



Universitat de Barcelona
Facultat de Química
Departament d'Enginyeria Química

COUPLED PHOTOCHEMICAL-BIOLOGICAL SYSTEM TO TREAT BIORECALCITRANT WASTEWATERS

Doctoral Thesis directed by Santiago Esplugas Vidal and
Esther Chamarro Aguilera

Jordi Bacardit Peñarroya

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Chapter 7: References

Alvarez, J. D., Gernjak, W., Malato, S., Berenguel, M., Fuerhacker, M. and Yebra, L. J. Dynamic models for hydrogen peroxide control in solar photo-fenton systems. *Journal of Solar Energy Engineering-Transactions of the Asme* **2007**, 129(1), 37-44.

Amat, A. M., Arques, A., Lopez, F. and Miranda, M. A. Solar photo-catalysis to remove paper mill wastewater pollutants. *Solar Energy* **2005**, 79(4), 393-401.

Arslan-Alaton, I. and Gurses, F. Photo-Fenton-like and photo-fenton-like oxidation of Procaine Penicillin G formulation effluent. *Journal of Photochemistry and Photobiology a-Chemistry* **2004**, 165(1-3), 165-175.

ASTM. *ASTM D1252-06: Standard Test Methods for Chemical Oxygen Demand (Dichromate Oxygen Demand) of Water*. ASTM, **2006**.

ATSDR. *Toxicological Profile for Chlorophenols*. U.S. Department of Health and Human Services. Public Health Service. Agency for Toxic Substances and Disease Registry. Report n°: --. **1999**.

Aubanell, A., Benseny, A. and Delshams, A. *Eines bàsiques de càlcul numèric. Amb 87 problemes resoltos*. Publicacions de la Universitat Autònoma de Barcelona, Bellaterra, **1991**.

Barcelo, D. Emerging pollutants in water analysis. *Trac-Trends in Analytical Chemistry* **2003**, 22(10), Xiv-Xvi.

Bauer, R. and Fallmann, H. The Photo-Fenton oxidation - A cheap and efficient wastewater treatment method. *Research on Chemical Intermediates* **1997**, 23(4), 341-354.

Beltran, F. J., González, M. and Álvarez, P. Tratamiento de aguas mediante oxidación avanzada (I): Procesos con ozono, radiación ultravioleta y combinación ozono/radiación ultravioleta. *Ingeniería Química* **1997**, 25(331), 161-164.

Benitez, F. J., Beltran-Heredia, J., Acero, J. L. and Rubio, F. J. Rate constants for the reactions of ozone with chlorophenols in aqueous solutions. *Journal of Hazardous Materials* **2000**, 79(3), 271-285.

Bianco, G. and Gehlen, M. H. Synthesis of poly(N-vinyl-2-pyrrolidone) and copolymers with methacrylic acid initiated by the photo-Fenton reaction. *Journal of Photochemistry and Photobiology a-Chemistry* **2002**, 149(1-3), 115-119.

Blanco, J. *Desarrollo de colectores solares CPC para aplicaciones fotoquímicas de degradación de contaminantes persistentes en agua*. Colección Documentos Ciemat. Editorial Ciemat, Madrid, **2002**.

Boncz, M. A., Bruning, H., Rulkens, W. H., Sudholter, E. J. R., Harmsen, G. H. and Bijsterbosch, J. W. Kinetic and mechanistic aspects of the oxidation of chlorophenols by ozone. *Water Science and Technology* **1997**, 35(4), 65-72.

Bossmann, S. H., Oliveros, E., Gob, S., Siegwart, S., Dahlen, E. P., Payawan, L., Straub, M., Worner, M. and Braun, A. M. New evidence against hydroxyl radicals as reactive intermediates in the thermal

- and photochemically enhanced fenton reactions. *Journal of Physical Chemistry A* **1998**, 102(28), 5542-5550.
- Box, G. E. P. and Wilson, K. B. On the Experimental Attainment of Optimum Conditions. *Journal of the Royal Statistical Society Series B-Statistical Methodology* **1951**, 13(1), 1-45.
- Braun, A. M., Jacob, J., Oliveros, E. and Nascimento, C. A. O. *Up-scaling photochemical reactions*. In: Volman, D., Hammond, G. S. and Neckers, D. C. (Ed), *Advances in Photochemistry*. New York: Wiley, **1993**, pp 235-313.
- Buitron, G., Gonzalez, A. and Lopez-Marin, L. M. Biodegradation of phenolic compounds by an acclimated activated sludge and isolated bacteria. *Water Science and Technology* **1998**, 37(4-5), 371-378.
- Buitron, G., Quezada, M. and Moreno, G. Aerobic degradation of the azo dye acid red 151 in a sequencing batch biofilter. *Bioresource Technology* **2004**, 92(2), 143-149.
- Calza, P., Minero, C. and Pelizzetti, E. Photocatalytically assisted hydrolysis of chlorinated methanes under anaerobic conditions. *Environmental Science & Technology* **1997**, 31(8), 2198-2203.
- CESARS. *Chemical Evaluation Search and Retrieval System*. Canadian Centre for Occupational Health and Safety, **1989**.
- Chamarro, E., Marco, A. and Esplugas, S. Use of Fenton reagent to improve organic chemical biodegradability. *Water Research* **2001**, 35(4), 1047-1051.
- Chen, R. Z. and Pignatello, J. J. Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidations of aromatic compounds. *Environmental Science & Technology* **1997**, 31(8), 2399-2406.
- Chu, W., Kwan, C. Y., Chan, K. H. and Kam, S. K. A study of kinetic modelling and reaction pathway of 2,4-dichlorophenol transformation by photo-fenton-like oxidation. *Journal of Hazardous Materials* **2005**, 121(1-3), 119-126.
- Contreras, S., Rodriguez, M., Al Momani, F., Sans, C. and Esplugas, S. Contribution of the ozonation pre-treatment to the biodegradation of aqueous solutions of 2,4-dichlorophenol. *Water Research* **2003**, 37(13), 3164-3171.
- Davis, A. P. and Green, D. L. Photocatalytic oxidation of cadmium-EDTA with titanium dioxide. *Environmental Science & Technology* **1999**, 33(4), 609-617.
- De Laat, J., Le, G. T. and Legube, B. 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* **2004**, 55(5), 715-723.
- Devinny, J. S. and Ramesh, J. A phenomenological review of biofilter models. *Chemical Engineering Journal* **2005**, 113(2-3), 187-196.

