 0,003 KWh Lamp 0,0161 KWh** | | **INPUTS SUM** |
|---|---|---|---|---|---|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 0,063414189 | 3,53E-05 | 0,026872774 | 4,06E-06 | 0,064209959 | 1,28E-08 | 0,03970402 | 7,58E-04 | 7,98E-04 |
| climate change:GWP100 (kg CO2-Eq) | 1,1423356 | 6,36E-04 | 0,26060464 | 3,94E-05 | 0,50430928 | 1,01E-07 | 0,46997944 | 8,98E-03 | 9,65E-03 |
| fossil depletion:FDP (kg oil-Eq) | 0,41260208 | 2,30E-04 | 0,072955402 | 1,10E-05 | 0,19146189 | 3,83E-08 | 0,14099153 | 2,69E-03 | 2,93E-03 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 0,037654205 | 2,10E-05 | 0,010686618 | 1,61E-06 | 0,014622691 | 2,92E-09 | 0,021929677 | 4,19E-04 | 4,41E-04 |
| freshwater eutrophication:FEP (kg P-Eq) | 0,000447069 | 2,49E-07 | 0,000190388 | 2,88E-08 | 0,000356328 | 7,13E-11 | 0,000148001 | 2,83E-06 | 3,10E-06 |
| human toxicity:HTPinf (kg 1,4-DC.) | 0,49946072 | 2,78E-04 | 0,24566418 | 3,71E-05 | 0,54405679 | 1,09E-07 | 0,1556088 | 2,97E-03 | 3,29E-03 |
| ionising radiation:IRP_HE (kg U235-Eq) | 0,12958364 | 7,21E-05 | 0,046500058 | 7,03E-06 | 0,14449425 | 2,89E-08 | 0,20320668 | 3,88E-03 | 3,96E-03 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 0,034833942 | 1,94E-05 | 0,010032565 | 1,52E-06 | 0,015538406 | 3,11E-09 | 0,019239411 | 3,67E-04 | 3,88E-04 |
| marine eutrophication:MEP (kg N-Eq) | 0,001111767 | 6,19E-07 | 0,000354052 | 5,35E-08 | 0,000601743 | 1,20E-10 | 0,000530836 | 1,01E-05 | 1,08E-05 |
| metal depletion:MDP (kg Fe-Eq) | 0,084310195 | 4,69E-05 | 0,054964385 | 8,31E-06 | 0,062444013 | 1,25E-08 | 0,016650484 | 3,18E-04 | 3,73E-04 |
| natural land transformation:NLTP (m2) | 0,000152537 | 8,49E-08 | 5,0931E-05 | 7,70E-09 | 8,46004E-05 | 1,69E-11 | 5,88219E-05 | 1,12E-06 | 1,22E-06 |
| ozone depletion:ODPinf (kg CFC-11.) | 1,092E-07 | 6,08E-11 | 2,56413E-08 | 3,87E-12 | 2,55444E-07 | 5,11E-14 | 6,41326E-08 | 1,22E-09 | 1,29E-09 |
| particulate matter formation:PMFP (kg PM10-Eq) | 0,002299229 | 1,28E-06 | 0,000827292 | 1,25E-07 | 0,001105543 | 2,21E-10 | 0,001026994 | 1,96E-05 | 2,10E-05 |
| photochemical oxidant formation:POFP (kg NMVOC) | 0,00349058 | 1,94E-06 | 0,001005159 | 1,52E-07 | 0,001685695 | 3,37E-10 | 0,001527486 | 2,92E-05 | 3,13E-05 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 0,004701736 | 2,62E-06 | 0,001500081 | 2,27E-07 | 0,002907428 | 5,81E-10 | 0,002915916 | 5,57E-05 | 5,85E-05 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 7,41005E-05 | 4,13E-08 | 3,6858E-05 | 5,57E-09 | 0,000297583 | 5,95E-11 | 3,09778E-05 | 5,92E-07 | 6,39E-07 |
| urban land occupation:ULOP (m2a) | 0,009500703 | 5,29E-06 | 0,005849213 | 8,84E-07 | 0,008062482 | 1,61E-09 | 0,003393926 | 6,48E-05 | 7,10E-05 |
| water depletion:WDP (m3) | 0,005372 | 2,99E-06 | 0,001029333 | 1,56E-07 | 0,002276097 | 4,55E-10 | 0,002089115 | 3,99E-05 | 4,30E-05 |

b)

| | **Incineration Iron sludge 55,7 E-06 Kg Fe** | | **Malonic acid 1,1 E-06 Kg** | | **Acetic acid 150 E-06 Kg** | | **OUTPUTS SUM** |
|---|---|---|---|---|---|---|---|
| **agricultural land occupation:ALOP (m2a)** | 0,24075018 | **1,34E-05** | | | | | **1,34E-05** |
| **climate change:GWP100 (kg CO2-Eq)** | 2,8889828 | **1,61E-04** | | | | | **1,61E-04** |
| **fossil depletion:FDP (kg oil-Eq)** | 0,53354981 | **2,97E-05** | | | | | **2,97E-05** |
| **freshwater ecotoxicity:FETPinf (kg 1,4-DC.)** | 0,02533157 | **1,41E-06** | 2,8E-10 | **3,10E-16** | 3,4E-07 | **5,08E-11** | **1,41E-06** |
| **freshwater eutrophication:FEP (kg P-Eq)** | 0,0009831 | **5,48E-08** | | | | | **5,48E-08** |
| **human toxicity:HTPinf (kg 1,4-DC.)** | 0,85556333 | **4,77E-05** | | | | | **4,77E-05** |
| **ionising radiation:IRP_HE (kg U235-Eq)** | 0,02956685 | **1,65E-06** | | | | | **1,65E-06** |
| **marine ecotoxicity:METPinf (kg 1,4-DC.)** | 0,02487669 | **1,39E-06** | 1,9E-03 | **2,13E-09** | 3,0E-03 | **4,53E-07** | **1,84E-06** |
| **marine eutrophication:MEP (kg N-Eq)** | 0,0011326 | **6,31E-08** | | | | | **6,31E-08** |
| **metal depletion:MDP (kg Fe-Eq)** | 0,01956331 | **1,09E-06** | | | | | **1,09E-06** |
| **natural land transformation:NLTP (m2)** | 0,00027883 | **1,55E-08** | | | | | **1,55E-08** |
| **ozone depletion:ODPinf (kg CFC-11.)** | 5,5918E-08 | **3,11E-12** | | | | | **3,11E-12** |
| **particulate matter formation:PMFP (kg PM10-Eq)** | 0,00360465 | **2,01E-07** | | | | | **2,01E-07** |
| **photochemical oxidant formation:POFP (kg NMVOC** | 0,01198468 | **6,68E-07** | | | | | **6,68E-07** |
| **terrestrial acidification:TAP100 (kg SO2-Eq)** | 0,011294 | **6,29E-07** | | | | | **6,29E-07** |
| **terrestrial ecotoxicity:TETPinf (kg 1,4-DC.)** | 0,00011478 | **6,39E-09** | 6,4E-09 | **7,05E-15** | 6,2E-06 | **9,28E-10** | **7,32E-09** |
| **urban land occupation:ULOP (m2a)** | 0,02598317 | **1,45E-06** | | | | | **1,45E-06** |
| **water depletion:WDP (m3)** | 0,00690007 | **3,84E-07** | | | | | **3,84E-07** |

Table 7.6. Inventory analysis and impacts of photocatalysis process in PW taking into account a) the inputs, and b) the outputs

a) **PHOTOCATALYSIS**

| **ReCiPe Midpoint (H)** | **$TiO_2$ (P25): 500 E-06 Kg** | | **Electricity: Agitation 0,0103 KWh Lamp 0,0444 KWh** | | **INPUTS SUM** |
|---|---|---|---|---|---|
| **agricultural land occupation:ALOP (m2a)** | 0,82203681 | **4,11E-04** | 0,03970402 | **2,17E-03** | **2,58E-03** |
| **climate change:GWP100 (kg CO2-Eq)** | 5,5751215 | **2,79E-03** | 0,46997944 | **2,57E-02** | **2,85E-02** |
| **fossil depletion:FDP (kg oil-Eq)** | 1,5261742 | **7,63E-04** | 0,14099153 | **7,71E-03** | **8,48E-03** |
| **freshwater ecotoxicity:FETPinf (kg 1,4-DC.)** | 0,14440837 | **7,22E-05** | 0,021929677 | **1,20E-03** | **1,27E-03** |
| **freshwater eutrophication:FEP (kg P-Eq)** | 0,002510952 | **1,26E-06** | 0,000148001 | **8,10E-06** | **9,35E-06** |
| **human toxicity:HTPinf (kg 1,4-DC.)** | 2,8028348 | **1,40E-03** | 0,1556088 | **8,51E-03** | **9,91E-03** |
| **ionising radiation:IRP_HE (kg U235-Eq)** | 0,67947599 | **3,40E-04** | 0,20320668 | **1,11E-02** | **1,15E-02** |
| **marine ecotoxicity:METPinf (kg 1,4-DC.)** | 0,13697459 | **6,85E-05** | 0,019239411 | **1,05E-03** | **1,12E-03** |
| **marine eutrophication:MEP (kg N-Eq)** | 0,007004917 | **3,50E-06** | 0,000530836 | **2,90E-05** | **3,25E-05** |
| **metal depletion:MDP (kg Fe-Eq)** | 0,38089 | **1,90E-04** | 0,016650484 | **9,11E-04** | **1,10E-03** |
| **natural land transformation:NLTP (m2)** | 0,001331737 | **6,66E-07** | 5,88219E-05 | **3,22E-06** | **3,88E-06** |
| **ozone depletion:ODPinf (kg CFC-11.)** | 7,26506E-07 | **3,63E-10** | 6,41326E-08 | **3,51E-09** | **3,87E-09** |
| **particulate matter formation:PMFP (kg PM10-Eq)** | 0,01690367 | **8,45E-06** | 0,001026994 | **5,62E-05** | **6,46E-05** |
| **photochemical oxidant formation:POFP (kg NMVOC)** | 0,022027459 | **1,10E-05** | 0,001527486 | **8,36E-05** | **9,46E-05** |
| **terrestrial acidification:TAP100 (kg SO2-Eq)** | 0,056581749 | **2,83E-05** | 0,002915916 | **1,60E-04** | **1,88E-04** |
| **terrestrial ecotoxicity:TETPinf (kg 1,4-DC.)** | 0,00064682 | **3,23E-07** | 3,09778E-05 | **1,69E-06** | **2,02E-06** |
| **urban land occupation:ULOP (m2a)** | 0,09591767 | **4,80E-05** | 0,003393926 | **1,86E-04** | **2,34E-04** |
| **water depletion:WDP (m3)** | 0,10868968 | **5,43E-05** | 0,002089115 | **1,14E-04** | **1,69E-04** |

