ENHANCED EXCESS SLUDGE DIGESTION USING THERMAL AND CHEMICAL PETREATMENTS

Esther Torrens Serrahima

Dipòsit Legal: T. 1420-2013

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DOCTORAL THESIS

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I, Dr. José Font Capafons, associate professor in the Department of Chemical Engineering of the Rovira i Virgili University,

CERTIFY:

That the present study, entitled "ENHANCED EXCESS SLUDGE DIGESTION USING THERMAL AND CHEMICAL PRETREATMENTS", presented by Esther Torrens Serrahima for the award of the degree of Doctor, has been carried out under my supervision at the Department of Chemical Engineering of this university, and that it fulfils all the requirements to be eligible for the European Doctorate Label.

Tarragona, 27th May 2013

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The most beautiful day: Today
The easiest thing: To make a mistake
The biggest obstacle: Fear
The gravest error: To give up, to despair
The root of all evils: Egoism
The most beautiful occupation: Work
The worst route to follow: Faintheartedness
The best teachers: Children
The first necessity: To communicate
The greatest happiness: To be useful to others
The greatest mystery: Death
The worst defect: Bad temper
The most dangerous being: The liar'
The most wretched feeling: The grudge
The most beautiful gift: Forgiveness
The most indispensable: Home
The quickest way: The correct one
The most comfortable feeling: Interior peace
The most powerful weapon: The smile
The best remedy: Optimism
The greatest satisfaction: The duty done
The most powerful force: Faith
The most needed beings: Parents
The most beautiful of all: Love

(Mother Teresa)

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Resum

Aquesta tesi versa sobre la problemàtica de la gestió de llots de purga generats a les depuradores urbanes. L'adopció de la directiva Europea sobre tractament d'aigües residuals urbanes 91/271/EEC imposa que els llots de depuradora siguin tractats. El procés clàssic d'incineració no pot ser acceptat per a una quantitat tan elevada de llots produïts dins de la Unió Europea. En particular la directiva 86/278/EEC, referent als llots de depuradora, regula l'ús i les propietats dels llots estabilitzats, tant si són reutilitzats com si són dipositats. Concretament la directiva recomana la reutilització i valorització de fangs en front a la deposició en abocador.

La proposta d'aquesta tesi està dirigida a desenvolupar estratègies per a la reutilització i valorització de llots de depuradora. Es pretén desenvolupar diferents processos per reduir tant la toxicitat com la quantitat de llots generats, i simultàniament estudiar la seva transformació en vectors d'energia verda, com ara el metà.

Actualment, a digestió anaeròbia és el procés de tractament de llots més utilitzat en les estacions depuradores d'aigües residuals (EDAR) urbanes per estabilitzar els fangs generats en l'etapa primària i secundària de tractament d'aigües. Els processos anaeròbics més estesos es duen a terme a temperatura mesòfila (~33ºC), ja que requereixen menys energia i són més estables. El procés de digestió anaeròbia, en les gammes termòfiles es caracteritza per reaccions bioquímiques accelerades, una producció de biogàs superior i una major taxa de creixement dels microorganismes que porten a una possible disminució del temps de retenció hidràulica (TRH), cosa que pot reduir l'espai del reactor. D'altra banda, la digestió anaeròbica termòfila pot conduir a la obtenció de biosòlids de classe A (és a dir; <1000 NMP de coliformes fecals/g TS; < 3 NMP/4g TS de *Salmonella*), classificació que es dóna a llots adequats per a ús fertilitzant. No obstant això, les condicions termòfiles poden no ser suficients per garantir les condicions sanitàries imposades per aquesta classe de biosòlids, que previsiblement serà obligatòria en un futur proper als abocadors d'Europa.

La digestió anaeròbia és l'oxidació microbiològica de la matèria orgànica sense la presència d'aire. El procés consisteix en un conjunt coordinat i interdependent de reaccions promogudes per diferents poblacions de bacteris que degraden la matèria orgànica en productes intermedis, al seu torn convertits en metà. El procés de digestió es divideix en quatre etapes: hidròlisi, acidogènesi, acetogénesis i la metanogènesi. La hidròlisi és considerada l'etapa limitant de la digestió anaeròbica. Per tal de millorar la digestió anaeròbica, una de les estratègies a seguir és precisament maximitzar aquesta etapa, en la que es du a terme la conversió de les partícules i substàncies complexes solubles en productes solubles com ara

aminoàcids, sucres i àcids grassos per enzims extracel lulars secretats per els microorganismes. Pretractaments químics, biològics, mecànics i tèrmics i la seva combinació s'han investigat amb la finalitat de millorar aquesta etapa. La hipòtesis de treball, es basa en aconseguir incrementar la matèria biodegradable disponible per a que les altres etapes de la digestió es portin a terme i, per tant, augmentar la l'eficiència de la digestió, reduint la quantitat de sòlids resultants, incrementar la producció de biogàs; és a dir, bàsicament obtenir un fang més estable.

Tot i haver diferents estudis previs de l'efecte dels tractaments, n'hi ha pocs que s'hagin combinat amb la digestió termòfila i que hagin avaluat la higienització del fang. Es pensa que una combinació de digestió termòfila utilitzant un llot tèrmicament o químicament pretractat pot ser una opció pràctica per a aquelles EDAR amb la digestió mesòfila implementada, ja que només requeriria un re-disseny mínim. Aquest treball té per objecte l'avaluació d'aquesta opció.

El fang a tractar ha estat proporcionat per la depuradora urbana de Reus, i correspon a una barreja de 35% de llots procedents de tractament aeròbic secundari i un 65% de tractament fisicoquímic, prèviament espessits, composició típica que genera aquesta depuradora. L´inòcul anaerobi mesòfil ha esta proporcionat també per la depuradora obtingut d'un dels seus digestors, i l'inòcul termòfil a 55ºC es va obtenir aclimatant fang anaeròbic mesòfil.

S'ha construït una planta pilot a escala de laboratori per a la digestió anaeròbia de fangs amb tres reactors operant en semi-continu, totalment independents, on s'ha estudiat la digestió anaeròbica en rang mesòfil i a tres temperatures termòfiles (50, 55 i 60ºC). També s'ha construït una planta pilot autotèrmica on s'ha estudiat el tractament aerobi en rang termòfil també en condicions d'operació semi-contínues.

Amb l'objectiu de millorar la digestió anaeròbica termòfila, s'han avaluat l'efecte del pretractament tèrmic sobre el fang en un rang de 30-200ºC així com l'efecte del pretractament químic amb peròxid d'hidrogen, afegit contínuament a la dosi de 0-1.0 g de H_2O_2/g DQO a 30ºC i 60ºC. El temps de reacció es va fixar finalment en 30 min, però també va ser avaluat. Per mesurar la digestió del fang pretractat s'han realitzar tests per determinar el potencial de biometà en condicions termòfiles.

L'impacte més notable en el pretractament tèrmic és la solubilització de la matèria orgànica, que augmenta cada vegada més amb la temperatura. Es pot observar que la producció de biogàs es veu reforçada per pretractament tèrmic, excepte per a 200ºC. Després d'avaluar l'efecte del temps de pretractament, es va decidir establir la durada del pretractament tèrmic a 1 h a la temperatura desitjada, ja que un augment addicional del temps de tractament, especialment a temperatures inferiors a 110ºC, no va millorar la solubilització de la matèria orgànica. Amb tan sols 80ºC tant els STD (sòlids

totals dissolts) com els SVD (sòlids volàtils dissolts) van augmentar fins a quatre vegades respecte al contingut inicial i a 170ºC es va aconseguir fins a set vegades més. Només el fang pretractat per sobre de 110 º C pot ser classificat com a biosòlid de classe A. Tot i així, a 50ºC ja es va observar una considerable reducció de patògens amb gairebé el 50% de la reducció *d'Escherichia Coli* i nul·la presència de *Salmonella.*

Encara que no s'observa eliminació rellevant de matèria orgànica després de l'addició de peròxid d'hidrogen a 30ºC a concentracions menors de 0.87 g de H_2O_2/g DQO, sembla produir-se una solubilització que es tradueix en un augment de la DQO soluble i els STD. La concentració de 0.03 g de H_2O_2/g DQO és suficient per augmentar la DQO soluble en més d'un 70%. A concentracions més altes, 1.16 i 1.45 g de H_2O_2/g DQO, ja s'observa la destrucció de matèria orgànica. El peròxid d'hidrogen promou la destrucció de *Salmonella*, però pràcticament no té cap efecte sobre les densitats de coliformes fecals, fins i tot a la dosi més alta provada de 0.6 g de H_2O_2/g DQO. Cal assenyalar que la addició del peròxid implica augment de volum del residu, ja que el peròxid es sol trobar en solució aquosa.

Per als estudis en digestió semi-contínua anaeròbica termòfila, s'han escollit el pretractament tèrmic a 80ºC i la peroxidació amb una dosi de 0.2 g de H_2O_2/g DQO.

Pel que fa al tractament aeròbic termòfil, s'ha observat una alta reducció de la DQO, a un valor mitjà de 62%, tot i que es van observar fluctuacions importants. Al seu torn, el ST (sòlids totals) i el contingut en SV (sòlids volàtils) va disminuir fins a un 34% i 40%, respectivament. El fang digerit es pot classificar com a bisòlid de classe A. Malgrat la desaparició de la matèria orgànica, no es van poder aconseguir veritables condicions autotèrmiques ja que per mantenir la temperatura termòfila (55ºC), es va haver d'aportar calefacció extra. Això va ser causat per la grandària del reactor, en tractar volums de fangs tant petits (5 L), l'àrea en relació al volum és massa gran i produeix una pèrdua excessiva de calor per les parets. No obstant això, la eliminació de la DQO assolida assegura (en el balanç d'energia) que en plantes a escala superior (>1 m^3) treballarien en funcionament auto-sostingut.

S'ha estudiat la digestió anaeròbica termòfila a 50ºC, 55ºC i 60ºC a TRH d'entre 15 a 25 dies, però aquestes condicions no són suficients per a la destrucció de patògens a nivell de biosòlids de classe A. La temperatura a 60ºC ha resultat poc òptima donat la poca producció de biogàs i no presenta avantatges en comparació amb les altres temperatures estudiades en termes d'eliminació de sòlids. El període d'aclimatació per canviar les condicions de temperatura al reactor anaeròbic ha estat més llarg de l'esperat. Al voltant de 5 vegades el TRH han estat necessaris per aclimatar les condicions de 60ºC a 55ºC en una TRH = 20 dies. En canvi l'aclimatació dels reactors als canvis de TRH afecten molt menys.

S'ha estudiat també la digestió anaeròbica dividint-la en dues etapes individuals, primer una etapa termòfila (55ºC, TRH=5 dies) i una segona etapa mesòfila (33ºC, TRH=15 dies). Si comparem aquest sistema dual amb els individuals mesòfils i termòfils a TRH=20dies, els millors resultats es van obtenir en el sistema dual. Aquests últims van mostrar un millor rendiment en termes de destrucció de DQO (66%), SV (48%) i ST (63%). Igualment, millora l'estabilitat del procés ja que el contingut de matèria orgànica soluble i d'AGV (àcids grassos volàtils) del efluent final es menor. Sembla que la digestió en dues etapes és prou eficient per obtenir biosòlids de classe A, però només es va realitzar un anàlisi. El principal inconvenient del sistema dual és que es necessita una construcció d'un nou reactor anaeròbic en el cas d'adaptació de les instal·lacions existents.

Es va estudiar l'efecte del pretractament tèrmic a 80ºC durant 1 h, i també l'efecte del pretractament químic amb peròxid d'hidrogen a una dosi de 0.2 g de H_2O_2/g COD a 30ºC en combinació amb la digestió anaeròbia semi-contínua a tres temperatures diferents, 33ºC (rang mesòfil), 50ºC i 55ºC (rang termòfil) amb un TRH=20 dies. No es pot concloure cap efecte clar pel que fa als resultats obtinguts en l'avaluació la reducció dels sòlids o matèria orgànica dels diferents rangs de temperatura estudiats, però el l'efluent final en rangs termòfils sempre presenta una càrrega de matèria soluble més gran que en el mesòfil. Els pretractaments semblen augmentar la producció de biogàs, especialment en el rang mesòfil, on s'observa un augment del 60% quan s'alimenta amb fang pretractat tèrmicament i d'un 52% quan és pretractat químicament. En el rang termòfil de 55ºC l'increment de biogàs és al voltant d'un 22% per tèrmic i un 8% per el químic. El contingut de metà del biogàs és sempre superior a 68% sent un biogàs d'alta qualitat per al seu possible ús en les unitats de cogeneració.