EC. *Report from the Water issue group as a contribution to the Environmental Technologies Action Plan*. European Commission, Brussels, **2003**.

EC. *Work Programme Sub-Priority 1.1.6.3 "Global Change and Ecosystems". 4th Call for Proposals. Call Identifier: FP6-2005-Global-4*. European Commission, **2005**.

EM-Entitat Metropolitana. *Reglament Metropolità d'abocament d'aigües residuals*. CM 3/06/2004. BOP N°: 142 14/06/2004, **2004**.

EPA. *Ambient Water Quality Criteria for Chlorinated Phenols*. USEPA. Report n°: EPA-440/5-80-032 (NITS PB81 117434) and EPA-440/5-80-034 (NITS PB81 117459). **1980**.

EPA. *TRI On-site and Off-site Reported Disposed of or Otherwise Released in pounds for facilities in All Industries for All Chemicals in United States*. **1988**. From <http://www.epa.gov/tri/>

EPA. *TRI On-site and Off-site Reported Disposed of or Otherwise Released in pounds for facilities in All Industries for All Chemicals in United States*. **2000**. From <http://www.epa.gov/tri/>

EPA. *TRI On-site and Off-site Reported Disposed of or Otherwise Released in pounds for facilities in All Industries for All Chemicals in United States*. **2005**. From <http://www.epa.gov/tri/>

Esplugas, S., Contreras, S. and Ollis, D. F. Engineering aspects of the integration of chemical and biological oxidation: Simple mechanistic models for the oxidation treatment. *Journal of Environmental Engineering-Asce* **2004**, 130(9), 967-974.

EU-European Parliament. *Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption*. Official Journal L 330/32, 5.12.1998. **1998**.

EU-European Parliament. *Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy*. Official Journal L 327/1, 22.12.2000. **2000**.

EU-European Parliament. *Decision 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC*. Official Journal L 331/1, 15.12.2001. **2001**.

EU-European Parliament. *Council Decision 2006/507/EC of 14 October 2004 concerning the conclusion, on behalf of the European Community, of the Stockholm Convention on Persistent Organic Pollutants*. Official Journal L 209/1, 31.7.2006. **2006a**.

EU-European Parliament. *Directive 2006/11/EC of the European Parliament and of the Council of 15 February 2006 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community*. Official Journal L 64/52, 4.3.2006. **2006b**.

EU-European Parliament. *Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration*. Official Journal L 372/19, 27.12.2006. **2006c**.