b)

| | Incineration $TiO_2$ sludge 500 E-06 Kg $TiO_2$ | | Malonic acid 1,1 E-06 Kg | | Acetic acid 150 E-06 Kg | | OUTPUTS SUM |
|---|---|---|---|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 0,24075018 | 1,34E-05 | | | | | 1,34E-05 |
| climate change:GWP100 (kg CO2-Eq) | 2,8889828 | 1,61E-04 | | | | | 1,61E-04 |
| fossil depletion:FDP (kg oil-Eq) | 0,53354981 | 2,97E-05 | | | | | 2,97E-05 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 0,02533157 | 1,41E-06 | 2,8E-10 | 3,10E-16 | 3,4E-07 | 5,08E-11 | 1,41E-06 |
| freshwater eutrophication:FEP (kg P-Eq) | 0,0009831 | 5,48E-08 | | | | | 5,48E-08 |
| human toxicity:HTPinf (kg 1,4-DC.) | 0,85556333 | 4,77E-05 | | | | | 4,77E-05 |
| ionising radiation:IRP_HE (kg U235-Eq) | 0,02956685 | 1,65E-06 | | | | | 1,65E-06 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 0,02487669 | 1,39E-06 | 1,9E-03 | 2,13E-09 | 3,0E-03 | 4,53E-07 | 1,84E-06 |
| marine eutrophication:MEP (kg N-Eq) | 0,0011326 | 6,31E-08 | | | | | 6,31E-08 |
| metal depletion:MDP (kg Fe-Eq) | 0,01956331 | 1,09E-06 | | | | | 1,09E-06 |
| natural land transformation:NLTP (m2) | 0,00027883 | 1,55E-08 | | | | | 1,55E-08 |
| ozone depletion:ODPinf (kg CFC-11.) | 5,5918E-08 | 3,11E-12 | | | | | 3,11E-12 |
| particulate matter formation:PMFP (kg PM10-Eq) | 0,00360465 | 2,01E-07 | | | | | 2,01E-07 |
| photochemical oxidant formation:POFP (kg NMVOC | 0,01198468 | 6,68E-07 | | | | | 6,68E-07 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 0,011294 | 6,29E-07 | | | | | 6,29E-07 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 0,00011478 | 6,39E-09 | 6,4E-09 | 7,05E-15 | 6,2E-06 | 9,28E-10 | 7,32E-09 |
| urban land occupation:ULOP (m2a) | 0,02598317 | 1,45E-06 | | | | | 1,45E-06 |
| water depletion:WDP (m3) | 0,00690007 | 3,84E-07 | | | | | 3,84E-07 |

Table 7.7. Inventory analysis and impacts of Fenton at 70ºC in PW taking into account a) the inputs, and b) the outputs

a) **FENTON AT 70ºC**

| ReCiPe Midpoint (H) | $H_2O_2$: 556,75 E-06 Kg | | $FeSO_4*7H_2O$: 276,41 E-06 Kg (FeSO4: 151,1 E-06 Kg) | | HCl: 20 µL | | Electricity: Agitation + heating (70 ºC): total 1,204 KWh | | INPUTS SUM |
|---|---|---|---|---|---|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 0,063414189 | 3,53E-05 | 0,026872774 | 4,06E-06 | 0,064209959 | 1,28E-08 | 0,03970402 | 4,78E-02 | 4,78E-02 |
| climate change:GWP100 (kg CO2-Eq) | 1,1423356 | 6,36E-04 | 0,26060464 | 3,94E-05 | 0,50430928 | 1,01E-07 | 0,46997944 | 5,66E-01 | 5,67E-01 |
| fossil depletion:FDP (kg oil-Eq) | 0,41260208 | 2,30E-04 | 0,072955402 | 1,10E-05 | 0,19146189 | 3,83E-08 | 0,14099153 | 1,70E-01 | 1,70E-01 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 0,037654205 | 2,10E-05 | 0,010686618 | 1,61E-06 | 0,014622691 | 2,92E-09 | 0,021929677 | 2,64E-02 | 2,64E-02 |
| freshwater eutrophication:FEP (kg P-Eq) | 0,000447069 | 2,49E-07 | 0,000190388 | 2,88E-08 | 0,000356328 | 7,13E-11 | 0,000148001 | 1,78E-04 | 1,78E-04 |
| human toxicity:HTPinf (kg 1,4-DC.) | 0,49946072 | 2,78E-04 | 0,24566418 | 3,71E-05 | 0,54405679 | 1,09E-07 | 0,1556088 | 1,87E-01 | 1,88E-01 |
| ionising radiation:IRP_HE (kg U235-Eq) | 0,12958364 | 7,21E-05 | 0,046500058 | 7,03E-06 | 0,14449425 | 2,89E-08 | 0,20320668 | 2,45E-01 | 2,45E-01 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 0,034833942 | 1,94E-05 | 0,010032565 | 1,52E-06 | 0,015538406 | 3,11E-09 | 0,019239411 | 2,32E-02 | 2,32E-02 |
| marine eutrophication:MEP (kg N-Eq) | 0,001111767 | 6,19E-07 | 0,000354052 | 5,35E-08 | 0,000601743 | 1,20E-10 | 0,000530836 | 6,39E-04 | 6,40E-04 |
| metal depletion:MDP (kg Fe-Eq) | 0,084310195 | 4,69E-05 | 0,054964385 | 8,31E-06 | 0,062444013 | 1,25E-08 | 0,016650484 | 2,00E-02 | 2,01E-02 |
| natural land transformation:NLTP (m2) | 0,000152537 | 8,49E-08 | 5,0931E-05 | 7,70E-09 | 8,46004E-05 | 1,69E-11 | 5,88219E-05 | 7,08E-05 | 7,09E-05 |
| ozone depletion:ODPinf (kg CFC-11.) | 1,092E-07 | 6,08E-11 | 2,56413E-08 | 3,87E-12 | 2,55444E-07 | 5,11E-14 | 6,41326E-08 | 7,72E-08 | 7,73E-08 |
| particulate matter formation:PMFP (kg PM10-Eq) | 0,002299229 | 1,28E-06 | 0,000827292 | 1,25E-07 | 0,001105543 | 2,21E-10 | 0,001026994 | 1,24E-03 | 1,24E-03 |
| photochemical oxidant formation:POFP (kg NMVOC) | 0,00349058 | 1,94E-06 | 0,001005159 | 1,52E-07 | 0,001685695 | 3,37E-10 | 0,001527486 | 1,84E-03 | 1,84E-03 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 0,004701736 | 2,62E-06 | 0,001500081 | 2,27E-07 | 0,002907428 | 5,81E-10 | 0,002915916 | 3,51E-03 | 3,51E-03 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 7,41005E-05 | 4,13E-08 | 3,6858E-05 | 5,57E-09 | 0,000297583 | 5,95E-11 | 3,09778E-05 | 3,73E-05 | 3,73E-05 |
| urban land occupation:ULOP (m2a) | 0,009500703 | 5,29E-06 | 0,005849213 | 8,84E-07 | 0,008062482 | 1,61E-09 | 0,003393926 | 4,09E-03 | 4,09E-03 |
| water depletion:WDP (m3) | 0,005372 | 2,99E-06 | 0,001029333 | 1,56E-07 | 0,002276097 | 4,55E-10 | 0,002089115 | 2,52E-03 | 2,52E-03 |

| b) | Incineration Iron sludge 55,7 E-06 Kg Fe | | Malonic acid 1,1 E-06 Kg | | Acetic acid 150 E-06 Kg | | OUTPUTS SUM |
|---|---|---|---|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 0,24075018 | 1,34E-05 | | | | | 1,34E-05 |
| climate change:GWP100 (kg CO2-Eq) | 2,8889828 | 1,61E-04 | | | | | 1,61E-04 |
| fossil depletion:FDP (kg oil-Eq) | 0,53354981 | 2,97E-05 | | | | | 2,97E-05 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 0,02533157 | 1,41E-06 | 2,8E-10 | 3,10E-16 | 3,4E-07 | 5,08E-11 | 1,41E-06 |
| freshwater eutrophication:FEP (kg P-Eq) | 0,0009831 | 5,48E-08 | | | | | 5,48E-08 |
| human toxicity:HTPinf (kg 1,4-DC.) | 0,85556333 | 4,77E-05 | | | | | 4,77E-05 |
| ionising radiation:IRP_HE (kg U235-Eq) | 0,02956685 | 1,65E-06 | | | | | 1,65E-06 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 0,02487669 | 1,39E-06 | 1,9E-03 | 2,13E-09 | 3,0E-03 | 4,53E-07 | 1,84E-06 |
| marine eutrophication:MEP (kg N-Eq) | 0,0011326 | 6,31E-08 | | | | | 6,31E-08 |
| metal depletion:MDP (kg Fe-Eq) | 0,01956331 | 1,09E-06 | | | | | 1,09E-06 |
| natural land transformation:NLTP (m2) | 0,00027883 | 1,55E-08 | | | | | 1,55E-08 |
| ozone depletion:ODPinf (kg CFC-11.) | 5,5918E-08 | 3,11E-12 | | | | | 3,11E-12 |
| particulate matter formation:PMFP (kg PM10-Eq) | 0,00360465 | 2,01E-07 | | | | | 2,01E-07 |
| photochemical oxidant formation:POFP (kg NMVOC | 0,01198468 | 6,68E-07 | | | | | 6,68E-07 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 0,011294 | 6,29E-07 | | | | | 6,29E-07 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 0,00011478 | 6,39E-09 | 6,4E-09 | 7,05E-15 | 6,2E-06 | 9,28E-10 | 7,32E-09 |
| urban land occupation:ULOP (m2a) | 0,02598317 | 1,45E-06 | | | | | 1,45E-06 |
| water depletion:WDP (m3) | 0,00690007 | 3,84E-07 | | | | | 3,84E-07 |