La màxima eliminació de SV (sòlids volàtils) s'obté amb el tractament anaerobi mesòfil de 33ºC dels llots de pretractats tèrmicament a 80ºC, amb una eliminació del 60%. No obstant això, es recomana treballar a 55ºC, ja que si també s'avalua el contingut de patògens, és el que presenta els resultats més òptims. S'observa que el contingut d'*E-coli* està per sota dels requisits dels biosòlids de classe A, es va trobar presència de *Salmonella* en l'efluent final malgrat que no es va detectar en els fangs pretractats a 80ºC. Sembla ser que en la digestió es podria produir una reactivació dels patògens, però l'anàlisi dels patògens en la fase estacionària de l'experiment es va realitzar només una vegada, i caldrien més anàlisis per confirmar aquesta hipòtesis.

La transformació dels digestors mesòfils a termòfils juntament amb la unitat de pretractament tèrmic en condicions no severes (T<110ºC, 1 h) és econòmicament viable ja que l'augment dels costos operació són àmpliament compensats per l'increment de la producció de biogàs i l'ús dels llots estabilitzats per a ús agrícola. Aquesta opció requereix una re-enginyeria mínima de les plantes i és especialment interessant per a les

plantes amb unitats de cogeneració d'energia ja aplicades. En aquest tipus de plantes l'estalvi s'estima en 1 € per habitant equivalent i any. Aquest estalvi cobriria qualsevol inversió necessària, fins i tot un sistema de cogeneració, amb un període de recuperació de menys de quatre anys.

Summary

This thesis deals with the problem of excess sludge management generated in urban wastewater treatment plants. The adoption of the European directive on urban wastewater treatment 91/271/EEC requires that sewage sludge has to be treated. The classic incineration process can not be accepted for such a large quantity of sludge produced in the European Union. In particular, Directive 86/278/EEC concerning sewage sludge regulates the use and properties of stabilized sludge, whether reused or deposited. Specifically, the board recommended the reuse and recovery of sludge in facing elimination at the tip.

The proposal of this thesis is to develop strategies for reuse and upgrading of sewage sludge. It aims to develop different processes for reducing both the toxicity and the amount of sludge produced and simultaneously study their transformation into green energy vectors such as methane.

Anaerobic digestion is a sludge treatment process used in wastewater treatment plants (WWTP) to stabilize urban sludge generated at the stage of primary and secondary water treatment. The most common anaerobic processes are carried out at mesophilic temperature (~33°C) as they require less energy and are more stable. But the anaerobic digestion at thermophilic ranges is characterized by accelerated biochemical reactions, higher biogas production and higher growth rate of microorganisms that may lead to a decrease in the hydraulic retention time (HRT), which can reduce the volume reactor. Moreover, thermophilic anaerobic digestion can lead to the production of Class A biosolids (i.e. , <1000 MPN fecal coliforms/g TS; <3 NMP/4g *Salmonella*), a classification given to the sludge considered for suitable fertilize use. However, thermophilic conditions may not be sufficient to ensure sanitary conditions imposed by this type of biosolids, which should be expected in the near future in Europe landfills.

Anaerobic digestion is the microbial oxidation of organic matter in the absence of air. The process consists of a set of coordinated and interdependent reactions promoted by different populations of bacteria that degrade organic intermediates in turn converted into methane. The digestion process is divided into four stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis. Hydrolysis is considered the limiting step in anaerobic digestion. To improve the anaerobic digestion, one of the strategies to be followed is maximizing the hydrolysis stage; in this step, it occurs the conversion of complex substances into soluble and simpler particles such as amino acids, sugars and fatty acids by extracellular enzymes secreted by microorganisms. Pre-treatment chemical, biological and mechanical heat and their combination have been investigated to improve this stage. Chemical, biological, mechanical an thermal sludge pretreatments and their combination have been investigated to improve this

step. The working hypothesis is based on increase the biodegradable material available for the other digestion stages and therefore increasing the efficiency of digestion by reducing the amount of solids, then enhancing biogas production; basically to obtain a more stable sludge.

Despite several previous studies over the effect of pretreatments, there are few that have been combined with thermophilic digestion and have evaluated sludge sanitation. It is thought that a combination of thermophilic digestion using a thermally or chemically pretreated sludge can be a practical option for those WWTP with an implemented mesophilic digestion as it only would require a minimal re-design. This work aims at evaluating this option.

The raw sludge was provided by the municipal WWTP of Reus, and corresponds to a mixture of 35% of WAS and 65% of sludge from the primary physicochemical treatment, both previously thickened. This relation is the typical composition generated by this WWTP. The mesophilic anaerobic inoculum was also provided by Reus WWTP from one of its anaerobic digesters. The thermophilic innoculum at 55°C was obtained by acclimating the mesophilic anaerobic sludge.

It was constructed a laboratory scale pilot plant for the anaerobic digestion of sludge with three independent reactors operating in a semi-continuous mode. It was studied the mesophilic anaerobic digestion at 33ºC and three thermophilic anaerobic temperatures (50, 55 and 60°C). It was also built a pilot plant where autothermal aerobic treatment was also studied at thermophilic range, at semi-continuous operation.

With the aim of improving the thermophilic anaerobic digestion, it was evaluated the effect of thermal pretreatment over the sludge in the range of 30-200 ° C and the effect of chemical pretreatment with hydrogen peroxide added continuously at a dose of 1.0 g of H_2O_2/g COD at 30ºC and 60ºC. The reaction time was set at 30 min, but time influence was also explored. To measure the anaerobic digestion performance of pretreated sludge, biomethane potential tests (BMP) were evaluated at thermophilic conditions.

The most noticeable impact on the thermal pretreatment is the solubilisation of organic matter, which increases with raising temperature. It can be seen that biogas production is enhanced by thermal pretreatment, except at 200°C. After evaluating the effect of pretreatment time, it was decided to establish the duration of the thermal pretreatment at 1 h, as an additional increase of treatment time, especially at temperatures below 110°C, did not improve the solubilization of organic matter. With only 80°C, both TDS and DVS were more than four times larger than the initial content, and at 170°C it was achieved up to seven times. Only sludge pretreated above 110°C can be classified as Class A. biolsolid. Anyway, at only 50ºC, it was observed a considerable decline of pathogens with almost 50% of the reduction of *Escherichia coli* and null presence of *Salmonella*.

Although irrelevant organic removal is observed after the addition of hydrogen peroxide at 30ºC at concentration below 0.87 gH_2O_2/gCOD, it seems to undergo a solubilisation of the solid part, which results in an increase of soluble COD and TDS. A dose of 0.03 g H_2O_2/g COD is enough to solubilize more than 70% of the initial soluble COD, which goes from 9% to 15% of the total COD. At higher concentrations, 1.16 and 1.45 g H_2O_2/g COD, organic destruction is already found. Hydrogen peroxide highly promotes the destruction of *Salmonella*, but practically has no effect on the densities of fecal coliforms, even at the highest dose tested of 0.6 g H_2O_2/g COD. Note that the addition of hydrogen implies increasing of the waste volume, as the peroxide is usually found in aqueous solution

For studies in the semi-continuous anaerobic thermophilic digestion, It was selected thermal pretreatment at 80ºC and peroxidation with a dose of 0.2 g H_2O_2/g COD.

Regarding the thermophilic aerobic treatment, a high reduction of COD, average of 62%, was found although significant fluctuations were also observed. In turn, the TS and VS removal content were up to 34% and 40%, respectively. The digested sludge can be classified as Class A. biosolid. Despite disappearance of organic matter does exist, true autothermal conditions were not achieved as extra-heating was added to sustain the thermophilic temperature. This was caused by the small size of the bench-scale reactor (5 L), with too high area to volume ratio, which leads to excessive wall heat loss. However, the COD removal achieved assures (by energy balance) that higher scale plants (> 1 m^3) would work under auto-sustained operation.

Thermophilic anaerobic digestion was studied at 50°C, 55°C and 60°C and HRT from 15 to 25 days, but these conditions not yet enough for obtaining class A biosolids. Temperature of 60°C leads to poor results, as it produced very low biogas generation and had no advantages when compared with other temperatures studied in terms of solids removal. The period of acclimation due to changing temperature conditions in the anaerobic reactor was longer than expected. About 5 times the HRT were necessary to acclimate conditions from 60°C to 55°C with an HRT=20 days. Instead, changes in HRT affect less to the system stability.

It was also studied the anaerobic digestion dividing the overall process into two individual stages, the first stage thermophilic (55°C, HRT=5 days) and a second. mesophilic stage (33°C, HRT=15 days). Comparing dual digestion with single mesophilic and thermophilic at HRT=20 days, the best results were obtained in the dual system. The latter showed a better performance in terms of destruction of COD (66%), VS (48%) and TS (63%). Also process stability was improved as the organic content of the effluent, like VFA and soluble COD where lower. It seems that the two-stage digestion is efficient enough to obtain Class A biosolids, but only one analysis was performed.

The main disadvantage of the dual system is that it requires the construction of a new anaerobic reactor in the case of adapting existing facilities.

It was studied the effect of the thermal pre-treatment at 80ºC for 1 h and also the effect of the chemical pre-treatment with hydrogen peroxide at a dose of 0.2 $gH_2O_2/gCOD$ at 30ºC in combination with the anaerobic digestion at three different temperatures, 33ºC (mesophilic range), and two different thermophilic temperatures 50ºC and 55ºC with an hydraulic retention time of 20 days. No clear effect can be concluded regarding the evaluation of reduction of solid or organic matter at the different temperature ranges studied, but the soluble organic matter in the final effluent at thermophilic range was always higher than in the mesophilic range. Pretreatments appear to enhance the production of biogas, especially in the mesophilic range, where there is a 60% of increase when the digester was fed with thermally pretreated sludge and 52% when chemically pretreated. In the thermophilic range of 55°C, the increase in biogas production was around 22% and 8% for thermal and peroxidated pretreatment, respectively. Methane content of the biogas is always higher than 68% being a high quality biogas for possible use in co-generation units.

The maximum VS removal is obtained with the mesophilic anaerobic treatment at 33ºC of thermal pre-treated sludge at 80ºC, with 60% of VS removal. However, it is recommended to work at 55 ºC, as if pathogen content is also assessed, thermophilic digestion at 55ºC presents better results. It is observed that the content of *E-coli* is below the requirements of Class A biosolids, however *Salmonella* was found in the final effluent despite it was not detected at sludge previously pre-treated at 80ºC. Apparently in digestion it may result in reactivation of pathogens, but the analysis of pathogens in the stationary phase of the experiment was performed only once, and it would take more analyses to confirm this hypothesis.

The transformation of mesophilic units into thermophilic units adding a thermal pre-treatment at non severe conditions (T<110ºC, 1 h) is economically viable as the higher operating costs are widely compensated by the increase of biogas production and the extended use of the stabilised sludge for agricultural land use. This option requires minimum re-engineering of the plants and is especially interesting for plants with power cogeneration units already implemented. As for those, the savings can be estimated in 1 € per equivalent inhabitant and year, which must cover any investment needed with a payback period of less than four years, even when a cogeneration plant must be build up.

Resumen

Esta tesis trata sobre la problemática de la gestión de lodos de purga generados en las depuradoras urbanas. La adopción de la directiva Europea sobre tratamiento de aguas residuales urbanas 91/271/EEC impone que los lodos de depuradora sean tratados. El proceso clásico de incineración no puede ser aceptado para una cantidad tan elevada de lodos producidos dentro de la Unión Europea. En particular la directiva 86/278/EEC referente a los lodos de depuradora, regula el uso y las propiedades de los lodos estabilizados, tanto si son reutilizados como si son depositados. Concretamente la directiva recomienda la reutilización y valorización de lodos frente a la deposición en vertedero.

La propuesta de esta tesis está dirigida a desarrollar estrategias para la reutilización y revalorización de lodos de depuradora. Se pretende desarrollar diferentes procesos para reducir tanto la toxicidad como la cantidad de lodos generados, y simultáneamente estudiar su transformación en vectores de energía verde, tales como el metano.