- Eurochlor. *The European Chlor-alkali industry. Steps towards sustainable development*. Euro Chlor. **2006**. From www.eurochlor.org
- Eurochlor. *European chlorine industry. Chlorine*. Euro Chlor. **2007**. From www.eurochlor.org
- Exon, J. H. A Review of Chlorinated Phenols. *Veterinary and Human Toxicology* **1984**, 26(6), 508-520.
- Fallmann, H., Krutzler, T., Bauer, R., Malato, S. and Blanco, J. Applicability of the Photo-Fenton method for treating water containing pesticides. *Catalysis Today* **1999**, 54(2-3), 309-319.
- Fenton, H. J. H. Oxidation of tartaric acid in presence of iron. *Journal of the Chemical Society* **1894**, 65, 899-910.
- Ferguson, S. H., Woinarski, A. Z., Snape, I., Morris, C. E. and Reville, A. T. A field trial of in situ chemical oxidation to remediate long-term diesel contaminated Antarctic soil. *Cold Regions Science and Technology* **2004**, 40(1-2), 47-60.
- Foussard, J. N., Debellefontaine, H. and Besombesvaille, J. Efficient Elimination of Organic Liquid Wastes - Wet Air Oxidation. *Journal of Environmental Engineering-Asce* **1989**, 115(2), 367-385.
- Freitas, A. R., Vidotti, G. J., Rubira, A. F. and Muniz, E. C. Polychloroprene degradation by a Photo-Fenton process. *Polymer Degradation and Stability* **2005**, 87(3), 425-432.
- Gantzer, C. J. Inhibitory Substrate Utilization by Steady-State Biofilms. *Journal of Environmental Engineering-Asce* **1989**, 115(2), 302-319.
- García-Molina, V. *Wet Oxidation Processes for Water Pollution Remediation*. Doctoral Thesis. University of Barcelona, Barcelona, **2006**.
- Garcia-Molina, V., Barcardit, J., Kallas, J. and Esplugas, S. Kinetics of wet oxidation reactions. *Journal of Advanced Oxidation Technologies* **2006**, 9(1), 20-26.
- Garcia-Molina, V., Lopez-Arias, M., Florczyk, M., Chamarro, E. and Esplugas, S. Wet peroxide oxidation of chlorophenols. *Water Research* **2005**, 39(5), 795-802.
- Gernjak, W. *Solar Photo-Fenton Treatment of EU Priority Substances. Process Parameters and Control Strategies*. Doctoral Thesis. Universität für Bodenkultur Wien, Vienna, **2006**.
- Gernjak, W., Fuerhacker, M., Fernandez-Ibanez, P., Blanco, J. and Malato, S. Solar photo-Fenton treatment - Process parameters and process control. *Applied Catalysis B-Environmental* **2006**, 64(1-2), 121-130.
- Glaze, W. H., Kang, J. W. and Chapin, D. H. The Chemistry of Water-Treatment Processes Involving Ozone, Hydrogen-Peroxide and Ultraviolet-Radiation. *Ozone-Science & Engineering* **1987**, 9(4), 335-352.

Gob, S., Oliveros, E., Bossmann, S. H., Braun, A. M., Guardani, R. and Nascimento, C. A. O. Modeling the kinetics of a photochemical water treatment process by means of artificial neural networks. *Chemical Engineering and Processing* **1999**, 38(4-6), 373-382.

Goldstein, S., Meyerstein, D. and Czapski, G. The Fenton Reagents. *Free Radical Biology and Medicine* **1993**, 15(4), 435-445.

Gonzalez, M. G., Oliveros, E., Worner, M. and Braun, A. M. Vacuum-ultraviolet photolysis of aqueous reaction systems. *Journal of Photochemistry and Photobiology C-Photochemistry Reviews* **2004**, 5(3), 225-246.

Gottschalk, C., Libra, J. A. and Saupe, A. *Ozonation of Water and Waste Water: A Practical Guide to Understanding Ozone and Its Application*. Gottschalk, C., Libra, J. A. and Saupe, A., (Eds). Weinheim: Wiley-VCH, **2000**.

Grady, C. P. L. Biodegradation of Toxic Organics - Status and Potential. *Journal of Environmental Engineering-Asce* **1990**, 116(5), 805-828.

Gurney, B. F. and Lautenschlager, D. P. Nearly non-toxic parachlorophenol antiseptics. *The Journal of the Dental Association of South Africa* **1982**, 37(12), 815-818.

Haber, F. and Weiss, J. The catalytic decomposition of hydrogen peroxide by iron salts. *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences* **1934**, 147(861), 332-351.

Hancock, F. E. Catalytic strategies for industrial water re-use. *Catalysis Today* **1999**, 53(1), 3-9.

Herrmann, J. M. Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catalysis Today* **1999**, 53(1), 115-129.

Hoigne, J. and Bader, H. Ozonation of Water - Role of Hydroxyl Radicals as Oxidizing Intermediates. *Science* **1975**, 190(4216), 782-784.

Hoigne, J. and Bader, H. Role of Hydroxyl Radical Reactions in Ozonation Processes in Aqueous-Solutions. *Water Research* **1976**, 10(5), 377-386.

HSDB. *Hazardous Substances Data Bank*. National Toxicology Information Program, Bethesda, MD. USA., **1998**.

Hunsberger, J. F. *Standard reduction potentials*. In: Weast, R. C. (Ed), *Handbook of Chemistry and Physics*. Ohio: CRC Press, **1977**, pp D141-144.

Huston, P. L. and Pignatello, J. J. Reduction of perchloroalkanes by ferrioxalate-generated carboxylate radical preceding mineralization by the photo-fenton reaction. *Environmental Science & Technology* **1996**, 30(12), 3457-3463.

ILO. *International Occupational Safety and Health Information Centre*. **1999**. From <http://www.ilo.org>