Table 7.8. Inventory analysis and impacts of ozonation process in PW taking into account a) the inputs, and b) the outputs

a) **OZONATION**

| **ReCiPe Midpoint (H)** | **$H_2O_2$: 1500 E-06 Kg** | | **$O_2$: 50L/h (0,143 Kg)** | | **Electricity: Agitation (0,004KWh)+ $O_3$ (0,08KWh). Total 0,084 KWh** | | **NaOH 0.0002 Kg** | | **potassium iodide trap 3,8 E-03 Kg I** | | **INPUTS SUM** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 0,063414189 | 9,51E-05 | 0,096304591 | 1,37E-02 | 0,03970402 | 3,34E-03 | 0,091499067 | 1,83E-05 | 0,10205656 | 3,88E-04 | 1,76E-02 |
| climate change:GWP100 (kg CO2-Eq) | 1,1423356 | 1,71E-03 | 0,6739925 | 9,62E-02 | 0,46997944 | 3,95E-02 | 1,181576 | 2,36E-04 | 4,614206 | 1,75E-02 | 1,55E-01 |
| fossil depletion:FDP (kg oil-Eq) | 0,41260208 | 6,19E-04 | 0,19191845 | 2,74E-02 | 0,14099153 | 1,18E-02 | 0,31473342 | 6,29E-05 | 1,4013006 | 5,32E-03 | 4,52E-02 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 0,037654205 | 5,65E-05 | 0,014205316 | 2,03E-03 | 0,021929677 | 1,84E-03 | 0,024652914 | 4,93E-06 | 0,037742722 | 1,43E-04 | 4,07E-03 |
| freshwater eutrophication:FEP (kg P-Eq) | 0,000447069 | 6,71E-07 | 0,000587465 | 8,38E-05 | 0,000148001 | 1,24E-05 | 0,000697654 | 1,40E-07 | 0,001102676 | 4,19E-06 | 1,01E-04 |
| human toxicity:HTPinf (kg 1,4-DC.) | 0,49946072 | 7,49E-04 | 0,41488327 | 5,92E-02 | 0,1556088 | 1,31E-02 | 0,71296281 | 1,43E-04 | 1,1750045 | 4,47E-03 | 7,76E-02 |
| ionising radiation:IRP_HE (kg U235-Eq) | 0,12958364 | 1,94E-04 | 0,33204307 | 4,74E-02 | 0,20320668 | 1,71E-02 | 0,20200255 | 4,04E-05 | 0,31097054 | 1,18E-03 | 6,59E-02 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 0,034833942 | 5,23E-05 | 0,013270735 | 1,89E-03 | 0,019239411 | 1,62E-03 | 0,022713639 | 4,54E-06 | 0,037466164 | 1,42E-04 | 3,71E-03 |
| marine eutrophication:MEP (kg N-Eq) | 0,001111767 | 1,67E-06 | 0,000596723 | 8,52E-05 | 0,000530836 | 4,46E-05 | 0,001364216 | 2,73E-07 | 0,003153755 | 1,20E-05 | 1,44E-04 |
| metal depletion:MDP (kg Fe-Eq) | 0,084310195 | 1,26E-04 | 0,01764147 | 2,52E-03 | 0,016650484 | 1,40E-03 | 0,077750756 | 1,56E-05 | 0,11802781 | 4,49E-04 | 4,51E-03 |
| natural land transformation:NLTP (m2) | 0,000152537 | 2,29E-07 | 6,76771E-05 | 9,66E-06 | 5,88219E-05 | 4,94E-06 | 0,000151302 | 3,03E-08 | 0,000851302 | 3,23E-06 | 1,81E-05 |
| ozone depletion:ODPinf (kg CFC-11.) | 1,092E-07 | 1,64E-10 | 7,86488E-08 | 1,12E-08 | 6,41326E-08 | 5,39E-09 | 6,53186E-07 | 1,31E-10 | 8,10017E-07 | 3,08E-09 | 2,00E-08 |
| particulate matter formation:PMFP (kg PM10-Eq) | 0,002299229 | 3,45E-06 | 0,000968812 | 1,38E-04 | 0,001026994 | 8,63E-05 | 0,003582783 | 7,17E-07 | 0,007306354 | 2,78E-05 | 2,56E-04 |
| photochemical oxidant formation:POFP (kg NMVOC) | 0,00349058 | 5,24E-06 | 0,001440385 | 2,06E-04 | 0,001527486 | 1,28E-04 | 0,00351137 | 7,02E-07 | 0,009934886 | 3,78E-05 | 3,78E-04 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 0,004701736 | 7,05E-06 | 0,002863532 | 4,09E-04 | 0,002915916 | 2,45E-04 | 0,00633309 | 1,27E-06 | 0,018476657 | 7,02E-05 | 7,32E-04 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 7,41005E-05 | 1,11E-07 | 5,13765E-05 | 7,33E-06 | 3,09778E-05 | 2,60E-06 | 0,000109197 | 2,18E-08 | 0,000560539 | 2,13E-06 | 1,22E-05 |
| urban land occupation:ULOP (m2a) | 0,009500703 | 1,43E-05 | 0,004093125 | 5,84E-04 | 0,003393926 | 2,85E-04 | 0,013763692 | 2,75E-06 | 0,024587149 | 9,34E-05 | 9,80E-04 |
| water depletion:WDP (m3) | 0,005372 | 8,06E-06 | 0,004282286 | 6,11E-04 | 0,002089115 | 1,75E-04 | 0,004611826 | 9,22E-07 | 0,008935897 | 3,40E-05 | 8,30E-04 |

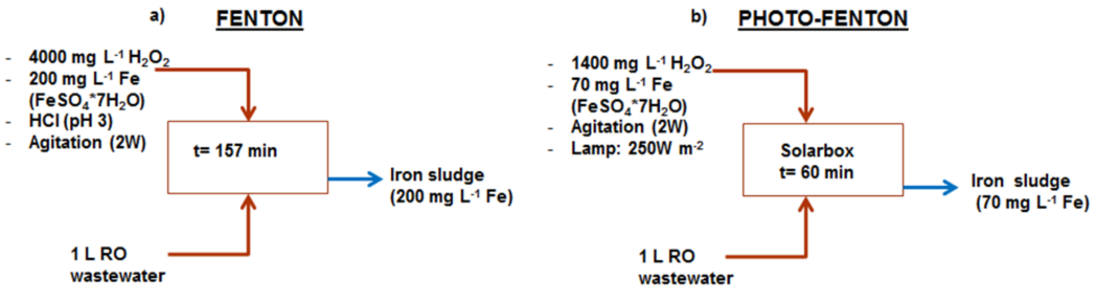
| b) | Acetic acid 33,3 E-06 Kg | | OUTPUTS SUM |
|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | | | |
| climate change:GWP100 (kg CO2-Eq) | | | |
| fossil depletion:FDP (kg oil-Eq) | | | |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 3,4E-07 | 1,13E-11 | 1,10E-11 |
| freshwater eutrophication:FEP (kg P-Eq) | | | |
| human toxicity:HTPinf (kg 1,4-DC.) | | | |
| ionising radiation:IRP_HE (kg U235-Eq) | | | |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 3,0E-03 | 1,01E-07 | 1,00E-07 |
| marine eutrophication:MEP (kg N-Eq) | | | |
| metal depletion:MDP (kg Fe-Eq) | | | |
| natural land transformation:NLTP (m2) | | | |
| ozone depletion:ODPinf (kg CFC-11.) | | | |
| particulate matter formation:PMFP (kg PM10-Eq) | | | |
| photochemical oxidant formation:POFP (kg NMVOC) | | | |
| terrestrial acidification:TAP100 (kg SO2-Eq) | | | |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 6,2E-06 | 2,06E-10 | 2,10E-10 |
| urban land occupation:ULOP (m2a) | | | |
| water depletion:WDP (m3) | | | |

Table 7.9. Total impact of each AOP for PW treatment and category

| | PHOTO-FENTON | PHOTOCATALISIS | FENTON AT 70ºC | OZONATION |
|---|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 8,11E-04 | 2,60E-03 | 4,79E-02 | 1,76E-02 |
| climate change:GWP100 (kg CO2-Eq) | 9,81E-03 | 2,87E-02 | 5,67E-01 | 1,55E-01 |
| fossil depletion:FDP (kg oil-Eq) | 2,96E-03 | 8,51E-03 | 1,70E-01 | 4,52E-02 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 4,43E-04 | 1,27E-03 | 2,64E-02 | 4,07E-03 |
| freshwater eutrophication:FEP (kg P-Eq) | 3,16E-06 | 9,41E-06 | 1,79E-04 | 1,01E-04 |
| human toxicity:HTPinf (kg 1,4-DC.) | 3,34E-03 | 9,96E-03 | 1,88E-01 | 7,76E-02 |
| ionising radiation:IRP_HE (kg U235-Eq) | 3,96E-03 | 1,15E-02 | 2,45E-01 | 6,59E-02 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 3,90E-04 | 1,12E-03 | 2,32E-02 | 3,71E-03 |
| marine eutrophication:MEP (kg N-Eq) | 1,09E-05 | 3,26E-05 | 6,40E-04 | 1,44E-04 |
| metal depletion:MDP (kg Fe-Eq) | 3,74E-04 | 1,10E-03 | 2,01E-02 | 4,51E-03 |
| natural land transformation:NLTP (m2) | 1,23E-06 | 3,90E-06 | 7,09E-05 | 1,81E-05 |
| ozone depletion:ODPinf (kg CFC-11.) | 1,29E-09 | 3,87E-09 | 7,73E-08 | 2,00E-08 |
| particulate matter formation:PMFP (kg PM10-Eq) | 2,12E-05 | 6,48E-05 | 1,24E-03 | 2,56E-04 |
| photochemical oxidant formation:POFP (kg NMVOC) | 3,19E-05 | 9,52E-05 | 1,84E-03 | 3,78E-04 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 5,92E-05 | 1,88E-04 | 3,51E-03 | 7,32E-04 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 6,46E-07 | 2,03E-06 | 3,74E-05 | 1,22E-05 |
| urban land occupation:ULOP (m2a) | 7,24E-05 | 2,35E-04 | 4,09E-03 | 9,80E-04 |
| water depletion:WDP (m3) | 4,34E-05 | 1,69E-04 | 2,52E-03 | 8,30E-04 |

### 7.3.2. RO membranes cleaning waters

The AOPs applied for the treatment of RO membranes cleaning waters were Fenton, photo-Fenton, photocatalysis and UV-C/$H_2O_2$ (studied in chapters 5 and 6 of this thesis). Figure 7.3 shows the flowcharts of the best conditions obtained for each of these processes, including the inputs and outputs associated. It should be noted that in the outputs, residual TOC that remained after these treatments was not been taken into account since the specific components corresponding to that residual TOC were not identified.