La digestión anaerobia es el proceso de tratamiento de lodos más utilizado en las estaciones depuradoras de aguas residuales (EDAR) urbanas para estabilizar los lodos generados en la etapa primaria y secundaria del tratamiento de aguas. Los procesos anaeróbicos más extendidos se llevan a cabo a temperatura mesófila (~33ºC) ya que requieren menos energía y son más estables. El proceso de digestión anaerobia en las gamas termófilas se caracteriza por reacciones bioquímicas aceleradas, una producción de biogás superior y una mayor tasa de crecimiento de los microorganismos que llevan a una posible disminución del tiempo de retención hidráulico (TRH), lo que puede reducir el volumen del reactor. Por otra parte, la digestión anaeróbica termófila puede conducir a la obtención de biosólidos de clase A (es decir, <1000 NMP de coliformes fecales /g ST; <3 NMP/4g ST de *Salmonella*), clasificación que se da a lodos adecuados para a su uso como fertilizante. Sin embargo, las condiciones termófilas pueden no ser suficientes para garantizar las condiciones sanitarias impuestas para esta clase de biosólidos, que previsiblemente será obligatoria en un futuro próximo en vertederos de Europa.

La digestión anaerobia es la oxidación microbiológica de la materia orgánica sin la presencia de aire. El proceso consiste en un conjunto coordinado e interdependiente de reacciones promovidas por diferentes poblaciones de bacterias, que degradan la materia orgánica en productos intermedios, a su vez convertidos en metano. El proceso de digestión se divide en cuatro etapas: hidrólisis, acidogénesis, acetogénesis y la metanogénesis. La hidrólisis es considerada la etapa limitante de la digestión anaeróbica. Para mejorar la digestión anaeróbica una de las estrategias a seguir es precisamente maximizar esta etapa, en la que se

lleva a cabo la conversión de las partículas y sustancias complejas solubles en productos solubles i/o más simples tales como aminoácidos, azúcares y ácidos grasos por parte de enzimas extracelulares secretados por los microorganismos. Se han estudiado pretratamientos químicos, biológicos, mecánicos y térmicos y su combinación con el fin de mejorar esta etapa. La hipótesis de trabajo, se basa en conseguir incrementar la materia biodegradable disponible para que las otras etapas de la digestión se lleven a cabo y, por lo tanto, aumentar la eficiencia de la digestión, reduciendo la cantidad de sólidos resultantes, incrementar la producción de biogás; es decir, básicamente obtener un fango más estable

A pesar de existir diferentes estudios previos del efecto de los pretratamientos sobre el fango, hay pocos que se hayan combinado con la digestión termófila y que hayan evaluado la higienización del lodo. Se piensa que una combinación de digestión termófila utilizando un lodo térmicamente o químicamente pretratado puede ser una opción práctica para aquellas EDAR con la digestión mesófila implementada, ya que sólo requeriría un rediseño mínimo. Este trabajo tiene por objeto la evaluación de esta opción.

El lodo a tratar fue suministrado por la depuradora urbana de Reus, y corresponde a una mezcla de 35% de lodos procedentes de tratamiento aeróbico secundario y un 65% de tratamiento fisicoquímico, previamente espesados, composición típica que genera esta depuradora. El inóculo anaerobio mesófilo fue proporcionado también por la depuradora de uno de sus digestores, y el inóculo termófilo a 55ºC se obtuvo aclimatando el lodo anaeróbico mesófilo.

Se construyó una planta piloto a escala de laboratorio para la digestión anaerobia de fangos con tres reactores operando en estado semi-continuo totalmente independientes donde se estudió la digestión anaeróbica en rango mesófilo y a tres temperaturas termófilas (50, 55 y 60ºC). También se construyó una planta piloto autotérmica donde se estudió el tratamiento aerobio en rango termófilo también en condiciones de operación semi-continuas.

Con el objetivo de mejorar la digestión anaeróbica termófila se ha evaluado el efecto del pretratamiento térmico sobre el lodo en un rango de 30 a 200ºC así como el efecto del pretratamiento químico con peróxido de hidrógeno, añadido continuamente a la dosis de 0-1.0 g de H_2O_2 / g DQO a 30ºC y 60ºC. El tiempo de reacción se fijó en 30 min, aunque el impacto del tiempo también fue evaluado. Para caracterizar la digestión del lodo pretratado, se han realizado tests para determinar el potencial de biometano en condiciones termófilas.

El impacto más notable en el pretratamiento térmico es la solubilización de la materia orgánica, que aumenta cada vez más con la temperatura. Se puede observar que la producción de biogás se ve reforzada por

pretratamiento térmico, excepto para 200ºC. Después de evaluar el efecto del tiempo de pretratamiento, se decidió establecer la duración en 1 h a la temperatura deseada, ya que un aumento adicional del tiempo de tratamiento, especialmente a temperaturas inferiores a 110 º C, no mejoró la solubilización de la materia orgánica. Con tan sólo 80ºC, tanto los SDT (sólidos disueltos totales) como los SDV (sólidos disueltos volatiles) fueron más de cuatro veces mayores que el contenido inicial y a 170ºC se consiguió que fuese hasta siete veces superior. Sólo el lodo pretratado por encima de 110ºC puede ser clasificado como biosólido de clase A. quede todas formas, a tan sólo 50ºC ya se observó una considerable reducción de patógenos con casi el 50% de la reducción de *Escherichia Coli* y nula presencia de *Salmonella*.

Aunque no se observa eliminación relevante de materia orgánica después de la adición de peróxido de hidrógeno a 30ºC en concentraciones menores de 0.87 g de H_2O_2/g DQO, parece producirse una solubilización de la materia, que se traduce en un aumento de la DQO soluble y de los SDT. La concentración de 0.03 g de H_2O_2/g DQO es suficiente para aumentar la DQO soluble en más de un 70%. A concentraciones más altas, 1.16 y 1.45 g de H_2O_2/g DQO, ya se observa la destrucción de materia orgánica. El peróxido de hidrógeno promueve la destrucción de *Salmonella*, pero prácticamente no tiene ningún efecto sobre las densidades de coliformes fecales, incluso a la dosis más alta probada de 0.6 g de H_2O_2/g DQO. Cabe señalar que la adición del peróxido implica un aumento de volumen del residuo, ya que el peróxido se suele encontrar en solución acuosa.

Para los estudios en digestión semi-continua anaeróbica termófila, se escogieron el pretratamiento térmico a 80ºC y la peroxidación con una dosis de 0.2 g de H_2O_2/g DQO.

En cuanto al tratamiento aeróbico termófilo, se ha obtenido una alta reducción de la DQO, a un valor medio de 62%, aunque se observaron fluctuaciones importantes. A su vez, los ST (sólidos totales) y el contenido en SV (sólidos volátiles) disminuyeron hasta un 34% y 40%, respectivamente. El fango digerido se puede clasificar como biosólido de clase A. A pesar de la desaparición de la materia orgánica, no se pudieron conseguir condiciones autotérmicas ya que para mantener la temperatura termófila (55ºC), se tuvo que aportar calor extra. Esto fue causado por el tamaño del reactor, al tratar volúmenes de lodos tanto pequeños (5 L) el área en relación al volumen es demasiado grande y produce una pérdida excesiva de calor por las paredes. Sin embargo, la eliminación de la DQO alcanzada asegura (en el balance de energía) que en plantas a escala superior (>1 m^3) se trabajase en funcionamiento auto-sostenido.

Se ha estudiado la digestión anaeróbica termófila a 50ºC, 55ºC y 60ºC a TRH de entre 15 a 25 días, pero estas condiciones no son suficientes para la destrucción de patógenos a nivel de biosólidos de clase A. La temperatura a 60ºC ha resultado poco interesante dada la poca producción

de biogás y no presenta ventajas en comparación con las otras temperaturas estudiadas en términos de eliminación de sólidos. El período de aclimatación para cambiar las condiciones de temperatura en el reactor anaeróbico fue más largo de lo esperado. Alrededor de cinco veces el TRH fue necesario para aclimatar las condiciones de 60ºC a 55ºC a un TRH=20 días. En cambio la aclimatación de los reactores a cambios de TRH afecta mucho menos.

Se ha estudiado también la digestión anaeróbica dividiéndola en dos etapas individuales, primero una etapa termófila (55ºC, TRH=5 días) y una segunda etapa mesófila (33ºC, TRH=15 días). Si comparamos este sistema dual con los individuales mesófilos y termófilos a TRH = 20 días, los mejores resultados se obtuvieron en el sistema dual. Estos últimos mostraron un mejor rendimiento en términos de destrucción de DQO (66%), SV (48%) y ST (63%). De igual manera, la estabilidad del proceso mejora ya que el contenido de materia orgánica soluble y de AGV (ácidos grasos volátiles) del efluente final es menor. Parece que la digestión en dos etapas es suficientemente eficiente para obtener biosólidos de clase A, pero sólo se realizó un análisis. El principal inconveniente del sistema dual es que se necesita la construcción de un nuevo reactor anaeróbico en caso de adaptación de las instalaciones existentes.

Se estudió el efecto del pretratamiento térmico a 80ºC durante 1 h y también el efecto del pretratamiento químico con peróxido de hidrógeno a una dosis de 0.2 g de H_2O_2/g COD a 30ºC en combinación con la digestión anaerobia semi-continua a tres temperaturas diferentes, 33ºC (rango mesófilo), 50ºC y 55ºC (rango termófilo) con un TRH=20 días. No se puede concluir ningún efecto claro en cuanto a los resultados obtenidos en la evaluación de la reducción de los sólidos o materia orgánica de los diferentes rangos de temperatura estudiados, pero se observa que el efluente final en rangos termófilos siempre presenta una carga de materia soluble mayor que en el mesófilo. Los pretratamientos parecen aumentar la producción de biogás, especialmente en el rango mesófilo, donde se observa un incremento del 60% cuando se alimenta con lodo pretratado térmicamente y de un 52% cuando es pretratado químicamente. En el rango termófilo de 55ºC, el incremento de biogás es alrededor de un 22% para térmico y un 8% para el químico. El contenido de metano del biogás es siempre superior a 68% siendo un biogás de alta calidad para su posible uso en las unidades de cogeneración

La máxima eliminación de SV se obtiene con el tratamiento anaerobio mesófilo de 33ºC de lodos pretratados térmicamente a 80ºC, con una eliminación del 60%. Sin embargo, se recomienda trabajar a 55ºC, ya que si también se evalúa el contenido de patógenos, es el que presenta los mejores resultados. Se observa que el contenido de *E-coli* está por debajo de los requisitos de los biosólidos de clase A. Se encontró presencia de *Salmonella* en el efluente final a pesar de que no se detectó en los lodos

pretratados a 80ºC. Parece ser que en la digestión se podría producir una reactivación de los patógenos, pero el análisis de los patógenos en la fase estacionaria del ensayo se realizó sólo una vez y harían falta más análisis para confirmar esta hipótesis

La transformación de los digestores mesófilos a termófilos juntamente con la unidad de pre-tratamiento térmico en condiciones no severas (T <110ºC, 1 h) es económicamente viable ya que el aumento de los costes operación son ampliamente compensados por el incremento de la producción de biogás y el uso de los lodos estabilizados para uso agrícola. Esta opción requiere una reingeniería mínima de las plantas y es especialmente interesante para las plantas con unidades de cogeneración de energía ya aplicadas. En este tipo de plantas el ahorro se estima en 1€ por habitante equivalente y año. Este ahorro cubriría cualquier inversión necesaria, incluso un sistema de cogeneración, con un periodo de recuperación de menos de cuatro años.

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Nomenclature

A_{max}	Max. specific substrate utilization rate $\left(g\,CH_4 / g\,VSS \cdot day \right)$
BMP	Biochemical methane potential
BOD_5	Biochemical oxygen demand $\left(mg\,O_2 / L \right)$
BP	Biogas production
COD	Chemical oxygen demand $\left(mg\,O_2 / L \right)$
CSTR	Continuous stirred tank reactor
DMS	Dissolved mineral solids $\left(g / L \right)$
FDS	Fixed dissolved solids $\left(g / L \right)$
FSS	Fixed suspended solids $\left(g / L \right)$
GC	Gas chromatography
HRT	Hydraulic retention time *(days)*
k_h	Hydrolysis constant
k_{max}	Maximum specific substrate utilization rate $\left(g\,substrate / g\,VSS \cdot day \right)$
k_s	Half saturation concentration $\left(g\,substrate / L \right)$
MSS	Mineral suspended solids $\left(g / L \right)$
OLR	Organic loading rate $\left(g\,COD / g\,VSS \right)$
ORR	Organic removal rate $\left(g\,COD / g\,VSS \right)$

PS	Primary sludge
TOC	Total Organic Carbon $\left(mg\,C/L\right)$
TC	Total Carbon $\left(mg\,C/L\right)$
TDS	Total dissolved solidls $\left(g/L\right)$
TFS	Total fixed solids $\left(g/L\right)$
TPAD	Thermophilic phased anaerobic digestion
TS	Total solids $\left(g/L\right)$
TSS	Total suspended solids $\left(g/L\right)$
TVS	Total volatile solids or volatile solids $\left(g/L\right)$
S_{COD}	Solubilisation rate of COD *(%)*
S_{TS}	Solubilisation rate of TS *(%)*
S_{VS}	Solubilisation rate of VS *(%)*
SMA	Specific methanogenic activity
SRT	Sludge retention time *(day)*
STP	Standard conditions
URV	Universitat Rovira i Virgili
VFA	Volatile fatty acids $\left(mg\,eq.\,Acetic\,Ac./L\right)$
V	Volume *(ml; L)*
VDS	Volatile dissolved solids $\left(g/L\right)$
VS	Volatile solids or total volatile solids $\left(g/L\right)$

VSS	Volatile suspended solids $\left(g/L\right)$
WAS	Waste activated sludge
WWTP	Waste water treatment plant
Y_{biogas}	Biogas yield
Y_{CH4}	Methane yield

CHAPTER 1

Introduction

Water is essential for life. What we know as wastewater (contaminated or polluted water) results from the incorporation of substances and microorganisms in water that alter their natural quality, caused by human action. The natural water quality is determined by a series of physical, chemical and microbiological characteristics that vary with its location (inland waters and groundwater, marine waters, etc.) and its final use.