- Kavitha, V. and Palanivelu, K. The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol. *Chemosphere* **2004**, 55(9), 1235-1243.
- Klimiuk, E. and Kulikowska, D. Organics removal from landfill leachate and activated sludge production in SBR reactors. *Waste Management* **2006**, 26(10), 1140-1147.
- Krutzler, T., Fallmann, H., Maletzky, P., Bauer, R., Malato, S. and Blanco, J. Solar driven degradation of 4-chlorophenol. *Catalysis Today* **1999**, 54(2-3), 321-327.
- Kuhn, H. J., Braslavsky, S. E. and Schmidt, R. Chemical actinometry. *Pure and Applied Chemistry* **2004**, 76(12), 2105-2146.
- Lee, C. H. and Yoon, J. Y. Temperature dependence of hydroxyl radical formation in the hv/Fe³⁺/H₂O₂ and Fe³⁺/H₂O₂ systems. *Chemosphere* **2004**, 56(10), 923-934.
- Lei, L. C., Hu, X. J., Yue, P. L., Bossmann, S. H., Gob, S. and Braun, A. M. Oxidative degradation of polyvinyl alcohol by the photochemically enhanced Fenton reaction. *Journal of Photochemistry and Photobiology a-Chemistry* **1998**, 116(2), 159-166.
- Li, L. X., Chen, P. S. and Gloyna, E. F. Generalized Kinetic-Model for Wet Oxidation of Organic-Compounds. *Aiche Journal* **1991**, 37(11), 1687-1697.
- Lipczynskakochany, E., Sprah, G. and Harms, S. Influence of Some Groundwater and Surface Waters Constituents on the Degradation of 4-Chlorophenol by the Fenton Reaction. *Chemosphere* **1995**, 30(1), 9-20.
- Lu, M. C., Chang, Y. F., Chen, I. M. and Huang, Y. Y. Effect of chloride ions on the oxidation of aniline by Fenton's reagent. *Journal of Environmental Management* **2005**, 75(2), 177-182.
- Maciel, R., Sant'Anna, G. L. and Dezotti, M. Phenol removal from high salinity effluents using Fenton's reagent and photo-Fenton reactions. *Chemosphere* **2004**, 57(7), 711-719.
- Malato, S., Blanco, J., Vidal, A. and Richter, C. Photocatalysis with solar energy at a pilot-plant scale: an overview. *Applied Catalysis B-Environmental* **2002**, 37(1), 1-15.
- Malato, S., Caceres, J., Fernandez-Alba, A. R., Piedra, L., Hernando, M. D., Aguera, A. and Vial, J. Photocatalytic treatment of diuron by solar photocatalysis: Evaluation of main intermediates and toxicity. *Environmental Science & Technology* **2003**, 37(11), 2516-2524.
- Martin, D. I., Margaritescu, I., Cirstea, E., Togoec, I., Ighigeanu, D., Nemtanu, M. R., Oproiu, C. and Iacob, N. Application of accelerated electron beam and microwave irradiation to biological waste treatment. *Vacuum* **2005**, 77(4), 501-506.
- Masarwa, M., Cohen, H., Meyerstein, D., Hickman, D. L., Bakac, A. and Espenson, J. H. Reactions of Low-Valent Transition-Metal Complexes with Hydrogen-Peroxide - Are They Fenton-Like or Not .1. The Case of Cu⁺Aq and Cr²⁺Aq. *Journal of the American Chemical Society* **1988**, 110(13), 4293-4297.

Mason, R. L. *Statistical design and analysis of experiments: with applications to engineering and science*. Mason, R. L., Gunst, R. F. and Hess, J. L., (Eds). New York: Wiley, **1989**.

Melin, E. S., Jarvinen, K. T. and Puhakka, J. A. Effects of temperature on chlorophenol biodegradation kinetics in fluidized-bed reactors with different biomass carriers. *Water Research* **1998**, 32(1), 81-90.

Metcalf and Eddy, Eds. *Wastewater engineering : treatment, disposal, and reuse*. McGraw-Hill series in water resources and environmental engineering. New York, McGraw-Hill, **1991**.

Millioli, V. S., Freire, D. D. C. and Cammarota, M. C. Petroleum oxidation using Fenton's reagent over beach sand following a spill. *Journal of Hazardous Materials* **2003**, 103(1-2), 79-91.

Moraes, J. E. F., Quina, F. H., Nascimento, C. A. O., Silva, D. N. and Chiavone, O. Treatment of saline wastewater contaminated with hydrocarbons by the photo-Fenton process. *Environmental Science & Technology* **2004**, 38(4), 1183-1187.

Moreno-Andrade, I., Buitron, G. N., Betancur, M. J. and Moreno, J. A. Optimal degradation of inhibitory wastewaters in a fed-batch bioreactor. *Journal of Chemical Technology and Biotechnology* **2006**, 81(4), 713-720.

Moreno, G. and Buitron, G. Influence of the origin of the inoculum and the acclimation strategy on the degradation of 4-chlorophenol. *Bioresource Technology* **2004**, 94(2), 215-218.

Muschaweck, J., Spirkel, W., Timinger, A., Benz, N., Dorfler, M., Gut, M. and Kose, E. Optimized reflectors for non-tracking solar collectors with tubular absorbers. *Solar Energy* **2000**, 68(2), 151-159.

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

NIOSH. *Registry of Toxic Effects of Chemical Substances (RTECS)*. National Institute for Occupational Safety and Health, Cincinnati (Ohio), **1983**.

Oliveros, E., Legrini, O., Hohl, M., Muller, T. and Braun, A. M. Industrial waste water treatment: large scale development of a light-enhanced Fenton reaction. *Chemical Engineering and Processing* **1997**, 36(5), 397-405.

Oller, I., Gernjak, W., Maldonado, M. I., Perez-Estrada, L. A., Sanchez-Perez, J. A. and Malato, S. Solar photocatalytic degradation of some hazardous water-soluble pesticides at pilot-plant scale. *Journal of Hazardous Materials* **2006**, 138(3), 507-517.