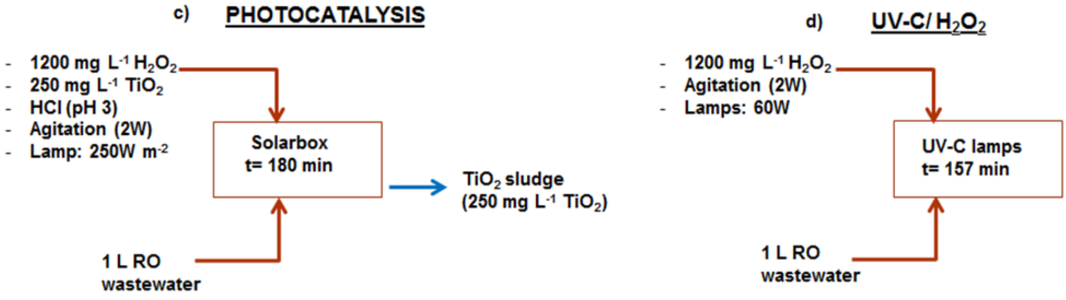


Figure 7.3. Flowcharts of the optimum conditions obtained of the AOPs for the RO membranes cleaning waters: a) Fenton, b) Photo-Fenton c) Photocatalysis and c) UV-C/ $H_2O_2$ for applying the LCA that are the basis for the inventory analysis

Table 7.10 shows the inventory analysis and the impact of the Fenton process applied to the RO membranes cleaning waters. The inputs were 4000 mg $L^{-1}$ $H_2O_2$, 993 mg $L^{-1}$ $FeSO_4{\cdot}7H_2O$, HCl to acidify until pH 3 and electricity for 157 min of agitation (Table 7.10 (a)).

In these processes applied in the RO membranes cleaning waters, the outputs considered were only the iron or $TiO_2$ sludge that was generated (in the case where iron or $TiO_2$ had been added, respectively), since after these treatments, only the final TOC was analyzed and not the components that may remain in the treated water (although the SDS, that was the component of interest, was eliminated).

In the case of Fenton process, the output is 200 mg $L^{-1}$ Fe (as iron sludge) (Table 7.10 (b)).

Table 7.11 (a) shows the inputs for the photo-Fenton process that were 1400 mg $L^{-1}$ $H_2O_2$, 348 mg $L^{-1}$ $FeSO_4{\cdot}7H_2O$, HCl to acidify until pH 3 and electricity for 60 min of agitation and performing 2 experiments using the same lamp radiation at a time. The output will be the 70 mg $L^{-1}$ Fe (sludge) (Table 7.11 (b)).

Table 7.12 (a) presents the inputs for the photocatalysis process that were 1200 mg $L^{-1}$ $H_2O_2$, 250 mg $L^{-1}$ $TiO_2$, HCl to acidify until pH 3 and electricity for 157 min of agitation and carrying out 2 experiments in the Solarbox. The output will be 250 mg $L^{-1}$ $TiO_2$ (7.12 (b)).

Finally, Table 7.13 (a) shows the inventory analysis and the impact for the UV-C/ $H_2O_2$ process where 1200 mg $L^{-1}$ $H_2O_2$ and electricity for 157 min of agitation and for the UV-C lamps consumption. In this process there is not any output.

Table 7.14 shows the total impacts for each AOP applied to RO membranes cleaning waters in each category. Among the AOPs applied in the treatment of RO membranes cleaning waters, Fenton process was the least polluting. In all impact categories the values were lower than in the other treatments, although similar to the photo-Fenton process. In Fenton process the reagents consumption ($H_2O_2$ and Fe) were a little higher than in photo-Fenton (with the consequent higher iron sludge generation), but the electricity consumption was less (0.005 KW h in Fenton process versus 0.013 KW h in photo-Fenton). The AOP that generated the most impacts is UV-C/ $H_2O_2$ due to the lamps energy consumption.

Table 7.10. Inventory analysis and impacts of Fenton process in RO membranes cleaning water taking into account a) the inputs, and b) the outputs

a) **FENTON**

| **ReCiPe Midpoint (H)** | **$H_2O_2$: 4000 E-06 Kg** | | **$FeSO_4$*$7H_2O$: 993 E-06 Kg ($FeSO_4$: 543 E-06 Kg)** | | **HCl: 20 µL** | | **Electricity: Agitation 0,005 KWh** | | **INPUTS SUM** |
|---|---|---|---|---|---|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 0,06341419 | 2,54E-04 | 0,026872774 | 1,46E-05 | 0,064209959 | 1,28E-08 | 0,03970402 | 1,99E-04 | 4,67E-04 |
| climate change:GWP100 (kg CO2-Eq) | 1,1423356 | 4,57E-03 | 0,26060464 | 1,42E-04 | 0,50430928 | 1,01E-07 | 0,46997944 | 2,35E-03 | 7,06E-03 |
| fossil depletion:FDP (kg oil-Eq) | 0,41260208 | 1,65E-03 | 0,072955402 | 3,96E-05 | 0,19146189 | 3,83E-08 | 0,14099153 | 7,05E-04 | 2,40E-03 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 0,03765421 | 1,51E-04 | 0,010686618 | 5,80E-06 | 0,014622691 | 2,92E-09 | 0,02192968 | 1,10E-04 | 2,66E-04 |
| freshwater eutrophication:FEP (kg P-Eq) | 0,00044707 | 1,79E-06 | 0,000190388 | 1,03E-07 | 0,000356328 | 7,13E-11 | 0,000148 | 7,40E-07 | 2,63E-06 |
| human toxicity:HTPinf (kg 1,4-DC.) | 0,49946072 | 2,00E-03 | 0,24566418 | 1,33E-04 | 0,54405679 | 1,09E-07 | 0,1556088 | 7,78E-04 | 2,91E-03 |
| ionising radiation:IRP_HE (kg U235-Eq) | 0,12958364 | 5,18E-04 | 0,046500058 | 2,52E-05 | 0,14449425 | 2,89E-08 | 0,20320668 | 1,02E-03 | 1,56E-03 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 0,03483394 | 1,39E-04 | 0,010032565 | 5,45E-06 | 0,015538406 | 3,11E-09 | 0,01923941 | 9,62E-05 | 2,41E-04 |
| marine eutrophication:MEP (kg N-Eq) | 0,00111177 | 4,45E-06 | 0,000354052 | 1,92E-07 | 0,000601743 | 1,20E-10 | 0,00053084 | 2,65E-06 | 7,29E-06 |
| metal depletion:MDP (kg Fe-Eq) | 0,0843102 | 3,37E-04 | 0,054964385 | 2,98E-05 | 0,062444013 | 1,25E-08 | 0,01665048 | 8,33E-05 | 4,50E-04 |
| natural land transformation:NLTP (m2) | 0,00015254 | 6,10E-07 | 5,0931E-05 | 2,77E-08 | 8,46004E-05 | 1,69E-11 | 5,8822E-05 | 2,94E-07 | 9,32E-07 |
| ozone depletion:ODPinf (kg CFC-11.) | 1,092E-07 | 4,37E-10 | 2,56413E-08 | 1,39E-11 | 2,55444E-07 | 5,11E-14 | 6,4133E-08 | 3,21E-10 | 7,71E-10 |
| particulate matter formation:PMFP (kg PM10-Eq) | 0,00229923 | 9,20E-06 | 0,000827292 | 4,49E-07 | 0,001105543 | 2,21E-10 | 0,00102699 | 5,13E-06 | 1,48E-05 |
| photochemical oxidant formation:POFP (kg NMVOC | 0,00349058 | 1,40E-05 | 0,001005159 | 5,46E-07 | 0,001685695 | 3,37E-10 | 0,00152749 | 7,64E-06 | 2,21E-05 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 0,00470174 | 1,88E-05 | 0,001500081 | 8,15E-07 | 0,002907428 | 5,81E-10 | 0,00291592 | 1,46E-05 | 3,42E-05 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 7,41E-05 | 2,96E-07 | 3,6858E-05 | 2,00E-08 | 0,000297583 | 5,95E-11 | 3,0978E-05 | 1,55E-07 | 4,71E-07 |
| urban land occupation:ULOP (m2a) | 0,0095007 | 3,80E-05 | 0,005849213 | 3,18E-06 | 0,008062482 | 1,61E-09 | 0,00339393 | 1,70E-05 | 5,82E-05 |
| water depletion:WDP (m3) | 0,005372 | 2,15E-05 | 0,001029333 | 5,59E-07 | 0,002276097 | 4,55E-10 | 0,00208911 | 1,04E-05 | 3,25E-05 |

**b)**

| | Incineration Iron sludge 200 E-06 Kg Fe | | OUTPUTS SUM |
|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 0,24075018 | 4,82E-05 | 4,82E-05 |
| climate change:GWP100 (kg CO2-Eq) | 2,8889828 | 5,78E-04 | 5,78E-04 |
| fossil depletion:FDP (kg oil-Eq) | 0,53354981 | 1,07E-04 | 1,07E-04 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 0,02533157 | 5,07E-06 | 5,07E-06 |
| freshwater eutrophication:FEP (kg P-Eq) | 0,0009831 | 1,97E-07 | 1,97E-07 |
| human toxicity:HTPinf (kg 1,4-DC.) | 0,85556333 | 1,71E-04 | 1,71E-04 |
| ionising radiation:IRP_HE (kg U235-Eq) | 0,02956685 | 5,91E-06 | 5,91E-06 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 0,02487669 | 4,98E-06 | 4,98E-06 |
| marine eutrophication:MEP (kg N-Eq) | 0,0011326 | 2,27E-07 | 2,27E-07 |
| metal depletion:MDP (kg Fe-Eq) | 0,01956331 | 3,91E-06 | 3,91E-06 |
| natural land transformation:NLTP (m2) | 0,00027883 | 5,58E-08 | 5,58E-08 |
| ozone depletion:ODPinf (kg CFC-11.) | 5,5918E-08 | 1,12E-11 | 1,12E-11 |
| particulate matter formation:PMFP (kg PM10-Eq) | 0,00360465 | 7,21E-07 | 7,21E-07 |
| photochemical oxidant formation:POFP (kg NMVOC | 0,01198468 | 2,40E-06 | 2,40E-06 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 0,011294 | 2,26E-06 | 2,26E-06 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 0,00011478 | 2,30E-08 | 2,30E-08 |
| urban land occupation:ULOP (m2a) | 0,02598317 | 5,20E-06 | 5,20E-06 |
| water depletion:WDP (m3) | 0,00690007 | 1,38E-06 | 1,38E-06 |