It is often forgotten how humans affect the water and life cycle of the earth and how important is the quality of the resources that it has. Despite the important self-purification capacity of water, when the pollution level exceeds its autopurifying capacity, biological death occurs with the subsequence degradation and deterioration of rivers and lakes, overseas, coastal areas, etc.

Since ancient Greek writings dating back to 2000 BC (Petri et al. 2007), humans realised that the use of non-purified water caused diseases and already recommended the use of boiled water for human use. Waterborne diseases, such as cholera, typhoid, diarrheal disease etc. and some foodborne diseases are mainly caused by pathogenic microorganisms, which are directly transmitted when contaminated fresh water or poisoned

food is consumed. Around 589000 number of cholera cases were still detected in the world in 2011 (WHO) directly related to the lack of sanitary conditions and fresh water.

The reduction of the contaminants present in wastewaters to an environmentally supportable level is essential. It is now being imperative that residues produced as a result of human activity both from domestic and industrial origin to be treated before discharge into the environment.

Water treatment processes includes physical, chemical, and biological processes that produce a liquid waste stream environmentally-safe and often a solid waste also called sludge.

For regulating quality of final effluents discharged from a Wastewater Treatment Plant (WWTP) and final water disposal, European Union has given rules in the Municipal Waste Water Treatment Directive 91/271/EEC, which requires limits and processes to adequate collection, treatment and disposal systems for wastewater generated. In addition, the Sewage Sludge Directive 86/278/EEC regulates the uses and properties of stabilised sludge for being either recycled or disposed. Sludge treatment and disposal among the wastewater treatment corresponds to 50% of the operational costs (Pérez-Elvira et al. 2006) a plant. Concerning sludge management, both European directives drive specific actions in two complementary ways. Firstly, they promote actions in order to study in deep current sludge treatments, such as mesophilic, thermophilic or autothermophilic processes taking in account the particular considerations of each treatment facility. In second place, the development of new processes must be supported to open new alternatives that could valorise that waste.

The tendency is that the amount of WWTP will increase, as still there are many wastewater discharged into the environment without any treatment. Therefore, sludge production also will increase and also threshold limits for releasing contaminants will be stricter.

Water is essential for live, and water resources are limited. Minimize water pollution and improve decontamination are key issues for a sustainable world. It must be found equilibrium of environmental, social, and economic aspects: consume what needed, improve efficiency and minimize environmental impact.

1.1. Overview on sewage sludge origin, treatment and composition

1.1.1. Waste water treatment

What is known as sewage treatment is the treatment of domestic wastewater that includes: household waste liquid from toilets, baths, showers, kitchens, sinks and so forth that is disposed of via sewers. It is estimated that in average 144 litres of water per person was consumed in Spain for satisfying urban necessities during 2010 (INE).

A huge amount of water corresponds to those activities that are inherent in human kind such as cleaning, feed preparation and physiological needs. During 2010, potable water distribution is Spain was registered to be more than 4500 hm^3.

Figure 1.1 depicts de evolution of the collected and treated wastewater and the costs involved in its treatment and collection over the last 15 years in Spain. One can observe the huge investment made by the Government in order to accomplish with the regulations especially in 2008, where the investment (both in collection and treatment) were up to 1851 million of Euros. Annually, the amount of treated wastewater has increased around 8-12% except in 2004 when a sharp increase of about 60% was observed respect the previous year. Since then it has been maintained almost constant; thus, about 13.3 hm^3/day of waste water was treated in 2010. The average cost of the treatment have been 0.4 €/m^3, which is 1991 million of Euros in 2010.

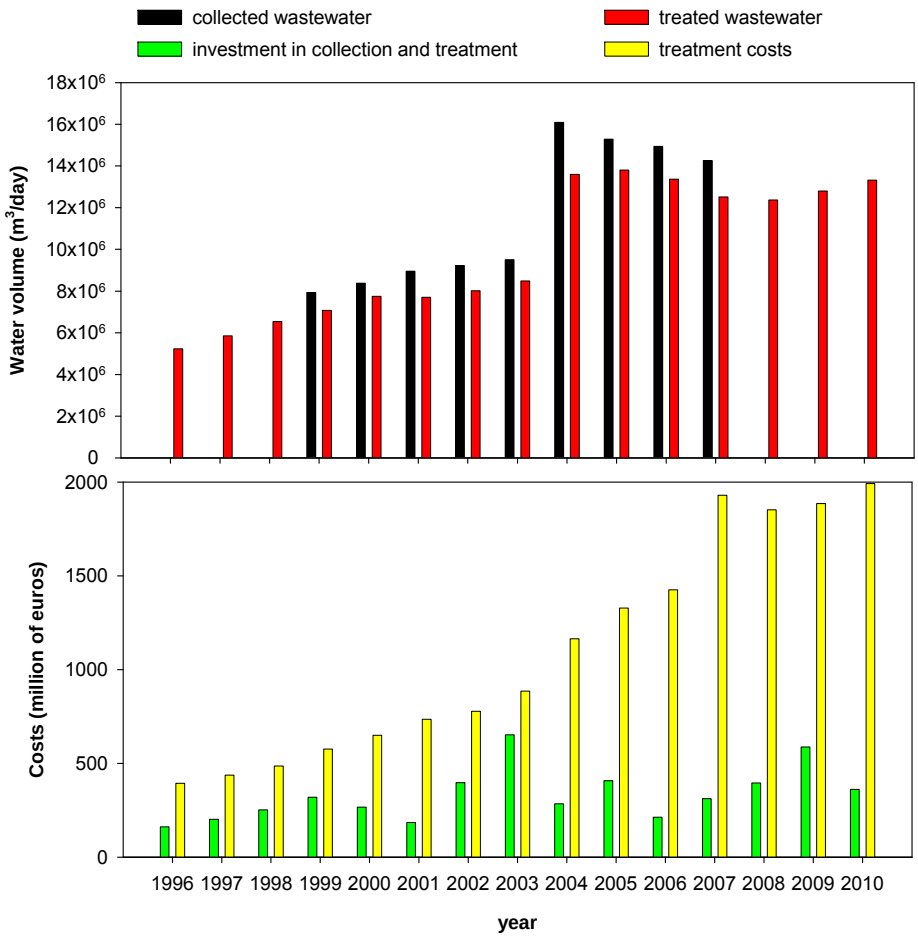

Figure 1.1. Evolution of the wastewater collected and treated and their costs in investment collection and treatment costs in Spain during 1996-2010.(INE)

The situation in Catalonia differs (see figure 1.2). Since 1996 the wastewater treatment has been maintained quite constant, however the costs have increased sharply since 2006. The treatment costs are 0.54 €/m^3 while before 2008 was around 0.2 €/m^3.

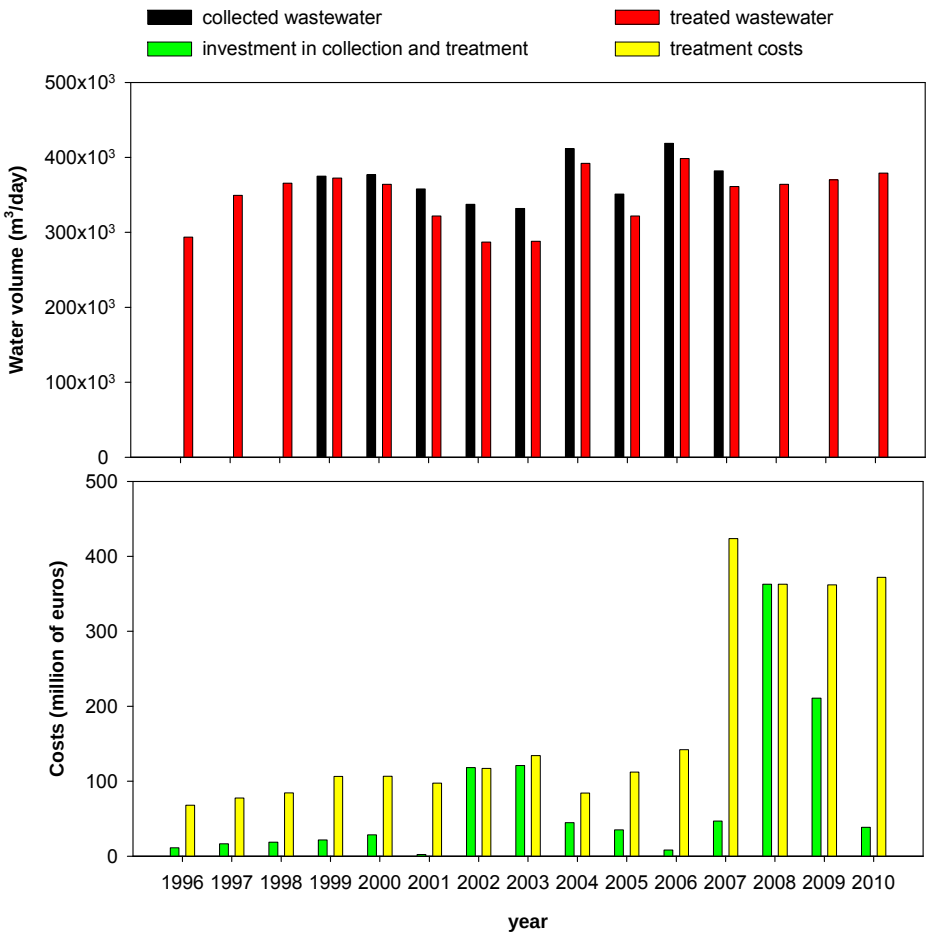

Figure 1.2. Evolution of the wastewater collected and treated and their costs in investment collection and treatment costs in Catalonia during 1996-2010.(INE)

Water treatments are overall well spread over the world in cities and populated centres. Waste Water Treatment Plants (WWTP) usually apply different technologies divided in three differentiated treatments: primary treatment, secondary treatments, and tertiary treatments. In figure 1.3 a scheme of a classical WWTP is shown.