Ollis, D. F. and Al-Ekabi, H., Eds. *Photocatalytic purification and treatment of water and air*. Amsterdam, Elsevier, **1993**.

Oppenländer, T. *Photochemical Purification of Water and Air: Advanced Oxidation Processes (AOPs): Principles, Reaction Mechanisms, Reactor Concepts*. Wiley-VCH, Weinheim, **2002**.

- Park, S. J., Yoon, T. I., Bae, J. H., Seo, H. J. and Park, H. J. Biological treatment of wastewater containing dimethyl sulphoxide from the semi-conductor industry. *Process Biochemistry* **2001**, 36(6), 579-589.
- Parsons, S. *Advanced Oxidation Processes for Water and Wastewater treatment*. Parsons, S., (Eds). London: IWA publishing, **2004**.
- Paterlini, W. C. and Nogueira, R. F. P. Multivariate analysis of photo-Fenton degradation of the herbicides tebuthiuron, diuron and 2,4-D. *Chemosphere* **2005**, 58(8), 1107-1116.
- Pera-Titus, M., Garcia-Molina, V., Banos, M. A., Gimenez, J. and Esplugas, S. Degradation of chlorophenols by means of advanced oxidation processes: a general review. *Applied Catalysis B-Environmental* **2004**, 47(4), 219-256.
- Perez, M., Torrades, F., Peral, J., Lizama, C., Bravo, C., Casas, S., Freer, J. and Mansilla, H. D. Multivariate approach to photocatalytic degradation of a cellulose bleaching effluent. *Applied Catalysis B-Environmental* **2001**, 33(2), 89-96.
- Peyton, B. M., Wilson, T. and Yonge, D. R. Kinetics of phenol biodegradation in high salt solutions. *Water Research* **2002**, 36(19), 4811-4820.
- Peyton, G. R. and Glaze, W. H. Destruction of Pollutants in Water with Ozone in Combination with Ultraviolet-Radiation .3. Photolysis of Aqueous Ozone. *Environmental Science & Technology* **1988**, 22(7), 761-767.
- Pignatello, J. J. Dark and Photoassisted Fe³⁺-Catalyzed Degradation of Chlorophenoxy Herbicides by Hydrogen-Peroxide. *Environmental Science & Technology* **1992**, 26(5), 944-951.
- Pignatello, J. J., Liu, D. and Huston, P. Evidence for an additional oxidant in the photoassisted Fenton reaction. *Environmental Science & Technology* **1999**, 33(11), 1832-1839.
- Pignatello, J. J., Oliveros, E. and MacKay, A. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Critical Reviews in Environmental Science and Technology* **2006**, 36(1), 1-84.
- Puhakka, J. A. and Jarvinen, K. Aerobic Fluidized-Bed Treatment of Polychlorinated Phenolic Wood Preservative Constituents. *Water Research* **1992**, 26(6), 765-770.
- Pulgarin, C., Invernizzi, M., Parra, S., Sarria, V., Polania, R. and Peringer, P. Strategy for the coupling of photochemical and biological flow reactors useful in mineralization of biorecalcitrant industrial pollutants. *Catalysis Today* **1999**, 54(2-3), 341-352.
- Quezada, M., Linares, I. and Buitron, G. Use of a sequencing batch biofilter for degradation of azo dyes (acids and bases). *Water Science and Technology* **2000**, 42(5-6), 329-336.

Raja, P., Bozzi, A., Jardim, W. F., Mascolo, G., Renganathan, R. and Kiwi, J. Reductive/oxidative treatment with superior performance relative to oxidative treatment during the degradation of 4-chlorophenol. *Applied Catalysis B-Environmental* **2005**, 59(3-4), 249-257.

Rao, N. N., Dubey, A. K., Mohanty, S., Khare, P., Jain, R. and Kau, S. N. Photocatalytic degradation of 2-chlorophenol: a study of kinetics, intermediates and biodegradability. *Journal of Hazardous Materials* **2003**, 101(3), 301-314.

Rios-Enriquez, M., Shahin, N., Duran-De-Bazua, C., Lang, J., Oliveros, E., Bossmann, S. H. and Braun, A. M. Optimization of the heterogeneous Fenton-oxidation of the model pollutant 2,4-xylidine using the optimal experimental design methodology. *Solar Energy* **2004**, 77(5), 491-501.

Rivas, F. J., Beltran, F. J., Gimeno, O. and Alvarez, P. Optimisation of Fenton's reagent usage as a pre-treatment for fermentation brines. *Journal of Hazardous Materials* **2003a**, 96(2-3), 277-290.

Rivas, F. J., Beltran, F. J., Gimeno, O. and Alvarez, P. Treatment of brines by combined Fenton's reagent-aerobic biodegradation II. Process modelling. *Journal of Hazardous Materials* **2003b**, 96(2-3), 259-276.

Rush, J. D. and Bielski, B. H. J. Pulse-Radiolysis Studies of Alkaline Fe(III) and Fe(VI) Solutions - Observation of Transient Iron Complexes with Intermediate Oxidation-States. *Journal of the American Chemical Society* **1986**, 108(3), 523-525.