Table 7.11. Inventory analysis and impacts of photo-Fenton process in RO membranes cleaning water taking into account a) the inputs, and b) the outputs

a) **PHOTO-FENTON**

| **METODOLOGÍA ReCiPe Midpoint (H)** | **$H_2O_2$: 1400 E-06 Kg** | | **$FeSO_4$*$7H_2O$: 348 E-06 Kg ($FeSO_4$: 190 E-06 Kg)** | | **HCl: 20 µL** | | **Electricity: Agitation + Lamp. Total 0,01275 KWh** | | **INPUTS SUM** |
|---|---|---|---|---|---|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 0,06341419 | 8,88E-05 | 0,026872774 | 5,11E-06 | 0,064209959 | 1,28E-08 | 0,03970402 | 5,06E-04 | 6,00E-04 |
| climate change:GWP100 (kg CO2-Eq) | 1,1423356 | 1,60E-03 | 0,26060464 | 4,95E-05 | 0,50430928 | 1,01E-07 | 0,46997944 | 5,99E-03 | 7,64E-03 |
| fossil depletion:FDP (kg oil-Eq) | 0,41260208 | 5,78E-04 | 0,072955402 | 1,39E-05 | 0,19146189 | 3,83E-08 | 0,14099153 | 1,80E-03 | 2,39E-03 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 0,03765421 | 5,27E-05 | 0,010686618 | 2,03E-06 | 0,014622691 | 2,92E-09 | 0,02192968 | 2,80E-04 | 3,34E-04 |
| freshwater eutrophication:FEP (kg P-Eq) | 0,00044707 | 6,26E-07 | 0,000190388 | 3,62E-08 | 0,000356328 | 7,13E-11 | 0,000148 | 1,89E-06 | 2,55E-06 |
| human toxicity:HTPinf (kg 1,4-DC.) | 0,49946072 | 6,99E-04 | 0,24566418 | 4,67E-05 | 0,54405679 | 1,09E-07 | 0,1556088 | 1,98E-03 | 2,73E-03 |
| ionising radiation:IRP_HE (kg U235-Eq) | 0,12958364 | 1,81E-04 | 0,046500058 | 8,84E-06 | 0,14449425 | 2,89E-08 | 0,20320668 | 2,59E-03 | 2,78E-03 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 0,03483394 | 4,88E-05 | 0,010032565 | 1,91E-06 | 0,015538406 | 3,11E-09 | 0,01923941 | 2,45E-04 | 2,96E-04 |
| marine eutrophication:MEP (kg N-Eq) | 0,00111177 | 1,56E-06 | 0,000354052 | 6,73E-08 | 0,000601743 | 1,20E-10 | 0,00053084 | 6,77E-06 | 8,39E-06 |
| metal depletion:MDP (kg Fe-Eq) | 0,0843102 | 1,18E-04 | 0,054964385 | 1,04E-05 | 0,062444013 | 1,25E-08 | 0,01665048 | 2,12E-04 | 3,41E-04 |
| natural land transformation:NLTP (m2) | 0,00015254 | 2,14E-07 | 5,0931E-05 | 9,68E-09 | 8,46004E-05 | 1,69E-11 | 5,8822E-05 | 7,50E-07 | 9,73E-07 |
| ozone depletion:ODPinf (kg CFC-11.) | 1,092E-07 | 1,53E-10 | 2,56413E-08 | 4,87E-12 | 2,55444E-07 | 5,11E-14 | 6,4133E-08 | 8,18E-10 | 9,75E-10 |
| particulate matter formation:PMFP (kg PM10-Eq) | 0,00229923 | 3,22E-06 | 0,000827292 | 1,57E-07 | 0,001105543 | 2,21E-10 | 0,00102699 | 1,31E-05 | 1,65E-05 |
| photochemical oxidant formation:POFP (kg NMVOC | 0,00349058 | 4,89E-06 | 0,001005159 | 1,91E-07 | 0,001685695 | 3,37E-10 | 0,00152749 | 1,95E-05 | 2,46E-05 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 0,00470174 | 6,58E-06 | 0,001500081 | 2,85E-07 | 0,002907428 | 5,81E-10 | 0,00291592 | 3,72E-05 | 4,40E-05 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 7,41E-05 | 1,04E-07 | 3,6858E-05 | 7,00E-09 | 0,000297583 | 5,95E-11 | 3,0978E-05 | 3,95E-07 | 5,06E-07 |
| urban land occupation:ULOP (m2a) | 0,0095007 | 1,33E-05 | 0,005849213 | 1,11E-06 | 0,008062482 | 1,61E-09 | 0,00339393 | 4,33E-05 | 5,77E-05 |
| water depletion:WDP (m3) | 0,005372 | 7,52E-06 | 0,001029333 | 1,96E-07 | 0,002276097 | 4,55E-10 | 0,00208911 | 2,66E-05 | 3,44E-05 |

b)

| | Incineration Iron sludge 70 E-06 Kg Fe | | OUTPUTS SUM |
|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 0,24075018 | 1,69E-05 | 1,69E-05 |
| climate change:GWP100 (kg CO2-Eq) | 2,8889828 | 2,02E-04 | 2,02E-04 |
| fossil depletion:FDP (kg oil-Eq) | 0,53354981 | 3,73E-05 | 3,73E-05 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 0,02533157 | 1,77E-06 | 1,77E-06 |
| freshwater eutrophication:FEP (kg P-Eq) | 0,0009831 | 6,88E-08 | 6,88E-08 |
| human toxicity:HTPinf (kg 1,4-DC.) | 0,85556333 | 5,99E-05 | 5,99E-05 |
| ionising radiation:IRP_HE (kg U235-Eq) | 0,02956685 | 2,07E-06 | 2,07E-06 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 0,02487669 | 1,74E-06 | 1,74E-06 |
| marine eutrophication:MEP (kg N-Eq) | 0,0011326 | 7,93E-08 | 7,93E-08 |
| metal depletion:MDP (kg Fe-Eq) | 0,01956331 | 1,37E-06 | 1,37E-06 |
| natural land transformation:NLTP (m2) | 0,00027883 | 1,95E-08 | 1,95E-08 |
| ozone depletion:ODPinf (kg CFC-11.) | 5,5918E-08 | 3,91E-12 | 3,91E-12 |
| particulate matter formation:PMFP (kg PM10-Eq) | 0,00360465 | 2,52E-07 | 2,52E-07 |
| photochemical oxidant formation:POFP (kg NMVOC | 0,01198468 | 8,39E-07 | 8,39E-07 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 0,011294 | 7,91E-07 | 7,91E-07 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 0,00011478 | 8,03E-09 | 8,03E-09 |
| urban land occupation:ULOP (m2a) | 0,02598317 | 1,82E-06 | 1,82E-06 |
| water depletion:WDP (m3) | 0,00690007 | 4,83E-07 | 4,83E-07 |

Table 7.12. Inventory analysis and impacts of photocatalysis process in RO membranes cleaning water taking into account a) the inputs, and b) the outputs

a) **PHOTOCATALYSIS**

| **METODOLOGÍA ReCiPe Midpoint (H)** | **$H_2O_2$: 1200 E-06 Kg** | | **$TiO_2$ (P25): 250 mg/L** | | **HCl: 20 µL** | | **Electricity: Agitation + Lamp: 0,03336 KW h** | | **INPUTS SUM** |
|---|---|---|---|---|---|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 0,06341419 | **7,61E-05** | 0,82203681 | **2,06E-04** | 0,064209959 | **1,28E-08** | 0,03970402 | **1,32E-03** | **1,61E-03** |
| climate change:GWP100 (kg CO2-Eq) | 1,1423356 | **1,37E-03** | 5,5751215 | **1,39E-03** | 0,50430928 | **1,01E-07** | 0,46997944 | **1,57E-02** | **1,84E-02** |
| fossil depletion:FDP (kg oil-Eq) | 0,41260208 | **4,95E-04** | 1,5261742 | **3,82E-04** | 0,19146189 | **3,83E-08** | 0,14099153 | **4,70E-03** | **5,58E-03** |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 0,03765421 | **4,52E-05** | 0,14440837 | **3,61E-05** | 0,014622691 | **2,92E-09** | 0,02192968 | **7,32E-04** | **8,13E-04** |
| freshwater eutrophication:FEP (kg P-Eq) | 0,00044707 | **5,36E-07** | 0,002510952 | **6,28E-07** | 0,000356328 | **7,13E-11** | 0,000148 | **4,94E-06** | **6,10E-06** |
| human toxicity:HTPinf (kg 1,4-DC.) | 0,49946072 | **5,99E-04** | 2,8028348 | **7,01E-04** | 0,54405679 | **1,09E-07** | 0,1556088 | **5,19E-03** | **6,49E-03** |
| ionising radiation:IRP_HE (kg U235-Eq) | 0,12958364 | **1,56E-04** | 0,67947599 | **1,70E-04** | 0,14449425 | **2,89E-08** | 0,20320668 | **6,78E-03** | **7,10E-03** |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 0,03483394 | **4,18E-05** | 0,13697459 | **3,42E-05** | 0,015538406 | **3,11E-09** | 0,01923941 | **6,42E-04** | **7,18E-04** |
| marine eutrophication:MEP (kg N-Eq) | 0,00111177 | **1,33E-06** | 0,007004917 | **1,75E-06** | 0,000601743 | **1,20E-10** | 0,00053084 | **1,77E-05** | **2,08E-05** |
| metal depletion:MDP (kg Fe-Eq) | 0,0843102 | **1,01E-04** | 0,38089 | **9,52E-05** | 0,062444013 | **1,25E-08** | 0,01665048 | **5,55E-04** | **7,52E-04** |
| natural land transformation:NLTP (m2) | 0,00015254 | **1,83E-07** | 0,001331737 | **3,33E-07** | 8,46004E-05 | **1,69E-11** | 5,8822E-05 | **1,96E-06** | **2,48E-06** |
| ozone depletion:ODPinf (kg CFC-11.) | 1,092E-07 | **1,31E-10** | 7,26506E-07 | **1,82E-10** | 2,55444E-07 | **5,11E-14** | 6,4133E-08 | **2,14E-09** | **2,45E-09** |
| particulate matter formation:PMFP (kg PM10-Eq) | 0,00229923 | **2,76E-06** | 0,01690367 | **4,23E-06** | 0,001105543 | **2,21E-10** | 0,00102699 | **3,43E-05** | **4,12E-05** |
| photochemical oxidant formation:POFP (kg NMVOC | 0,00349058 | **4,19E-06** | 0,022027459 | **5,51E-06** | 0,001685695 | **3,37E-10** | 0,00152749 | **5,10E-05** | **6,07E-05** |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 0,00470174 | **5,64E-06** | 0,056581749 | **1,41E-05** | 0,002907428 | **5,81E-10** | 0,00291592 | **9,73E-05** | **1,17E-04** |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 7,41E-05 | **8,89E-08** | 0,00064682 | **1,62E-07** | 0,000297583 | **5,95E-11** | 3,0978E-05 | **1,03E-06** | **1,28E-06** |
| urban land occupation:ULOP (m2a) | 0,0095007 | **1,14E-05** | 0,09591767 | **2,40E-05** | 0,008062482 | **1,61E-09** | 0,00339393 | **1,13E-04** | **1,49E-04** |
| water depletion:WDP (m3) | 0,005372 | **6,45E-06** | 0,10868968 | **2,72E-05** | 0,002276097 | **4,55E-10** | 0,00208911 | **6,97E-05** | **1,03E-04** |