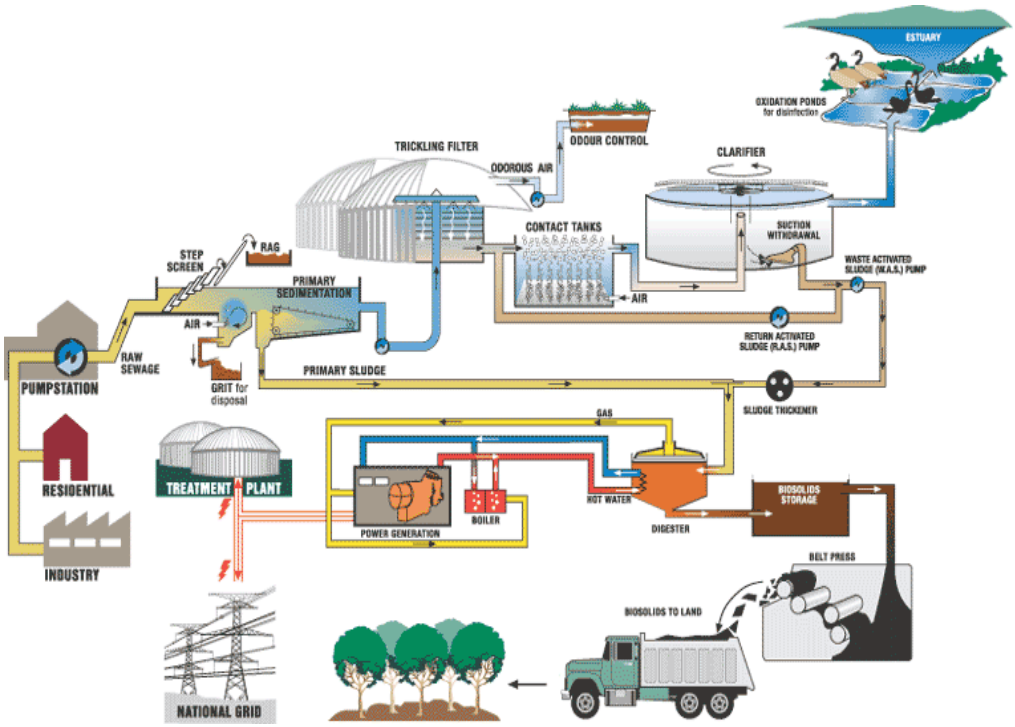

Figure 1.3. Classical WWTP scheme (Christchurch city council)

1.1.1.1. Primary treatment

Primary treatment consists in physical and chemical processes normally used to prepare waste water for the next treatment and is mainly devoted to remove coarse fraction such as oil, fatty acids and suspended solids. Water compounds are classified basically in three different categories: suspended solids, colloidal particles, which have less than 1 micron size, and dissolved substances which are less than several nanometers. Technologies in this primary treatment are:

Screens. Its purpose is to protect the structure downstream against large objects which could create obstructions in some of the facility's units. They easily separate and remove large matter carried along by the raw water, which might negatively affect the efficiency of later treatment procedures or make their implementation more difficult.

Coagulation. Coagulation is the destabilization of colloidal particles brought about by the addition of a chemical reagent called coagulant.

Flocculation. Flocculation is the agglomeration of destabilized particles into microfloc and after into bulky floccules which can be settled. The addition of another reagent called flocculant or a flocculant aid may promote the formation of the floc. The coagulation-flocculation processes facilitate the removal of suspended solids and colloidal particles. It is regularly used in the final stage solid-liquid separation.

Settling. It is a solid-liquid separation where particulates settle to the bottom of a liquid and form sediment.

Flotation. As opposed to settling, flotation is a solid-liquid or liquid-liquid separation procedure, which is applied to particles whose density is lower than that of the liquid where they are in.

Centrifugation. Centrifugation is a separation process taking advantage of the action of centrifugal force to promote accelerated settling of particles in a solid-liquid mixture. Two distinct major phases are formed in the vessel during centrifugation.

Fluidisation. This process consists in converting the solid-like state of a liquid into a fluid-like state by the addition of an agent.

Precipitation. Is the process that produces the formation of a solid in a solution or inside another solid during a chemical reaction.

1.1.1.2. Secondary treatment

In secondary water treatment, organics and suspended solids are removed using basically biological and chemical treatments. There are two main processes:

- Aerobic treatment is a microbiological process where organic waste is broken down in a controlled oxygen environment by bacteria naturally occurring in the waste material.
- Anaerobic treatment is a microbiological process where organic waste is broken down in a controlled oxygen-free environment by bacteria naturally occurring in waste material.

Temperature is one of the most important physico-chemical variables. It selects the predominant type of microorganisms present in the system. Also temperature has influence on microorganism's activity, gas solubility, reaction rates, etc.

1.1.1.3. Tertiary treatment

Tertiary treatments are those treatments applied to water coming from secondary treatment that needs to be more purified before discharge into the environment. These treatments are basically used for eliminating organic contaminants, nutrients such as phosphates and nitrates and mineral salt excess. Processes used are chlorination, ozonation, microfiltration, reverse osmosis, ionic exchange, adsorption, etc.

1.1.2. Origin and treatment of sewage sludge

1.1.2.1. Origin of sewage sludge

There are two types of sewage sludge depending on their origin. Thus their characteristics and composition are closely related to the step of the wastewater treatment where are generated.

Primary sludge is produced through the mechanical wastewater treatment process. It consists of unsolved wastewater contaminants. The composition of this sludge depends on the characteristics of the catchment area and it composed by a high portion of organic matters as faeces, vegetables, fruits, textiles, paper, etc. Primary sludge is solid organic matter composed mainly of carbohydrates (55%) proteins (18%), and lipids (10%) (Miron et al. 2000).

Secondary sludge or activated sludge is resulting from biological aerobic process during water treatment, where the interaction of different types of bacteria and microorganisms removes dissolved organic matter and nutrients from wastewater. It contains living and dead biomass as well as organic and mineral particles. To keep a stable aged population, a fraction of the sewage sludge must be periodically purged: the excess sludge. Secondary sludge mainly consists of bacterial cells, characterized by higher protein content (36%), carbohydrates (20%) (Dignac et al. 2000).

In table 1.1, it can be seen the typical characteristics of primary and activated sludge.

Table 1.1. Typical composition of primary and activated sludge (Metcalf and Eddy 2003).

Parameter	Primary sludge		Activated sludge	
	Range	Average	Range	Average
TS (%w/w)	2.0-8.0	5.0	6.0-12.0	10.0
VS (%w/w of TS)	60-80	65	30-60	40
pH	5.0-8.0	6.0	6.5-7.5	7.0
Alkalinity (mg $CaCO_3$/l)	500-1500	600	2500-3500	3000
Organic Acids (mg Acetic Acid/l)	200-2000	500	100-600	200

1.1.2.2. Sludge production and management

The Urban Waste Water Treatment Directive 91/271/EEC specifies that all agglomerations with a population equivalent to more than 2000 inhabitants must be provided with collecting systems for urban waste water and subjected to a subsequent secondary treatment before discharge. As a result of the implementation of this European directive, the number of WWTP in Catalonia has increased over the last decade and also the residue generated for water decontamination: the sludge.

Table 1.2 presents the evolution of the active WWTP in Catalonia, the amount of water treated and the sludge generated during 2002-2010. It can be seen that, in nearly a decade, almost 100 WWTP were built since 2002, not only new construction for treating more water, but also to improve the efficiency of the process, as the increase of more than 20% in the flow rate treated generates less amount sludge.

Table 1.2. Evolution of the Active WWTP in Catalonia during 2002-2010 (INE)

	2002	2003	2004	2005	2006	2007	2008	2009	2010
WWTP	290	297	314	328	330	335	340	368	389
Q treated (hm^3/year)	587	715	720	676	686	661	664	675	706
Sludge (tn/year)	567	523	518	554	539	547	594	585	548

The objectives of sludge treatment are to stabilise it and to obtain sludge with no odour, volume and weight reduction and no presence of pathogen organisms by means of the degradation of organic compounds in a controlled environment. What is wanted is to produce a residual sludge containing the maximum amount of non-biodegradable fraction, and a

minimum of biodegradable one. This final residue sludge should be easily dewaterable, and its content of pathogens or toxic chemicals should also be negligible. Sludge treatment comprises stabilisation, hygienisation and detoxification. Table 1.3 presents the different type and classes of sludge treatments. Processes are commonly categorized in sludge management as: thickening, stabilisation, dewatering, conditioning and drying.

A) THICKENING

Sludge thickening produces a concentrated product that essentially retains the properties of a liquid. Gravity thickening, or concentration by simple sedimentation, is the thickening process most commonly applied to municipal sludge. Alternatives to gravity thickening include flotation thickening (in which a gas is incorporated with sludge solids, causing them to float), as well as the use of gravity drainage belts, perforated rotating drums, and centrifuges. The amount volume reduction in sludge thickening processes is around one fifth of the total volume (Metcalf and Eddy, 2003). The separated water is recycled into the WWTP.

B) STABILISATION

In biological stabilization processes, the organic content of sludge is reduced by biological degradation in controlled processes. Most commonly, domestic wastewater sludge is biologically stabilized as a liquid in anaerobic digesters from which methane gas is a byproduct. Anaerobic digesters typically operate at mesophilic temperatures (at about 35°C) but can also operate at thermophilic temperatures.

Liquid sludge can also be biologically stabilized in aerobic digesters to which oxygen (or air) must be added; aerobic digesters can be made to operate thermophilically using autogenous heat.

Composting is a process that biologically stabilizes dewatered sludge. Composting is ordinarily an aerobic process, and an amendment, such as wood chips or sawdust, must be added to improve friability in order to promote aeration. Composting takes place at thermophilic temperatures (often, about 55°C) because of the heat released by biochemical transformations.

Chemical stabilization of sludge is aimed not at reducing the quantity of biodegradable organic matter, but at creating conditions that inhibit microorganisms in order to retard the degradation of organic materials and prevent odours. The most common chemical stabilization procedure is to raise the pH of sludge using lime or other alkaline material, such as cement kiln dust. Sludge can be chemically stabilized in liquid or dewatered forms. When dewatered sludge is used, the exothermic reaction of lime with water causes heating which helps destroy pathogens and evaporate water.

C) DEWATERABILITY

Sludge dewatering processes are used for dehydrated sludge; however the dewatered sludge is still mostly water -still the total solids content can improve only to 10-45% strongly dependent on the type of sludge and dewatering treatment (Metcalf and Eddy 2003). Dewatering may be accomplished on sand drying beds and, occasionally, in lagoons, where gravity drainage and evaporation remove moisture. More often, larger municipal installations use mechanical means for dewatering sludge. Mechanical sludge dewatering equipment includes filter presses, belt filter presses, vacuum filters, and centrifuges.

D) CONDITIONING AND DRYING

Conditioning alters the physical properties of sludge solids to facilitate the release of water in dewatering processes. Chemical and, less frequently, physical techniques are used to condition sludge. Chemical conditioning most commonly involves adding synthetic organic polyelectrolytes or polymers to sludge prior to dewatering. Inorganic chemicals (most commonly, ferric chloride and lime) can also be used. Physical conditioning techniques include heat treatment and freeze-thaw treatment.

Table 1.3.. Sludge treatments (Metcalf and Eddy 2003)

PRELIMINARY OPERATIONS	**THICKENING**
Sludge grinding	Rotary Drum thickening
Sludge bending	Gravity thickening
Sludge storage	Flotation thickening
Sludge degritting	Centrifugation
	Gravity belt thickening
STABILISATION	**CONDITIONING**
Chlorine oxidation	Chemical conditioning
Lime stabilisation	Sludge grinding
Heat Treatment	Elutriation
Anaerobic digestion	Heat Treatment
Aerobic digestion	
Composting	
DISINFECTION	**DEWATERING**
Pasteurization	Vacuum filter
Long term storage	Pressure filter
	Horizontal belt filter
	Centrifuge
	Drying bed
	Lagoon
DRYING	**THERMAL REDUCTION**
Multiple effect evaporator	Multiple Herat incineration
Flash drying	Fluidized-bed incineration
Spray drying	Flash combustion
Rotary drying	Co-incineration with solid wastes
Multiple Herat dryer	Vertical deep well reactor
	Wet air oxidation

Most of the sludge generated in Catalonia is treated at least with anaerobic digestion before final disposal. Table 1.4, presents the sludge generated by WWTP and table 1.5 shows the total treated sludge and sludge treatment. From the shown data, it can be observed that since 2006 practically above 90% of the sludge generated in Catalonia is treated. The evolution of the

sludge treatment in our country is clearly to maximize the post-treatment of the sludge after the first anaerobic digestion stabilization stage. In 2010, the most preferred option after mesophilic anaerobic digestion was thermal drying, followed by composting with almost 44% and 34% respectively (see table 1.4).

After treating the sludge, the selection of the best disposal route depends on the most secure and environmentally acceptable final destinations. Sewage Sludge Directive 86/278/EEC establishes a hierarchy of disposal outlets, and regulates the uses and properties of stabilised sludge for being either recycled or disposed. This dictates the type of treatment required.

Currently the sludge disposal outlets are:

a) Landfilling, burial with urban garbage, which can result in leaching problems.

b) Dumping in the sea, an option that is unavailable to land-locked countries and-locked in some countries;

c) Incineration, it requires supplementary fuel and results in air pollution and extensive land and surface water pollution. It must be no longer accepted from an environmental point of view.

d) Recycling as fertilizer. Either composting with other material or direct spread.

Traditionally, it has been used sludge as a fertilizer after digestion to reduce the fraction of readily biodegradable matter present prior to spreading, However, increasing concern on the grounds, public/veterinary health aspects and nuisance for odour problems arising from land application, is becoming evident and more effective and reliable sludge treatment processes are urgently required.