Sagawe, G., Lehnard, A., Lubber, M. and Bahnemann, D. The insulated solar Fenton hybrid process: Fundamental investigations. *Helvetica Chimica Acta* **2001**, 84(12), 3742-3759.

Sahinkaya, E. and Dilek, F. B. Effect of biogenic substrate concentration on chlorophenol degradation kinetics. *Journal of Chemical Technology and Biotechnology* **2006**, 81(9), 1530-1539.

Sarria, V., Kenfack, S., Guillod, O. and Pulgarin, C. An innovative coupled solar-biological system at field pilot scale for the treatment of biorecalcitrant pollutants. *Journal of Photochemistry and Photobiology a-Chemistry* **2003**, 159(1), 89-99.

Sarria, V., Parra, S., Adler, N., Peringer, P., Benitez, N. and Pulgarin, C. Recent developments in the coupling of photoassisted and aerobic biological processes for the treatment of biorecalcitrant compounds. *Catalysis Today* **2002**, 76(2-4), 301-315.

Scott, J. P. and Ollis, D. F. Integration of chemical and biological oxidation processes for water treatment: Review and recommendations. *Environmental Progress* **1995**, 14(2), 88-103.

Silva, A. M. T., Oliveira, A. C. M. and Quinta-Ferreira, R. M. Catalytic wet oxidation of ethylene glycol: kinetics of reaction on a Mn-Ce-O catalyst. *Chemical Engineering Science* **2004**, 59(22-23), 5291-5299.

Sima, J. and Makanova, J. Photochemistry of iron(III) complexes. *Coordination Chemistry Reviews* **1997**, 160, 161-189.

- SM. *Standard Methods for the examination of water and wastewater*. American Public Health Association, **1985**.
- Spigno, G., Zilli, M. and Nicoletta, C. Mathematical modelling and simulation of phenol degradation in biofilters. *Biochemical Engineering Journal* **2004**, 19(3), 267-275.
- Takeuchi, R., Suwa, Y., Yamagishi, T. and Yonezawa, Y. Anaerobic transformation of chlorophenols in methanogenic sludge unexposed to chlorophenols. *Chemosphere* **2000**, 41(9), 1457-1462.
- Tang, W. Z. and Tassos, S. Oxidation kinetics and mechanisms of trihalomethanes by Fenton's reagent. *Water Research* **1997**, 31(5), 1117-1125.
- Terada, H. Uncouplers of Oxidative-Phosphorylation. *Environmental Health Perspectives* **1990**, 87, 213-218.
- Theurich, J., Lindner, M. and Bahnemann, D. W. Photocatalytic degradation of 4-chlorophenol in aerated aqueous titanium dioxide suspensions: A kinetic and mechanistic study. *Langmuir* **1996**, 12(26), 6368-6376.
- Torrades, F., Perez, M., Mansilla, H. D. and Peral, J. Experimental design of Fenton and photo-Fenton reactions for the treatment of cellulose bleaching effluents. *Chemosphere* **2003**, 53(10), 1211-1220.
- Ullmann's. *Ullmann's Encyclopedia of Industrial Chemistry*. 5th edition, Germany: VCH Verlagsgesellschaft, **1991**.
- Ventosa, A. and Nieto, J. J. Biotechnological Applications and Potentialities of Halophilic Microorganisms. *World Journal of Microbiology & Biotechnology* **1995**, 11(1), 85-94.
- Verenich, S. and Kallas, J. Wet oxidation lumped kinetic model for wastewater organic burden biodegradability prediction. *Environmental Science & Technology* **2002**, 36(15), 3335-3339.
- Verenich, S., Laari, A. and Kallas, J. Parameter estimation and sensitivity analysis of lumped kinetic models for wet oxidation of concentrated wastewaters. *Industrial & Engineering Chemistry Research* **2003**, 42(21), 5091-5098.
- Verenich, S., Molina, V. G. and Kallas, J. Lipophilic wood extractives abatement from TMP circulation waters by wet oxidation. *Advances in Environmental Research* **2004**, 8(3-4), 293-301.
- Verenich, S., Roosalu, K., Hautaniemi, M., Laari, A. and Kallas, J. Kinetic modeling of the promoted and unpromoted wet oxidation of debarking evaporation concentrates. *Chemical Engineering Journal* **2005**, 108(1-2), 101-108.
- Vicente, M. and Esplugas, S. Calibration of the Ring Photoreactor. *Afinidad* **1983**, 40(387), 453-457.
- Wadley, S. and Waite, T. D. In: Parsons, S. (Ed), *Advanced Oxidation Processes for Water and Wastewater Treatment*. London: IWA Publishing, **2004**, pp 111-136.