**b)**

| | **Incineration $TiO_2$ 250 E-06 Kg $TiO_2$** | | **OUTPUTS SUM** |
|---|---|---|---|
| **agricultural land occupation:ALOP (m2a)** | 0,24075018 | **6,02E-05** | **6,02E-05** |
| **climate change:GWP100 (kg CO2-Eq)** | 2,8889828 | **7,22E-04** | **7,22E-04** |
| **fossil depletion:FDP (kg oil-Eq)** | 0,53354981 | **1,33E-04** | **1,33E-04** |
| **freshwater ecotoxicity:FETPinf (kg 1,4-DC.)** | 0,02533157 | **6,33E-06** | **6,33E-06** |
| **freshwater eutrophication:FEP (kg P-Eq)** | 0,0009831 | **2,46E-07** | **2,46E-07** |
| **human toxicity:HTPinf (kg 1,4-DC.)** | 0,85556333 | **2,14E-04** | **2,14E-04** |
| **ionising radiation:IRP_HE (kg U235-Eq)** | 0,02956685 | **7,39E-06** | **7,39E-06** |
| **marine ecotoxicity:METPinf (kg 1,4-DC.)** | 0,02487669 | **6,22E-06** | **6,22E-06** |
| **marine eutrophication:MEP (kg N-Eq)** | 0,0011326 | **2,83E-07** | **2,83E-07** |
| **metal depletion:MDP (kg Fe-Eq)** | 0,01956331 | **4,89E-06** | **4,89E-06** |
| **natural land transformation:NLTP (m2)** | 0,00027883 | **6,97E-08** | **6,97E-08** |
| **ozone depletion:ODPinf (kg CFC-11.)** | 5,5918E-08 | **1,40E-11** | **1,40E-11** |
| **particulate matter formation:PMFP (kg PM10-Eq)** | 0,00360465 | **9,01E-07** | **9,01E-07** |
| **photochemical oxidant formation:POFP (kg NMVOC** | 0,01198468 | **3,00E-06** | **3,00E-06** |
| **terrestrial acidification:TAP100 (kg SO2-Eq)** | 0,011294 | **2,82E-06** | **2,82E-06** |
| **terrestrial ecotoxicity:TETPinf (kg 1,4-DC.)** | 0,00011478 | **2,87E-08** | **2,87E-08** |
| **urban land occupation:ULOP (m2a)** | 0,02598317 | **6,50E-06** | **6,50E-06** |
| **water depletion:WDP (m3)** | 0,00690007 | **1,73E-06** | **1,73E-06** |

Table 7.13. Inventory analysis and impacts of UV-C/$H_2O_2$ process in RO membranes cleaning water

**UV-C/$H_2O_2$**

| **ReCiPe Midpoint (H)** | **$H_2O_2$: 1200 E-06 Kg** | | **Electricity: Agitation + Lamps UV-C. Total 0,1622 KWh** | | **INPUTS SUM** |
|---|---|---|---|---|---|
| **agricultural land occupation:ALOP (m2a)** | 0,06341419 | **7,61E-05** | 0,03970402 | **6,44E-03** | **6,52E-03** |
| **climate change:GWP100 (kg CO2-Eq)** | 1,1423356 | **1,37E-03** | 0,46997944 | **7,62E-02** | **7,76E-02** |
| **fossil depletion:FDP (kg oil-Eq)** | 0,41260208 | **4,95E-04** | 0,14099153 | **2,29E-02** | **2,34E-02** |
| **freshwater ecotoxicity:FETPinf (kg 1,4-DC.)** | 0,03765421 | **4,52E-05** | 0,021929677 | **3,56E-03** | **3,60E-03** |
| **freshwater eutrophication:FEP (kg P-Eq)** | 0,00044707 | **5,36E-07** | 0,000148001 | **2,40E-05** | **2,45E-05** |
| **human toxicity:HTPinf (kg 1,4-DC.)** | 0,49946072 | **5,99E-04** | 0,1556088 | **2,52E-02** | **2,58E-02** |
| **ionising radiation:IRP_HE (kg U235-Eq)** | 0,12958364 | **1,56E-04** | 0,20320668 | **3,30E-02** | **3,31E-02** |
| **marine ecotoxicity:METPinf (kg 1,4-DC.)** | 0,03483394 | **4,18E-05** | 0,019239411 | **3,12E-03** | **3,16E-03** |
| **marine eutrophication:MEP (kg N-Eq)** | 0,00111177 | **1,33E-06** | 0,000530836 | **8,61E-05** | **8,74E-05** |
| **metal depletion:MDP (kg Fe-Eq)** | 0,0843102 | **1,01E-04** | 0,016650484 | **2,70E-03** | **2,80E-03** |
| **natural land transformation:NLTP (m2)** | 0,00015254 | **1,83E-07** | 5,88219E-05 | **9,54E-06** | **9,72E-06** |
| **ozone depletion:ODPinf (kg CFC-11.)** | 1,092E-07 | **1,31E-10** | 6,41326E-08 | **1,04E-08** | **1,05E-08** |
| **particulate matter formation:PMFP (kg PM10-Eq)** | 0,00229923 | **2,76E-06** | 0,001026994 | **1,67E-04** | **1,69E-04** |
| **photochemical oxidant formation:POFP (kg NMVOC** | 0,00349058 | **4,19E-06** | 0,001527486 | **2,48E-04** | **2,52E-04** |
| **terrestrial acidification:TAP100 (kg SO2-Eq)** | 0,00470174 | **5,64E-06** | 0,002915916 | **4,73E-04** | **4,79E-04** |
| **terrestrial ecotoxicity:TETPinf (kg 1,4-DC.)** | 7,41E-05 | **8,89E-08** | 3,09778E-05 | **5,02E-06** | **5,11E-06** |
| **urban land occupation:ULOP (m2a)** | 0,0095007 | **1,14E-05** | 0,003393926 | **5,50E-04** | **5,62E-04** |
| **water depletion:WDP (m3)** | 0,005372 | **6,45E-06** | 0,002089115 | **3,39E-04** | **3,45E-04** |

Table 7.14. Total impact for each AOP applied to the treatment of RO membranes cleaning water and category

| | FENTON | PHOTO-FENTON | PHOTOCATALYSIS | UV-C/ H2O2 |
|---|---|---|---|---|
| agricultural land occupation:ALOP (m2a) | 5,15E-04 | 6,17E-04 | 1,67E-03 | 6,52E-03 |
| climate change:GWP100 (kg CO2-Eq) | 7,64E-03 | 7,84E-03 | 1,92E-02 | 7,76E-02 |
| fossil depletion:FDP (kg oil-Eq) | 2,50E-03 | 2,43E-03 | 5,71E-03 | 2,34E-02 |
| freshwater ecotoxicity:FETPinf (kg 1,4-DC.) | 2,71E-04 | 3,36E-04 | 8,19E-04 | 3,60E-03 |
| freshwater eutrophication:FEP (kg P-Eq) | 2,83E-06 | 2,62E-06 | 6,35E-06 | 2,45E-05 |
| human toxicity:HTPinf (kg 1,4-DC.) | 3,08E-03 | 2,79E-03 | 6,71E-03 | 2,58E-02 |
| ionising radiation:IRP_HE (kg U235-Eq) | 1,57E-03 | 2,78E-03 | 7,11E-03 | 3,31E-02 |
| marine ecotoxicity:METPinf (kg 1,4-DC.) | 2,46E-04 | 2,98E-04 | 7,24E-04 | 3,16E-03 |
| marine eutrophication:MEP (kg N-Eq) | 7,52E-06 | 8,47E-06 | 2,11E-05 | 8,74E-05 |
| metal depletion:MDP (kg Fe-Eq) | 4,54E-04 | 3,42E-04 | 7,57E-04 | 2,80E-03 |
| natural land transformation:NLTP (m2) | 9,88E-07 | 9,93E-07 | 2,55E-06 | 9,72E-06 |
| ozone depletion:ODPinf (kg CFC-11.) | 7,83E-10 | 9,79E-10 | 2,47E-09 | 1,05E-08 |
| particulate matter formation:PMFP (kg PM10-Eq) | 1,55E-05 | 1,67E-05 | 4,21E-05 | 1,69E-04 |
| photochemical oxidant formation:POFP (kg NMVOC | 2,45E-05 | 2,54E-05 | 6,36E-05 | 2,52E-04 |
| terrestrial acidification:TAP100 (kg SO2-Eq) | 3,65E-05 | 4,48E-05 | 1,20E-04 | 4,79E-04 |
| terrestrial ecotoxicity:TETPinf (kg 1,4-DC.) | 4,94E-07 | 5,14E-07 | 1,31E-06 | 5,11E-06 |
| urban land occupation:ULOP (m2a) | 6,33E-05 | 5,95E-05 | 1,55E-04 | 5,62E-04 |
| water depletion:WDP (m3) | 3,39E-05 | 3,48E-05 | 1,05E-04 | 3,45E-04 |

## 7.4. CONCLUSIONS AND DISCUSSION

LCA was used to compare the different treatments applied in this thesis to PW and RO membranes cleaning waters for reuse, to take into account, in addition to the elimination efficiency, the environmental impact of these technologies.