Table 1.5 depicts the evolution of the final sludge disposal in Catalonia during 2001-2010. It can bee seen that the final sludge destination mainly goes to agriculture and gardening. Land filling disposal is becoming less used and is tending to be minimized. In contrast is remarkable the latest increase in sludge disposal as energy revalorisation, mainly in the use of the sludge as a fuel source. This situation is attributed to the population distribution in Catalonia, most of the population lives in the Barcelona metropolitan area. For instance the Besos WWTP and the Prat WWTP, the nearest WWTP, produce more than 37% of the total sludge amount in 2010 (ACA). The most part of the cement production is located also in the same area, so transportation costs strongly decay, and environmentally is the best option for this type of sludge. (Nadal et al. 2009).

Table 1.4. Evolution of the used sludge treatment processes in Catalonia during 2001-2010 (Generalitat de Catalunya. Departament de Territori i Sostenibilitat. Agència Catalana de l'Aigua.)

Year	Composting (%)	Thermal drying (%)	Other Treatments [#](%)	Digestion no posttreatment (%)	TREATED SLUDGE (tn fresh sludge)
2001	28.3	26.7	-	45.0	343
2002	35.6	25.8	-	38.7	350
2003	32.4	32.1	-	35.5	401
2004	30.3	36.4	-	33.3	441
2005	36.5	41.3	-	22.1	491
2006	39.0	35.0	-	25.9	521
2007	52.9	19.4	2.50	25.1	564
2008	51.0	21.9	2.60	24.4	563
2009	48.1	27.3	1.30	23.3	535
2010	33.6	43.9	0.80	21.7	531

[#] lagoons, special treatments, grey compost

Table 1.5. Evolution of the final sludge disposal in Catalonia during 2001-2010 (Generalitat de Catalunya. Departament de Territori i Sostenibilitat. Agència Catalana de l'Aigua.)

Year	AGR./ GAR. (%)	QRRY. (%)	LAN. (%)	Others (%)	EMIS (%)	Energy revalorisation[#]	SLUDGE ELIMINATED (tn fresh sludge)
2001	68	1.0	27	0.6	4.1	-	499
2002	70	1.0	29	-	-	-	490
2003	70	0.1	30	-	-	0.1	403
2004	69	-	29	0.1	-	1.5	431
2005	74	-	19	-	-	6.5	366
2006	86	0.1	12	-	-	2.5	388
2007	89	0.1	8.9	-	-	1.6	479
2008	91	0.05	5.2	-	-	3.4	461
2009	91	-	2.7	-	-	6.5	411
2010	86	0.1	1.7	-	-	1.2	334

AGR-GAR: Agricultural and Gardening
QRRY: Restauration of quarries
LAN: Controlled landfilling
EMIS: Emissary
[#] Concrete industry

1.1.2.3. Legislation

Council directive of 12 June 1986 is about the protection of the environment, and in particular of the soil, where sewage sludge is used in agriculture (86/278/EEC). This directive regulates the use of sewage sludge in agriculture; it defines the limit values of heavy metals to avoid soil contamination due to sludge spreading. It also promotes that every Member State must protect its environment with more stringent regulations if needed.

Directive 2008/98/EC sets the basic concepts and definitions related to waste management, such as definitions of waste, recycling, recovery, and also the priority order of the waste management hierarchy for all State Members. Following this European directive law 15/2003 of June establishes hierarchy in sludge management presented en figure 1.4.

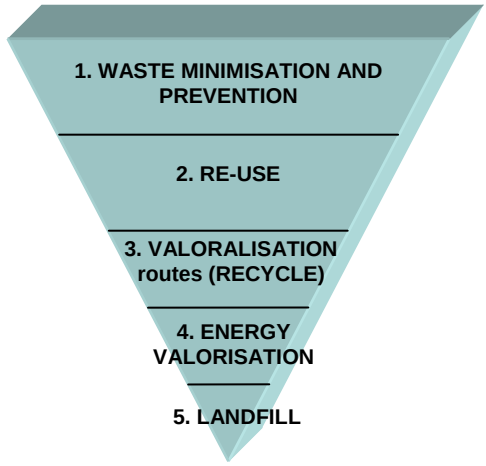

Figure 1.4. Management sludge hierarchy by Catalan law 15/2003

However each State member is responsible of the data compilation and the accomplishment of the directive with penalties for not meeting the objectives. In annex I, the specific legislation applied in Catalonia can be found.

Based in the re-use of biosolids, directive 86/278/EEC encourages the sewage sludge utilization in agriculture as fertilizer, and defines sludge treatments before agrarian use.

EPA Biosolids class A (EPA 40CFR Part 503 Rule)

This distinction, commonly used in literature, is given by the U.S. Environmental Protection Agency (EPA) to ensure that biosolids applied to the land do not threaten public health. Apart from giving pollutant limits of Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Molybdenum, Nickel, Selenium and Zinc, it basically categorizes the biosolids depending on the level of pathogenic organisms that are present in the material. Specifically Class A biosolids are those that accomplish values described in table 1.6.

Table 1.6. EPA biosolids class A limits

Organism	Limit value
Fecal coliform (FC)<	<1000 MPN/g TS
Salmonella	<3 MPN/ 4g TS

1.2. Anaerobic digestion

Anaerobic digestion is the most widely sludge treatment process used in municipal Waste Water Treatment Plants (WWTP) to stabilize primary and secondary (waste activated sludge, WAS) sludge generated in the wastewater treatment (Metcalf 2003). The most extended anaerobic process is at mesophilic temperatures (from ambient temperature to 45ºC) due to its low energy requirements. However anaerobic digestion process at thermophilic ranges are characterized by accelerated biochemical reactions, upper biogas production and higher growth rate of microorganisms (Speece 1996), leading a possible reduction of the hydraulic retention time or space requirements. Moreover, thermophilic anaerobic digestion can lead to EPAs class A biosolids which are suitable for land application (Watanabe et al. 1997, Zábranská et al. 2000) and according to the literature (Suh and Rousseaux 2002) the combination of anaerobic digestion and agricultural land application is the most environmentally friendly thanks to less emissions and less consumption of energy.

When the organic matter (sludge) is anaerobically digested, it suffers a microbiological oxidation. This process involves a coordinated and interdependent set of reactions promoted by different bacteria population, which degrades the organic matter into intermediary products in turn converted into methane. The digestion process can be divided in four steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Ros and Zupancic 2003; Gavala et al. 2003). Hydrolysis can be the rate limiting process for anaerobic digestion, especially for sludge with high solid content, while methanogenesis is considered rate limiting in the

fermentation of soluble substances (Pavlostathis and Giraldo-Gomez 1991; Wang et al. 1997; Gavala et al. 2003; Ros and Zupancic 2003; Puchadjda and Oleszkiewicz 2006). Thus, most of the strategies to enhance anaerobic digestion are based in improving the hydrolysis step.

1.2.1. Process fundamentals

Anaerobic digestion is the microbiological oxidation of organic matter without the presence of air. The process involves a coordinated and interdependent set of reactions promoted by different bacteria population as seen in figure 1.5, which degrades organic matter into intermediary products in turn converted into methane. The digestion process can be divided in four steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Ros and Zupancic 2003).

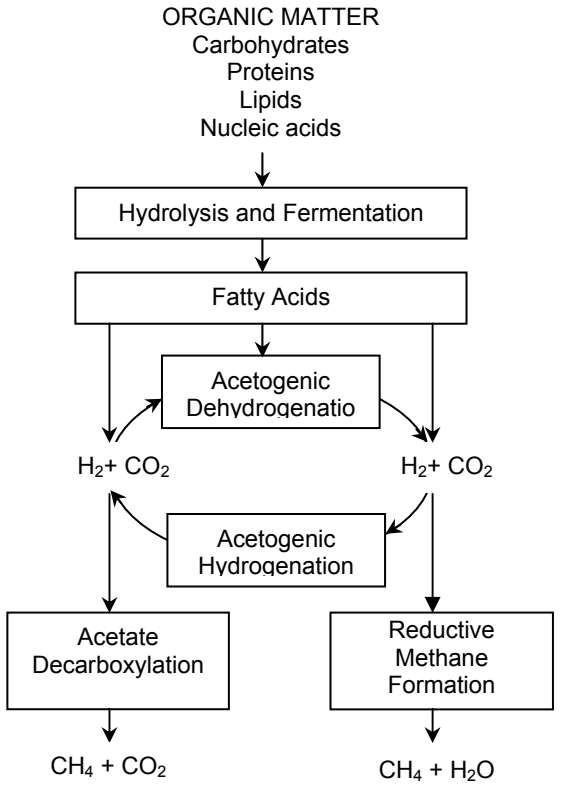

Figure 1.5. Multistep reactions in anaerobic digestion (Ros and Zupancic 2003).

The electron donor of the process is the biodegradable COD, as it provides the energy for the biomass activity. The electron acceptor of anaerobic processes is the CO_2 or sulphates as the process is taken in the absence of oxygen. Carbon dioxide reduction results in CH_4 production, while sulphate reduction results in H_2S production.

Hydrogen sulphide is malodorous and corrosive to metals. Combustion products are considered air pollutants. However, in contrast to methane, H_2S is highly soluble in water, 2650 mg/L at 35ºC.

1.2.1.1. Hydrolysis

This step is the conversion of particulate and soluble complex substances into soluble products such as amino acids, sugars and fatty acids by extracellular enzymes secreted by microorganisms. The microorganisms that produce the enzymes can be obligate or facultative anaerobes.

Hydrolysis can be the rate limiting process for anaerobic digestion, especially for sludge with high solid content, while methanogenesis is considered rate limiting in the fermentation of soluble substances (Pavlostathis and Giraldo-Gomez 1991, Puchadjda and Oleszkiewicz 2006).

1.2.1.2. Acidogenesis

Acetate, hydrogen and carbon dioxide as well as volatile fatty acids (VFA) and alcohols are produced from the soluble organic matter by acidogenic fermentative bacteria. These organisms are obligated and facultative anaerobes, and this step is often the fastest in the anaerobic digestion (Pavlostathis and Giraldo-Gomez 1991).

1.2.1.3. Acetogenesis

Acetogen bacteria are organisms that are able to reduce CO_2 to acetate via the acetyl coenzyme A (acetyl-CoA) or Wood-Ljungdahl metabolic pathway (Müller 2003). Acetogen bacteria are strictly anaerobic bacteria, which can derive energy only by fermentation and/or by ion gradient-driven phosphorylation (anaerobic respiration); these bacteria can grow by the

conversion of hexoses, C_2 and C_1 compounds, such as HCOOH and CO, into acetate.

They can inhabit in a wide range of ecosystems due to their high resistance to extreme conditions such as pH, temperature and salinity. In table 1.7, there are cited some acetogenic bacteria and their characteristics.

The fermentation of hexoses (equation 1.1) can exclusively yield acetate; this fermentation is referred to as homoacetogenesis (Müller 2003). Also other authors report that are capable of autotrophic growth on H_2/CO_2 (equations. 1.2 and 1.3). However, homoacetogenesis in digested sludge may be maintained as a result of heterotrophic growth on sugars or other organic compounds, equation. 1.4 (Ryan, 2005). Homoacetogenic bacteria utilize CO_2 as a terminal electron acceptor to produce acetate; electrons for reduction can come from H_2.

$$C_6H_{12}O_6 \rightarrow 3CH_3COOH \qquad \textit{Eq. 1.1}$$

$$4H_2 + 2CO_2 \rightarrow CH_3 - COOH + 2H_2O \qquad \textit{Eq. 1.2}$$

$$4CO + 2H_2O \rightarrow CH_3 - COOH + 2CO_2 \qquad \textit{Eq. 1.3}$$

$$4CH_3OH + 2CO_2 \rightarrow 3CH_3 - COOH + 2H_2O \qquad \textit{Eq. 1.4}$$

Table 1.7. Acetogenic bacteria (Gottschalk et al. 1986).

Organism	Thermophilic	Growth on	
		H_2+CO_2	Sugars
Clostridium aceticum	-	+	+
C. thermoautotrophicum	+	+	+
C. formicoaceticum	-	-	+
C. thermoaceticum	+	+	+
Acetobacterium woodii	-	+	+
A. wieringar	-	+	+
Acetogenium kivui	+	+	+
Sporomusa sphaeroides	-	+	-

Acetogenesis is an endotermic reaction and requires very low hydrogen partial pressure to favour the thermodynamics of the reaction. In anaerobic digestion processes, this is achieved by the combination with hydrogenotrophic methanogenesis where hydrogen is consumed and homoacetogenesis where hydrogen is used to reduce carbon dioxide to acetate.