- Walling, C. Fentons Reagent Revisited. *Accounts of Chemical Research* **1975**, 8(4), 125-131.
- Wei, C. Photodechlorination mechanism of DDT in a UV/surfactant system. *Environmental Science & Technology* **1999**, 33(3), 421-425.
- WHO. *Environmental Health Criteria 93. Chlorophenols other than pentachlorophenol*. World Health Organization, Geneva, Switzerland, **1989**.
- WHO. *Lack of water and inadequate sanitation*. World Health Organization. **2005**. From <http://www.who.int/en/>
- Wilderer, P. A. *Sequencing batch biofilm reactor technology. Harnessing biotechnology for the 21st century*. Ladisch, M. R. and Bose, A., (Eds). American Chemical Society, **1992**.
- Wilderer, P. A., Irvine, R. L. and Goronszy, M. C. *Sequencing Batch Reactor Technology*. IWA Publishing, London, **2001**.
- Wilderer, P. A. and McSwain, B. S. The SBR and its biofilm application potentials. *Water Science and Technology* **2004**, 50(10), 1-10.
- Wingender, J., Neu, T. R. and Flemming, H.-C., Eds. *Microbial Extracellular Polymeric Substances: Characterization, Structure and Function*. Berlin., Springer, **1999**.
- Yeber, M. C., Rodriguez, J., Freer, J., Baeza, J., Duran, N. and Mansilla, H. D. Advanced oxidation of a pulp mill bleaching wastewater. *Chemosphere* **1999**, 39(10), 1679-1688.
- Yoong, E. T., Lant, P. A. and Greenfield, P. F. In situ respirometry in an SBR treating wastewater with high phenol concentrations. *Water Research* **2000**, 34(1), 239-245.
- Zarook, S. M. and Shaikh, A. A. Analysis and comparison of biofilter models. *Chemical Engineering Journal* **1997**, 65(1), 55-61.
- Zepp, R. G., Faust, B. C. and Hoigne, J. Hydroxyl Radical Formation in Aqueous Reactions (Ph 3-8) of Iron(II) with Hydrogen-Peroxide - the Photo-Fenton Reaction. *Environmental Science & Technology* **1992**, 26(2), 313-319.

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*Chapter 9: Abbreviation and
Notation*

List of Abbreviations

2,4-D:	2,4-dichlorophenoxyacetic acid
2,4-DCP:	2,4-dichlorophenol
4-CP:	4-chlorophenol
AOPs:	Advanced Oxidation Processes
AOS:	Average Oxidation State (mol O ₂ .mol C ⁻¹)
AOTs:	Advanced Oxidation Technologies
ASM1:	Activated Sludge Model 1
ASTM	American Society for Testing and Materials
ATP:	Adenosine 5'-triphosphate
BOD:	Biochemical Oxygen Demand (mg.L ⁻¹)
BOD ₅ :	Biochemical Oxygen Demand after 5 days (mg.L ⁻¹)
CCD:	Central Composite Design
COD:	Chemical Oxygen Demand (mg.L ⁻¹)
COMMPS:	Combined Monitoring-based and Modelling-based Priority Setting
DO:	Dissolved Oxygen (mg.L ⁻¹)
EC:	European Commission
EC ₅₀ :	Median Effective Concentration (%)
EDCs:	Endocrine Disrupting Chemicals
EPER:	European Pollutant Emission Register
EU:	European Union
HRT:	Hydraulic Retention Time (hour; h)
ISA:	Ion Strength Adjustor
ISE:	Ion Selective Electrode
NBCS:	Non-Biodegradable Chlorinated Species
OC:	Consumed Oxygen per unit volume (mg.L ⁻¹)
ODEs:	Ordinary Differential Equations
OLR:	Organic Loading Rate (mg.L ⁻¹ .h ⁻¹)
OUR:	Oxygen Uptake Rate (mg.L ⁻¹ .h ⁻¹)
PAHs:	Polycyclic Aromatic Hydrocarbons
Ph-F.	Photo-Fenton
PPCPs:	Pharmaceuticals and Personal Care Products
PSA:	Plataforma Solar de Almería
POPs:	Persistent Organic Pollutants

RSM:	Response Surface Methodology
SBR:	Sequencing Batch Reactor
SBBR:	Sequencing Batch Biofilter Reactor
SCWO:	Supercritical Wet Oxidation
SEM:	Scanning Electron Microscope
SHE:	Standard Hydrogen Electrode
SUR	Substrate Uptake Rate
TOC:	Total Organic Carbon (mg.L ⁻¹)
TSS:	Total Suspended Solids (mass/unit volume)
TVSS:	Total Volatile Suspended Solids (mass/unit volume)
UV:	Ultraviolet radiation
Vis:	Visible light
WFD:	Water Framework Directive
WO:	Wet Oxidation
WPO:	Wet Peroxide Oxidation

Notation

[4-CP] ₀ :	4-chlorophenol initial concentration (mg.L ⁻¹ or mmol.L ⁻¹)
[Fe ²⁺] ₀ :	iron (II) initial concentration (mg.L ⁻¹ or mmol.L ⁻¹)
[H ₂ O ₂] ₀ :	hydrogen peroxide initial concentration (mg.L ⁻¹ or mmol.L ⁻¹)
S _O :	concentration of oxygen in solution (mg.L ⁻¹)
S _S :	concentration of biodegradable substrate in solution (mg.L ⁻¹)
T:	Temperature (°C)
t _{30W} :	normalized illumination time (min).
V _i :	irradiated volume (L).
V _T :	total system volume (L).
X:	concentration of microorganisms (mass/unit volume)
Q:	received or transmitted energy per volume (kJ.L ⁻¹).

Notation in Mechanistic models (Section 3.5):

(COD-BOD_5) : Concentration of non-biodegradable compounds (mg.L^{-1}).