For the PW treatment, first a pretreatment was carried and DAF, E-DAF and settling were studied. Because the reference unit is a small volume (1 L) and therefore, the consumptions of reagents, etc. are low, there are no significant differences between the three scenarios. The quantity of $FeCl_3$ and kW h of electricity in the inputs were similar for the three treatments with the difference in the microspheres addition in the E-DAF process, and the compressed air in DAF, although consumptions were low. In this last one, the required compressed air expense is compensated with the lowest generation of oil and grease sludge because this pretreatment was not effective for the oil and grease removal in PW.

In general, impacts were slighter minor in DAF process followed by settling process.

Concerning the AOPs in the PW treatment, that was the next step, photo-Fenton was the process that caused less environmental impacts in all the categories.

Comparing the photo-Fenton process and Fenton at 70ºC where the same doses of reagents were added, the difference was mainly related to the electric consumption, since for the photo-Fenton 0.019 KW h were required, while 1.20 KW h were required for Fenton process, due to the consumption of the heating plate for 2 h. For the photo-Fenton process, the lamp consumption was not very high with the advantage that two experiments can be performed at a time inside the solarbox and that the reaction time was 1.5 h.

After photo-Fenton, the treatment that generated the least impact was photocatalysis (although was not completely effective for the PW treatment). The electric consumption was 0.055 KW h because although the solarbox was used as in the photo-Fenton process, photocatalysis required more time (310 min instead of 90 min in photo-Fenton). Comparing Fenton at 70ºC and ozonation, the environmental impacts were higher in all categories for Fenton than for ozonation, therefore the AOP that generates the most impacts is Fenton with temperature.

Among the AOPs applied in the treatment of RO membranes cleaning waters, Fenton process was therefore the least polluting. In all impact categories the values were lower than in the other treatments, although similar to the photo-Fenton process. In Fenton process the reagents consumption ($H_2O_2$ and Fe) were a little higher than in photo-Fenton (with the consequent higher iron sludge generation), but the electricity consumption was less (0.005 KW h in Fenton process versus 0.013 KW h in photo-Fenton).

The AOP that generated the most impacts was UV-C/ $H_2O_2$ due to the lamps energy consumption.

It must be taken into account that these results correspond to treatments at laboratory scale. On an industrial scale, for example in the case of the ozonation, to remove the 80% ozone excess, thermal-catalytic ozone destroyer would be used instead of the potassium iodide trap. Regarding the case of the processes where a lamp for the radiation is used (for example UV-C lamps), in this work 1L of water has been treated and it does not take advantage of the total incident light of the lamp. Using more volume of wastewater contained in an elongated reactor of the same length as the vertical lamp, the energy consumption would be the same, therefore an optimization would take place.

## 7.5. REFERENCES

Consoli, F., Allen, D., Boustead, I., Fava, J., Franklin, W., Jensen, A.A., de Oude, N., Parrish, R., Perriman, R., Postlethwaite, D., Quay, Seâguin, J., Vigon, B. (eds.), 1993. Guidelines for Life-Cycle Assessment: A `Code of Practice', SETAC, Brussels.

Fava, J., Dennison, R., Jones, B., Curran, M.A., Vigon, B., Selke, S.,Barnum, J. (eds.), 1991. A Technical Framework for Life-Cycle Assessment, SETAC and SETAC Foundation for Environmental Education, Washington, DC.

ISO/DIS 14040, 1997. Environmental Management ± Life Cycle Assessment ± Part 1: Principles and Framework.

# Chapter 8. Conclusions

**Content**

## 8.1. CONCLUSIONS FOR THE TREATMENT OF PW

The treatment of PW for reuse purposes has been essayed through an integrated solution composed of individual treatment technologies consisting on a pretreatment for oil and grease (O&G) removal followed by an advanced oxidation process (AOP) (at the end there would be a reverse osmosis membrane).

➢ Dissolved air flotation (DAF), enhanced-DAF (E-DAF) and settling were studied as pretreatments, using synthetic PW composed of the O&G fraction and phenol as a representative dissolved organic compound found in PW, in a seawater matrix:

- For flotation experiments (DAF), the coagulant dose only affected COD removal, while pH levels did not impact on the process performance; this meant that pH control would not be necessary in this type of pretreatment. As phenol was barely eliminated, the optimal coagulant ($FeCl_3$) concentration only taking into account the COD removal, was 70 mg $L^{-1}$ to achieve 46.2% of COD elimination. Under these conditions, 53.6% of turbidity removal was obtained. Higher levels of removals were not achieved with this treatment since microbubbles break the formed flocs.
- In the settling process, the removal of COD and turbidity were significantly affected by coagulant dosage and settling time. Phenol removal was not influenced by any operational parameter, as in flotation. The optimal process conditions were 86 mg $L^{-1}$ of coagulant concentration and 83 min of settling time, leading to a 69% COD removal percentage and 90% turbidity removal. Comparison of these pretreatments showed that higher COD and turbidity removals were achieved by settling (86% of O&G was also eliminated with this pretreatment).
- Due to the fact that the rising velocity of the microbubbles caused floc breakup, a new process using microspheres instead of air

microbubbles was also studied. This enhanced DAF or E-DAF removed 87.2% of PW turbidity and 94% of O&G (similar to the settling treatment but requiring less operation time), using 57.9 mg $L^{-1}$ of coagulant, 300 mg $L^{-1}$ of microspheres and a flocculation rate of 40 rpm. In E-DAF experiments it was observed that the turbidity reduction of PW was correlated to its O&G concentration depletion. High O&G removal percentages were achieved (up to 90% of elimination) with this process, comparable to settling results. The use of microspheres in the flotation without the injection of microbubbles was shown to be more effective for the removal of turbidity and O&G (which also implies lower energy consumption).

➢ Since dissolved organic compounds present in PW, as phenol, are not removed in these pretreatments, an advanced oxidation process (AOP) is required.

Different AOPs such as photocatalysis, photo-Fenton, Fenton and ozonation were studied to include one of these processes after the PW pretreatment. The PW was also synthetized in a seawater matrix where 10 mg $L^{-1}$ toluene and 10 mg $L^{-1}$ xylene were added as representatives of the BTEX group, 3 mg $L^{-1}$ naphthalene as representative of the PAHs group, 150 mg $L^{-1}$ acetic acid and 10 mg $L^{-1}$ malonic acid 10 mg $L^{-1}$ as representatives of the acids group and 10 mg $L^{-1}$ phenol:

- Photocatalysis was not resulted effective for the treatment of PW since under solar simulated radiation and by adding 100 mg $L^{-1}$ P25, TOC and phenol removals were 9.8% and 50%, respectively, after 4 h and by adding 500 mg $L^{-1}$ P25, TOC and phenol removals were 18% and 100%, respectively, after 4 h. Besides, malonic acid remained and there was no degradation of acetic acid.
- With photo-Fenton process under simulated solar radiation at pH 3 and by adding 557 mg $L^{-1}$ $H_2O_2$ and 55.7 mg $L^{-1}$ Fe, a 16.5% of TOC removal was achieved after 90 min. With this process phenol was

completely eliminated and malonic acid was removed up to a 89%, however acetic acid remained unaltered. Furthermore dditional intermediates as benzaldehyde were formed.

- With the Fenton process at 70ºC, when adding 557 mg $L^{-1}$ $H_2O_2$ and 55.7 mg $L^{-1}$ Fe, a 18% of TOC removal was achieved after 60 min. Compared to the photo-Fenton processes using the same doses of reagents, it was observed that temperature had more influence than light over TOC decrease. As in the case of photo-Fenton, BTEX, naphthalene and phenol were rapidly eliminated but no acetic acid removal occurred. Also intermediates compounds were detected.
- Higher eliminations were obtained by ozonation combined with $H_2O_2$. Although TOC removal was still low (17%) and there was no degradation of acetic acid by just injecting $O_3$, its combination with $H_2O_2$ produced better results and acetic acid began to be eliminated. At free pH, 50% of TOC removal was achieved after 2 h by adding 4 g $h^{-1}$ $O_3$ and 1500 mg $L^{-1}$ $H_2O_2$ and a 56% by adding 4.8 g $h^{-1}$ $O_3$ and 1500 mg $L^{-1}$ $H_2O_2$. For these conditions all the components in PW were eliminated, including a 70% of acetic acid (45 mg $L^{-1}$ remains). $H_2O_2$ was consumed in these processes between the 60-90 min of reaction and the final pH of the treated PW was around 7.6.

The optimum result was obtained with 4 g $h^{-1}$ $O_3$ and 1500 mg $L^{-1}$ $H_2O_2$ at initial pH 10 where 74% of TOC removal was achieved after 2 h and the acetic acid elimination was 77.8%. $H_2O_2$ was consumed within 60 min and the final pH of this effluent was 8.4.

- After applying the Life Cycle Assessment (LCA) to the tested AOPs (since for the pretreatments there are no significant differences between the three scenarios), photo-Fenton resulted the process that caused less environmental impacts, and Fenton with temperature the one that implied more impacts.

photo-Fenton process comparison with Fenton at 70ºC, when the same doses of reagents were added, showed that the main difference for LCA results relies in the electric consumption of heating. For the photo-Fenton process, the lamp consumption is not very high with the advantage that two experiments can be performed at a time inside the solarbox and that the reaction time is 1.5 h.

After photo-Fenton, the treatment that generated the least impact was photocatalysis (although it was not completely effective for the PW treatment). The electric consumption was 0.055 KW h because although the solarbox was used as in the photo-Fenton process, photocatalysis required more time (310 min instead of 90 min in photo-Fenton). Comparing Fenton at 70ºC and ozonation, the environmental impacts were higher in all categories for Fenton, despite the ozonation was more effective for PW polishing. In the ozonation process the total electric consumption was 0.084 KW h and what generated the highest impacts was the consumption of $O_2$ (50 L $h^{-1}$).