1.2.1.4. Methanogenesis

Methanogens can be found in natural environments rich in organics but free from oxygen. Methanogens are strict anaerobes that obtain energy by converting carbon dioxide, hydrogen, formate, methanol, acetate and other organic compounds into methane and carbon dioxide. Hydrogenotrophic methanogens generate methane from CO_2 and H_2 following equation 1.5, while acetoclastic methanogens produce methane from acetate (see equation 1.6).

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \textit{Eq. 1.5}$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad \textit{Eq. 1.6}$$

About two thirds of the methane produced during the digestion directly comes from the degradation of acetate (Prescott et al. 1999). Methanogens have slow growth rates and are usually considered rate limiting for the anaerobic process (Pavlostathis and Giraldo-Gomez 1991).

1.2.2. Environmental factors of anaerobic digestion

Important environmental factors involving anaerobic digestion process are: (1) temperature, (2) availability of nutrients and trace material, (3) pH, (4) alkalinity, (5) toxics, (6) solids retention time (SRT) and (7) hydraulic retention time (HRT). This two later operational factors are based in anaerobic digester size, and based on provide enough residence time to allow digestion. HRT defines the time where microbes can 'attack' the material and it strongly depends on the substrate, while SRT determines which organisms are predominant and can replicate in the system and also maintain the amount of biomass. Basically the other parameters concern the 'optimal environment' for the organisms involving the fermentation process.

Three main temperature intervals are suitable for anaerobic populations to degrade organic matter. They are termed psychrophilic, mesophilic and thermophilic intervals (see table 1.8). The temperature is the most important parameter since it influences on the microorganism activity, equilibrium reactions, gas solubility, and the type of microorganisms present in the media. Temperature selects the predominant microorganisms in the reactor and also controls its growth rate. Mesophilic ranges are commonly used in anaerobic digestion; however methanogens species are reported to operate between 4 and 100ºC. At lower temperatures, more contact time and

biomass is required. Temperature of 45ºC is reported to have operational and stability problems (Bousková et al. 2005) so higher temperature thermophilic ranges are preferable.

Table 1.8. Temperature ranges for various anaerobic populations

Bacteria population	Temperature range
Psychrophilic	0-20ºC
Mesophilic	15-45ºC
Thermophilic	45-75ºC

Methanogens, especially *Methanogenic archaea* are very sensitive to temperature changes Thus, changes even at 1 ºC/day may cause disturbances and loss of stability in the process (Metcalf and Eddy 1995)

One of the principal issues for anaerobic digestion process is bacterial nutritional requirements. Nutrient deficiencies may result in an incomplete, unstable bioconversion of organic substances and cause digestion failure (Speecy 1996). Grow of microorganisms requires carbon, nitrogen and phosphor sources. Since most anaerobic systems are heterotrophs, the carbon source for synthesizing the biomass comes from the feedstock (the biodegradable COD), in the case of autotrophic hydrogen utilizers to produce methane, the carbon source could be the dissolved CO_2 in the reactor.

The amount of carbon has to be in balance with the amount of nitrogen. The optimum C:N ratio for anaerobic digestion is suggested to be in to the range of 20:1 to 30:1 (Stratford et al. 1980). Besides carbon and nitrogen, certain amounts of micronutrients such as sulphur, vitamins and trace of minerals (Fe, K, Na, Ni, Mg, Ca, Ba, Mo, Se and Co) are needed to stimulate growth (Mata-Álvarez et al. 2000).

For example, methanogens are reported to require sulphide and trace metals. Iron is needed in the highest concentrations over the other metals, while Co, Ni and Zn are stimulatory, although also tungsten, manganese, molybdenum, selenium and even boron are reported as well (Speecy 1996). However, the presence of these trace metals do not indicate bioavailability. It is think that these metals may be in chelated forms and thus not available for microbes due the very strong binding properties of these chelated compounds, in table 1.9, it can be seen the elemental composition of methanogens.

Table 1.9. Elemental composition of methanogens (mg/L) (Speece, 1996)

Element	Composition (mg/L)
C	370000-440000
H	55000-65000
N	95000-128000
Na	3000-40000
K	1300-50000
S	5600-12000
P	5000-28000
Ca	8-4500
Mg	900-5300
Fe	700-2800
Ni	65-180
Co	10-120
Mo	10-70
Zn	50-630
Cu	10-160
Mn	5-25
Se	14-320

The amount of trace materials may vary depending on the effluent treated; however, in table 1.10, recommended amounts are given.

Table 1.10. Trace nutrients recommended concentration in anaerobic digestion (Speecy 1996)

Compound	Concentration (mg/L)
$FeCl_2$	1.0
$CoCl_2$	0.1
$NiCl_2$	0.1
$ZnCl_2$	0.1

The pH in the digester is important since the microbial groups involved have optimal growth at different pH values. To maintain dynamic equilibrium in the anaerobic system pH between 6 and 8.2 (Speece 1996) are reported to be the best. However, methanogenic bacteria are known to be more sensible to pH changes than hydrolytic and acidogenesis ones. The pH is also important since certain compounds, e.g. NH_3, H_2S and VFA, can

become toxic at specific pH. Thus, an important parameter is the buffering capacity, usually measured as the alkalinity. Because the CO_2 generated in the anaerobic process (30-35% of CO_2), high alkalinity is needed to assure pH near neutrality, ranges between 3000 to 5000 mg/L as $CaCO_3$ (Metcalf and Eddy 1995) are commonly found. In general, it is not necessary to add basic compounds as sufficient alkalinity is produced by the breakdown of protein and amino acids present in the sludge (NH_3 combines with CO_2 and H_2O to form $NH_4(HCO_3)$).

Table 1.11 lists the principal control parameters in order to assure and maintain the optimum conditions and reach stable operation.

Table 1.11. Control parameters of anaerobic process (adapted from Ferrer 2008)

Parameter	Optimal Range	Potential Risk
pH	6.5-8.3	Digester acidification
		Requires external control if the reactor has low buffer capacity
0Alkalinity	3-5 g $CaCO_3$/L	< (alkalinity deficiency) not enough buffer capacity
Redox Potential	≤300mV	Indicates reductive atmosphere in the system
C/N	20:1-30:1	> (N deficiency) may decrease reaction rate
(Ammonia)	(>40-70mg/L)	< (N excess) may cause inhibition, especially due to ammonia N
C/P	150:1-300:1	> (P excess) do not cause inhibition
VFA	<5000 mg/L	> (VFA excess) inhibit methanogenesis
		> (VFA excess) Trace metal deficiency
		> (VFA excess) Toxicity
		> (VFA excess) Nitrogen or phosphorous limitations
		< (VFA decay) not enough biodegradable substrate available (not enough hydrolysis)
Sulphide	<20 mg/L	> (Sulphide excess) sulphate-reducing bacteria are enhanced and compete with methanogens, thus methane reduction is observed.

The Water Pollution Control Federation design manual for anaerobic digestion also suggests several recommendations about the VFA concentrations. These are:

- the butyrate concentration should be < 15 mg/L
- the acetate concentration should be < 800 mg/L

- the propionate/acetate ratio should be < 1.4
- the total VFA/alkalinity ratio should be < 0.4

Toxic compounds or toxic concentrations of certain compounds may cause dismiss in the reactor performance and might be in consideration. In tables 1.12 and 1.13, these toxic and inhibitory compounds are listed, table 1.12 for inorganic and table 1.13 for organic compounds.

Nevertheless, anaerobic biomass has a strong potential of being acclimated in the presence of toxic compounds. The key factor is to expose the biomass to relatively low concentrations, and then slightly increase it until the targeted concentrations. That means that the toxic compound does not inhibit anymore the right anaerobic digestion of the effluent. Especially in industrial effluents, anaerobic digestion is preferred to aerobic alternative, due to the acclimatising easiness and also because some compounds are only anaerobically biodegradable.

Table 1.12. Toxic and inhibitory inorganic compound in anaerobic digestion (Metcalf and Eddy 2003)

Substance	Moderately inhibitory concentration (mg/L)	Strongly inhibitory concentration (mg/L)
Na^+	3500-5500	8000
K^+	2500-4500	12000
Ca^{2+}	2500-4500	8000
Mg^{2+}	1000-1500	3000
Ammonia-nitrogen NH_4^+	1500-3000	3000
Sulphide, S^{2-}	200	200
Copper, Cu^{2+}		0.5 (soluble)
		50-70 (total)
Chromium, Cr (VI)		2.0 (soluble)
		180-420 (total)
Nickel, Ni^{2+}		30 (total)
Zinc, Zn^{2+}		1.0 (soluble)

Table 1.13. Toxic and inhibitory organic compound in anaerobic digestion (Metcalf and Eddy 2003)

Compound	Concentration resulting in 50% reduction in activity (mmol)
1-Chloropropene	0.1
Nitrobenzene	0.1
Acrolein	0.2
1-Chloropropane	1.9
Formaldehyde	2.4
Lauric acid	2.6
Ethyl benzene	3.2
Acrylonitrile	4
3-Chlorol-1,2-propanediol	6
Crotonaldehyde	6.5
2-Chloropropionic acid	8
Vinyl acetate	8
Acetaldehyde	10
Ethyl acetate	11
Acrylic acid	12
Catechol	24
Phenol	26
Aniline	26
Resorcinol	29
Propanol	90

Positive features for the anaerobic process (Speece, 1996), if compared with aerobic treatment, are:

- Process stability
- Reduction of waste biomass disposal costs
- Reduction of nitrogen and phosphorus supplementation costs
- Reduction of installation space requirements
- Conservation of energy, ensuring ecological and economic benefits
- Minimization of operational attention requirements
- Elimination of off-gas air pollution

- Avoidance of foaming with surfactant wastewaters
- Biodegradation of aerobic non-biodegradables
- Reduction of chlorinated organic toxicity levels
- Provision of seasonal treatment

On the other hand, disadvantages of anaerobic treatment are (Speece, 1996):

- Long start-up requirements for developing of biomass innoculum
- Insufficient alkalinity in dilute or carbohydrate effluents
- Insufficient methane generation form diluted effluents to provide the heating to optimal temperatures
- Sulphide and odour generation from sulphate feed stocks
- No nitrification
- Low kinetic rates at low temperatures
- High NH_4 concentrations (40-70 mg/L) required for maximum biomass activity

1.2.3. Thermophilic anaerobic digestion

Traditionally, mesophilic (~33ºC) anaerobic digesters in Municipal WWTP used for treating the sludge use continuous stirred tank reactors (CSTR) with biomass suspended along the reactor by means of mechanical agitation or/and in some cases biogas recirculation. However, this process does not assure hygienic regulations for being considered class A biosolids, and therefore its reuse in land, which is strongly recommended by the European Commission in order to recycle nutrients and organic matter content in the sludge.

The thermophilic process is reported to enhance biochemical reactions (Zábranská et al. 2000). Rate reaction increases with temperature in a factor of 2 or 3 times higher than in mesophilic conditions increasing the efficiency (Metcalf and Eddy, 1995). This means that less time is needed to reduce the same amount of organic matter (Zábranská et al. 2000) and the organic load rate can be potentially elevated. Additionally, it can be obtained the same organic matter reduction in shorter periods of time and consequently the reactor volume is smaller therefore reducing the investment cost (Romero et al. 1990)

Consequently, migration to higher temperatures, such as thermophilic range, can enhance excess sludge reduction, its further reuse as fertiliser accomplishing the sanitary conditions, and sludge revalorisation because of the biogas production.

Changes in temperature operation to thermophilic ranges can result in a better exploitation of the existing infrastructures. There are some studies about the different influencing parameters in thermophilic anaerobic digestion. De la Rubia et al. (2006), reported higher volatiles solids removal for thermophilic temperature range than for mesophilic at the same hydraulic retention time (HRT). In contrast, it is reported that COD removal has no significant differences when temperature changes (Garber et al. 1975); interestingly, other studies indicate that there are higher COD reduction at thermophilic temperatures.

Theoretically, as thermophilic bacteria give higher reaction rates, biogas production should be higher; this is not yet confirmed thus some authors report lower values (Rimikus et al. 1982) and other higher (Zábranská et al. 2000).

Pathogenic destruction in anaerobic treatments is clearly more efficient in thermophilic ranges. Wantanabe et al. (1997) reported 5 log units of pathogens (*Fecal coliform* and *Enterococcus*) decrease in thermophilic temperature with andHRT of only 10 days, whereas in mesophilic digestion with HRT of 30 days was only of 1-3 log units. Parallelly, Wantanabe et al. (1995) found inactivation of pathogenic bacteria at 55ºC and for HRT of 20 days, while at 35ºC was not observed complete inactivation. Also, it is reported that *E. coli* is inactivated at temperatures above 60ºC (Middelberg 1995).