$[(\text{COD-BOD}_5)]_0$: Initial Concentration of non-biodegradable compounds (mg.L^{-1}).

$(\text{COD-BOD}_5)_r$: Concentration of non-biodegradable species recalcitrant to oxidation (mg.L^{-1}).

$[\text{BOD}_5]$: Concentration of readily biodegradable matter (mg.L^{-1}).

$[\text{BOD}_5]_0$: Initial concentration of readily biodegradable matter (mg.L^{-1}).

$[\text{COD}]$: Concentration of organic matter (mg.L^{-1}).

$[\text{COD}]_0$: Concentration of organic matter (mg.L^{-1}).

$[\text{H}_2\text{O}_2]_0$: hydrogen peroxide initial concentration (mg.L^{-1}).

$[\text{H}_2\text{O}_2]_t$: hydrogen peroxide concentration at time “ t ” (mg.L^{-1}).

k_i : pseudo-stoichiometric or pseudo-kinetic constants

$K_{\text{H}_2\text{O}_2}$: hydrogen peroxide half-saturation concentration (mg.L^{-1})

$k_{\text{H}_2\text{O}_2}$: hydrogen peroxide decomposition pseudo-kinetic constant

*Chapter 10: Related
Publications and Works*

Publications

- Jordi Bacardit, Julia Stötzner, Esther Chamarro and Santiago Esplugas. *Effect of salinity on photo-Fenton process*. Accepted for its publication in the ACS's Industrial and Engineering Chemistry Research. Publication expected in November **2007**. DOI: 10.1021/ie070154o.
- Jordi Bacardit, Isabel Oller, Manuel I. Maldonado, Esther Chamarro, Sixto Malato, and Santiago Esplugas. *Simple Models for the control of Photo-Fenton by monitoring H₂O₂*. Accepted for publication in the Journal of Advanced Oxidation Technologies (JAOT) in the July **2007** issue.
- Jordi Bacardit, Verónica García-Molina, Bernardí Bayarri, Jaume Giménez, Esther Chamarro, Carme Sans, Santiago Esplugas. *Coupled photochemical-biological system to treat biorecalcitrant wastewater*. Published in the Proceedings book of the **2006** AOP4 Conference in Goslar, Germany. Submitted for its publication in the IWA's Water Science and Technology.
- Jordi Bacardit, Anders Hultgren, Verónica García-Molina, Santiago Esplugas. *Biodegradability Enhancement of Wastewater Containing 4-Chlorophenol by Means of Photo-Fenton*. Journal of Advanced oxidation Technologies (JAOT), **2006**, Volume 9(1), 27-34.
- Jordi Bacardit, Oscar González, Renato Falcao, Verónica García-Molina, Sandra Contreras, Ester Chamarro, Carme Sans, Santiago Esplugas. *Start-up of a Coupled chemical-biological system for the abatement of 4-chlorophenol. Preliminary Study*. Photocatalytic and Advanced Oxidation Processes for Treatment of Air, Water, Soil and Surfaces. Redox Technologies, Inc. **2005**. ISBN: 0-9738746-0-0.

Still in project:

- Mechanistic Models for the Oxidation by Photo-Fenton
- Characterization of a Sequencing Batch Biofilter Reactor (SBBR) combined with the AOP Photo-Fenton

Communications to Conferences

- Jordi Bacardit, Julia Stötzner, Verónica García-Molina, Esther Chamarro and Santiago Esplugas. *Effect of salinity on photo-fenton process*. Poster presentation in the 4th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA 4), Gran Canaria, Spain, November **2006**.
- Jordi Bacardit, Verónica García-Molina, Bernardí Bayarri, and Santiago Esplugas. *Coupled photochemical-biological system to treat biorecalcitrant wastewater*. Poster presentation in the AOP4 - 4th Conference on Oxidation Technologies for Water and Wastewater Treatment. Goslar, Germany May **2006**.
- Jordi Bacardit, Anders Hultgren, Oscar González, Renato Falcao, Carme Sans, Esther Chamarro and Santiago Esplugas. *Biodegradability Enhancement of wastewater containing 4-chlorophenol by means of photo-Fenton*. Presented as oral presentation in the Second European Conference on Oxidation and Reduction technologies for ex-situ and in-situ treatment of water, air and soil (ECOR-2). Göttingen, Germany, 12-15 June, **2005**.
- Jordi Bacardit, Óscar González, Verónica García-Molina, Renato Falcao, Sandra Contreras, Carme Sans, Esther Chamarro and Santiago Esplugas. *Start-up of a coupled chemical-biological treatment of aqueous solutions of 4-monochlorophenol*. Presented as a poster and in the 10th International Conference on Advanced Oxidation Technologies for Water and Air Remediation (AOTs-10), San Diego, California, USA, 24-28 October **2004**.
- Jordi Bacardit, Renato Falcao, Verónica García-Molina, Esther Chamarro, Carme Sans and Santiago Esplugas. *Comparison between Photo-Fenton and Wet Peroxide Oxidation for the removal of 4-monochlorophenol*. Poster presentation in the 3rd European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA 3), Barcelona, Spain, 30 June-2 July **2004**.