➢ **As final conclusion, the combination of settling pretreatment and ozonation process with 4 g $h^{-1}$ $O_3$ and 1500 mg $L^{-1}$ $H_2O_2$ at initial pH 10 could be suggested as a suitable polishing process for the reuse of PW, since O&G was eliminated in the pretreatment and the rest of organic compounds were at the ozonation process. Only 33 mg $L^{-1}$ of acetic acid remained (which would not pose much problem since it is biodegradable), and a suitable final pH to reuse the treated water after passing through a RO membrane for salts removal. Settling could be also substituted by E-DAF technology, without air injection, when there are limitations regarding reaction volumes and times.**

**In a future work a higher optimization of doses of $O_3$ and $H_2O_2$ could be carry out to achieve a complete or higher elimination of the acetic**

**acid, and also the combination of $O_3$/ $H_2O_2$ with UV-C radiation could be tested.**

## 8.2. CONCLUSIONS FOR THE TREATMENT OF THE CLEANING WATERS FROM SEAWATER DESALINATION RO MEMBRANES

AOPs were studied for treating cleaning simulated waters from seawater desalination RO membranes composed of 7.37 mg $L^{-1}$ starch, 200 mg $L^{-1}$ $Na_4$-EDTA and 150 mg $L^{-1}$ of SDS.

➢ With Fenton process, statistical analysis of the results showed that after 15 min of reaction, decreasing TOC was favored with increasing doses of $H_2O_2$ and $Fe^{2+}$ until a maximum dose of $Fe^{2+}$. Fe can also be chelated with EDTA, forming Fe-EDTA complexes.

After 157 min of reaction, $Fe^{2+}$ dose did not have significant influence on the final TOC, however, $H_2O_2$ itself favored the reduction of TOC.

Finally, after 300 min of reaction, lower TOC values were achieved by high doses of $H_2O_2$ and low doses of $Fe^{2+}$. When $H_2O_2$ concentration is low, iron can participate in other secondary reactions.

That is, for rapid organic matter degradation is necessary the use of high doses of both reagents, being able to achieve within 15 min a maximum TOC removal of 53.3%; while if it is left for longer reaction times, only $H_2O_2$ has influence and 64.4% of TOC can be removed adding 8280 mg $L^{-1}$ $H_2O_2$ and 414 mg $L^{-1}$ $Fe^{2+}$ after 157 min. After 300 min a TOC removal of 67.5% can be achieved with the lowest dose of $Fe^{2+}$ (8280 mg $L^{-1}$ of $H_2O_2$ and 50 mg $L^{-1}$ of $Fe^{2+}$), according to the statistical model obtained.

Among the three reaction times tested, 157 min is the optimum time for the Fenton process and a minimum TOC value could be achieved with a $H_2O_2$ concentration above 4000 mg $L^{-1}$ and a $H_2O_2$ / $Fe^{2+}$ (w/w) ratio between 1 and 20, which could be fixed to 20 to reduce the amount of

$Fe^{2+}$, corresponding to 200 mg $L^{-1}$ of $Fe^{2+}$. The maximum TOC removal obtained under these operating conditions was 67% and 14.8 mg $O_2$ $L^{-1}$ was the final $BOD_5$ value, that exceeds slightly the EPA recommendations for irrigation of raw food crops for human consumption. Nevertheless, the treated cleaning water could be used for irrigation of processed food crops or non-food crops, for reutilization in other processes and for industrial applications, once the iron has been removed by raising the pH and decanting.

➢ After the study of the photo-Fenton process at pH 3 under simulated solar radiation, the evaluated effluent TOC at three reaction times, indicated that 60 min of reaction were sufficient in the removal of a high TOC percentage. After a statistical analysis of the results, for the range of reagent concentrations studied, the optimal dose of reagents for optimal time of 60 min were 1400 mg $L^{-1}$ of $H_2O_2$ and 70 mg $L^{-1}$ of $Fe^{2+}$, achieving a 79.70% of TOC removal. An empirical equation was proposed to estimate the percentage of TOC removal after 60 min of reaction. Experimentally, the TOC removal at 60 min was 78.8% and with longer time (157 min) a 85.6% and all the $H_2O_2$ was consumed. This photo-Fenton reaction can be performed at pH 7 because, although until 60 min the reaction was slower at pH 7, at 157 min, the same elimination is reached.

By contrast, the addition of P25 accelerated this process both at pH 3 and at 7 in the first 30 min but after one hour, similar elimination was obtained, so there would be no need to add P25 that afterwards would have to be removed from the effluent.

SDS was analyzed in the water after the best treatments obtained and this component was not found. Final $BOD_5$ was 1 mg $L^{-1}$, therefore this water could be reused for irrigation according to EPA recommendations.

A high mineralization was also obtained under simulated solar radiation at pH 3 by adding 1200 mg $L^{-1}$ of $H_2O_2$ with 0.25 g $L^{-1}$ of P25 instead of Fe, where 76.9% of TOC removal was achieved at 180 min.

Under UV-C radiation and by adding 1200 mg $L^{-1}$ of $H_2O_2$ at free pH, 61% of TOC removal was achieved at 157 min.

➢ LCA indicated that Fenton process was the least polluting. In all impact categories the values were lower than in the other treatments, although similar than the photo-Fenton process. In Fenton process the reagents consumption ($H_2O_2$ and Fe) were a little higher than in photo-Fenton (with the consequent higher iron sludge generation), but the electricity consumption was much lower (0.005 KW h in Fenton process versus 0.013 KW h in photo-Fenton).The AOP that generates the most impacts is UV-C/ $H_2O_2$ due to the lamps energy consumption.

➢ **As conclusion, results showed that the best AOP to treat the cleaning waters from seawater desalination RO membranes is photo-Fenton. The optimal dose of reagents for optimal time of 60 min were 1400 mg $L^{-1}$ of $H_2O_2$ and 70 mg $L^{-1}$ of $Fe^{2+}$, achieving a 79.70% of TOC removal. With longer time (157 min) a 85.6% and all the $H_2O_2$ was consumed. This photo-Fenton reaction could be performed at pH 7 because, although until 60 min the reaction is slower at pH 7, at 157 min, the same elimination is reached as at pH 3. SDS content was depleted after this treatment, and final $BOD_5$ would allow the use of this treated effluent in irrigation of raw food crops for human consumption although other parameters of quality like salinity, hardness or alkalinity have to be measured.**

# Chapter 9. Publications and Communications

## PUBLISHED ARTICLE

Jiménez, S., Micó, M.M., Arnaldos, M., Ferrero, E., Malfeito, J.J., Medina, F., Contreras, S., 2017. Integrated processes for produced water polishing: Enhanced flotation/sedimentation combined with advanced oxidation processes. Chemosphere, 168, 309-317.

## SUBMITTED ARTICLES

Jiménez, S., Micó, M.M., Arnaldos, M., Medina, F., Contreras, S., 2017. State of the Art of Produced Water Treatment.

Jiménez, S., Micó, M.M., Arnaldos, M., Corzo, B., Navea, S., Ferrero, E., Medina, F., Contreras, S., 2017. Reverse Osmosis Membranes Cleaning Waters Treatment for Reutilization Purposes. Part I: Application of Fenton Process.

Jiménez, S., Micó, M.M., Corzo, B., Contreras, S., 2017. Reverse Osmosis Membranes Cleaning Waters Treatment for Reutilization Purposes. Part II: Application of Photo-Fenton and Photocatalysis Processes.

Jiménez, S., Micó, M.M., García-Álvarez, M., Contreras, S., 2017. Produced Water Treatment by Advanced Oxidation Processes.

## POSTER PRESENTATIONS

Jiménez, S., García-Álvarez, M., Micó, M.M., Medina, F., Contreras, S., 2017. “Application of Advanced Oxidation Processes for the Polishing of Produced Water”. 5th European Conference on Environmental Applications of Advanced Oxidation Processes. June 25-29, 2017, Prague, Czech Republic.

Jiménez, S., 2016. "Dissolved Air Flotation, Enhanced Flotation and Settling Processes Combined with Advanced Oxidation Processes for Emulsified Oil and Grease Removal in Produced Water Trains". 13 th Doctoral Day. Universitat Rovira i Virgili. PhD in Nanoscience, Materials and Chemical Engineering. Tarragona, 4 May 2016.

## ORAL COMMUNICATIONS

Arnaldos, M., Corzo, B., Jiménez, S., Micó, M.M., Ferrero, E., Malfeito, J.J., 2016. "Advanced oxidation processes to recover reverse osmosis cleaning waters for irrigation purposes". XI International Congress AEDyR. Valencia 19-21 October 2016.

Arnaldos, M., Jiménez, S., Micó, M.M., Ferrero, E., Contreras, S., Malfeito, J.J., 2016. "Produced Water Treatment and Reuse: Bridging Conventional Treatment and Polishing Technologies". Singapur International Water Week. The global platform to share and co create innovative water solutions. Sands Expo & Convention Center, Marina Bay Sands, Syngapore. 10-14 July 2016.

Jiménez, S., 2016. "Novel Process for Produced Water Polishing: Enhanced Flotation Combined With Advanced Oxidation Processes". Canada-Spain Workshop on AOPs. AOPs and Ozone Fundamental Updates and Current Industrial Applications. Faculty of Chemistry of the University of Barcelona from 7 to 8 July 2016.

Jiménez, S., Arnaldos, M., Bayona, C., Micó, M.M., Ferrero, E., Malfeito, J.J., Contreras, S., 2016. "Novel Process for Produced Water Polishing: Enhanced Flotation Combined With Advanced Oxidation Processes". European Desalination Society Congress. Desalination for the

Environment: Clean Water and Energy. Marriott Park Hotel, Rome, Italy, 22–26 May 2016.

Jiménez, S., Arnaldos, M., Corzo, B., Micó, M.M., Ferrero, E., de la Torre, T., Malfeito, J.J., 2016. “Advanced oxidation processes to recover reverse osmosis cleaning waters for irrigation purposes”. European Desalination Society Congress. Desalination for the Environment: Clean Water and Energy. Marriott Park Hotel, Rome, Italy, 22–26 May 2016.

Jiménez, S., 2015. “Dissolved air flotation and settling processes for emulsified oil and grease removal in produced water trains”. 7th European Meeting on Chemical Industry and Environment. Universitat Rovira i Virgili, Tarragona, Spain, 10-12 June 2015.

Jiménez, S., Micó, M.M., Ferrero, E., Navea, S., Medina, F., Contreras, S., Arnaldos, M., Malfeito, J., 2015. “Dissolved air flotation and settling processes for emulsified oil and grease removal in produced water trains”. EuroMed 2015 Congress. European Desalination Society. Desalination for Clean Water and Energy. Cooperation among Mediterranean Countries of Europe and the MENA Region. Palermo, Italy, 10–14 May 2015.

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