To summarize, the advantages and disadvantages of the thermophilic anaerobic digestion over mesophilic conditions are:

<u>Advantages</u>

- High organic matter removal efficiency
- Accelerated biochemical reactions.
- Higher growth rate of microorganisms
- Biogas enhancement
- Higienisation effects (pathogen reduction enhancement)
- Higher destruction of protein, as reflects the higher ammonia concentration.
- Lower solubilisation of CO_2, resulting in a reduction of the alkalinity requirement
- Improves dewaterability

- Increase bacterial destruction

Disadvantages

- Low net yield of biomass, only 50% of that possible at 35ºC
- Slow start-up acclimatising to OLR changes, or substrate changes.
- High VFA concentration in the effluent
- Higher energy requirement for heating
- Poor supernatant quality containing high quantities of dissolved solids and odours
- Less stability
- Odour effluent due to high VFA concentration

As most of the existing facilities for sludge treatment in WWTP operate at mesophilic conditions, the changing into thermophilic temperatures requires a minimum re-engineering of the plant, and the cost-benefit investment is clearly acceptable. Fang and Lau (1996) studied the start up of thermophilic UASB reactor using mesophilic seed sludge using one-step temperature change. Also Iranpur et al. (2002) presented full scale experiment results with a step-wise strategy, temperature rise of 3ºC/day up to 55ºC. Boušková et al. (2005) studied two temperature changing strategies in anaerobic CSTR reactors treating sewage sludge. It was found that despite the disturbance in the process parameters, one-step temperature increase required much lower time, only 30 days, than step-wise temperature increment (70 days). It was concluded that is possible to adapt mesophilic to thermophilic conditions under constant operation and loading rates, however anaerobic performance is not optimal.

It is also suggested that the rapid acclimatation to the new temperatures indicates that thermophilic microorganisms are already present in the mesophilic sludge.

1.2.4. Thermophilic-mesophilic co-digestion. Dual digestion process

In general, one step process has been commonly used in anaerobic digestion where in one single stage all anaerobic reactions take place. However, later studies are focus in intensifying the two main processes in anaerobic digestion: (1) the acidification step, where organic acids are generated and (2) the gasification stage (methane production).

This dual system aims at incorporating the advantages of both mesophilic (low concentrations of VFA) and thermophilic digestion (hydrolysis improvement, high destruction of pathogens and VFA) avoiding the disadvantages. It is reported to have better stabilisation conditions as it could prevent the system from possible inhibition problems, especially high VFA presence in methanogenic stage. Also, the metabolic activities of acidogenic (fast-growing) and methanogenic (slow-growing) microorganisms are not the most efficient under the operating conditions of a single digester (Rubio-Loza and Noyola 2010). It has also been reported that a two-stage process is better than a single-stage process because it separates faster acidogenesis reactions in the first-stage from the slower methanogenesis reactions in the second-stage (Solera et al. 2002). Such kinetic separation of different steps in anaerobic digestion enhances the overall process by improving the individual steps.

The TPAD (thermophilic phased anaerobic digestion) treatment process generally has a short retention time in the thermophilic and acidification step followed by a longer retention time mesophilic step, which provides major pathogen control and effective organic matter treatment (Han et al. 1997, Huyard et al. 2000).

There are several studies concerning the TPAD, however most of them have been developed on various wastes such as: dairy wastewater; cattle, and combinations of wastes like co-digestion of sewage sludge and confectionery waste; cattle waste co-digestion of sewage sludge and food waste etc. (Riau et al. 2010).

Concerning sewage sludge treatment, Huyard et al. (2000) obtained Class A biosolids and a VS reduction of 61% with thermophilic/mesophilic two phased anaerobic process of a feed mixture of PS 60% and 40% WAS with an HRT of thermophilic (55ºC) reactor of 2 days and 10 days for mesophilic (37ºC). Roberts et al. (1999) reported that was possible to reduce the HRT of acidogenic stage in thermophilic conditions (55ºC) at below12 h and had little effect on the properties of the sludge produced in the second mesophilic step (33ºC and TRH of 10 days). It was found that VS reduction was low 25-35% in all the different experimental case studies, even at the control mesophilic single stage (HRT = 20 days), and also reported specific methane yields between 0.35-1.13 (m^3/kg $VS_{removed}$) in dual digestion while in a mesophilic single stage was only between 0.30-0.45. Riau et al. (2010) experimented with different solid residence times when treating a mixture of primary and activated sludge to find the best combination in the dual digestion: TPAD 15/15, TPAD 5/15, TPAD 3/15 or TPAD 3/12 and compared them with single stage, either mesophilic or thermophilic. Temperature-phased anaerobic digestion systems showed better performance and process stability at total SRT of 15 days than single-stage mesophilic or thermophilic digestion at SRT 15 days. TPAD 3/15 was found to be the best, with 87% of volatile solid reduction, 0.62 LCH_4 /g $VS_{removed}$,

faecal coliform densities <103 MPN/g TS and *Salmonella* spp. of 1 MPN/4 g TS.

Two-phase or two-stage anaerobic processes showed good performance in the effluent quality, methane yield, volatile solid reduction and process stability (Roberts et al. 1999, Riau et al. 2010, Huyard et al. 2000). However applying this process into the existing WWTP would require re-engineering of the process, as an introduction of a new reactor would be required.

1.2.5. Anaerobic digestion enhancement. Pretreatments

One of the main operation drawbacks in wastewater treatment plants is related to the huge amount of excess sludge generated, which has become a serious disposal problem. Several efforts have been made following two main strategies in order to deal with this setback. The first strategy aims the minimisation of the sludge production from biological systems, based on lysis-crytic growth, uncoupling metabolism, maintenance metabolism, predation on bacteria, etc (Wei et al. 2003). Several processes have been studied in this field, such as oxic-settling-anaerobic process, high dissolved oxygen process, uncoupler-containing activated sludge process, ozonation-combined activated sludge processes, control of sludge retention time and biodegradation of sludge in membrane-assisted reactor, etc., so the sludge production can be reduced by 20-100% (Liu and Tay 2001). The second strategy is based on sludge post-treatment processes, its major main goal being to enhance the presence of organic substances in the aqueous phase for subsequent degradation. This latter strategy is the most widely used in WWTP and it is the premise followed here.

As previously commented, hydrolysis is known to be the rate limiting step for anaerobic digestion, so the strategy followed is to improve this step. A number of pre-treatment processes, i.e. thermal, chemical, biological and mechanical and their combination (Bougrier et al. 2007; Lu et al. 2007; Chen et al. 2007; Elliott and Mahmood 2007; Wong et al. 2006; Cacho Rivero and Suidan 2006, Vlyssides et al. 2004; Valo et al 2004), have been investigated in order to enhanced hydrolysis.

The main purpose of sludge pre-treatment is to facilitate the hydrolysis step. What is wanted is that the membrane cell brakes down, allowing the release of the complex organic compounds such as carbohydrates, lipids, proteins and nucleic acids for further hydrolysis so that easy-biodegradable substrates are more accessible for the anaerobe microorganisms (Kim et al. 2003; Müller 2001), as represented in figure 1.6. Moreover, as cell water is freed under hydrolysis, the viscosity of sludge is lowered. Therefore, sludge with about 12% TS can be handled in the same way as raw sludge with 5-

6% TS. This allows for a higher sludge concentration in the digester feed, higher buffer capacity and a stable digestion process (Bougrier et al. 2007)

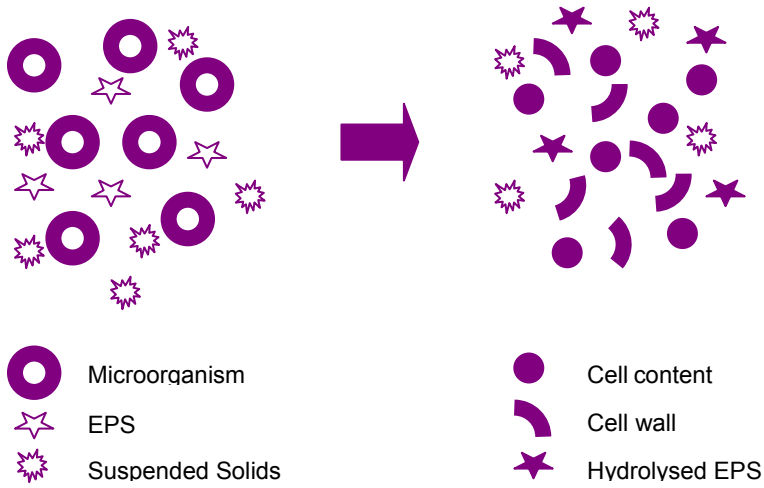

Figure 1.6. Hydrolysis

Hydrolysis results in a number of advantages:

- Enhanced biogas production, increase of organic matter converted to biogas
- High quality biogas, rich in methane, low in H_2S
- Ideal for green electricity, as renewable vehicle fuel, or substitute for natural gas
- Improved dewaterability after digestion
- Significant mass reduction
- Less water evaporation for sludge drying
- Improvement of pathogens elimination
- Increased stabilization of cake after digestion due to high organic matter conversion
- Nno negative odour associated to he digested sludge; odour nuisances prevented due to the closed process cycle
- Lower retention time and higher dry-solids content in digesters
- Reduced viscosity from thermal hydrolysis, making the sludge more fluid
- Increased rate of digestion

- Robust anaerobic digestion process
- Ideal feed for anaerobic digestion; consistent and free of unwanted micro-organisms
- High alkaline buffering capacity
- High active biomass concentration
- Compact design that makes THP easy to retrofit to existing sludge treatment plants
- Existing digester assets can be used to treat sludge or other biowastes from a wider region without further investment
- Existing digester systems can be fed at more than double conventional rates, thus increasing the capacity of existing plants or minimising capital expenditure for new digesters

Several methods and a combination of them have been applied to sludge in order to maximize hydrolysis (Müller 2001, Carrère et al. 2010):

- Heat treatment
- Chemical treatment: ozone, acids, alkali and H_2O_2
- Mechanical disintegration: ultrasounds, mills, homogenizers, lysate centrifuge disintegration.
- Freezing and thawing
- Biological hydrolysis with or without enzyme addition (Guellil et al. 2001; Thomas et al. 1993)

Most of the studies are focused to one pre-treatment at very specific conditions. Thus, those results may not be compared directly, as they strongly depend on the sludge (primary sludge, secondary sludge, mixed sludge, sludge age, sludge concentration, etc) and biodegradability performance (temperature, sludge activity, etc). Most of pretreaments have only been applied to WAS, maybe because WAS is known to be more difficult to digest than primary sludge (Bougrier et al. 2007), despite that most of WWTP generate both primary and secondary sludge and then are combined prior to anaerobic digestion.

Bougrier et al. (2006b) compared ultrasound, thermal hydrolysis (170ºC for 30 min) and ozonation pre-treatment on activated sludge and found that thermal treatment was the most efficient in terms of solubilisation, resulting in an improved biogas production at mesophilic conditions. Kim et al. (2003) also compared thermal (121ºC for 30 min) with chemical (NaOH) and ultrasound pre-treatment; the best results in terms of biodegradability in

mesophiilic conditions where for thermal > thermochemical pretreatents > ultrasound.

Camacho et al. (2002) tested thermal (60-95ºC), thermo-oxidative treatments with H_2O_2 (at 60ºC and 95ºC), and O_3 and mechanical treatment with a high pressure homogeneizer. Mechanical and thermo-oxidative treatments showed better performance in terms of organic matter released, around 60% of $COD_{released}$ (expressed as % COD_{tot}) and 60-65% of $TOC_{release}$, respectively. Thermal treatment leads only to 35% of $COD_{release}$ at 95ºC for a contact time of 24 h. Elimination of material was observed only in oxidative techniques.

Thermal pretreatments

Thermal pre-treatment studies are focused on the pre-treatment duration and temperature conditions, table 1.1 presents some works related to this treatment.

A few studies deal with temperatures below 100ºC, and usually focus in one treatment temperature. Most of the literature uses quite high contact time, from 1 to 7 days (Ferrer et al. 2008, Gavala et al. 2003, Lu et al. 2007, Ge et al. 2010, Skiadas et al. 2005), although there are studies at much lower contact times <7h (Paul et al. 2008 and Wang et al. 1997) obtaining that large quantity of soluble organic substrates were eluted within the first 10 min, later slightly increasing with time, and with not remarkable increase over 30 min (Wang et al. 1997).

Gavala et al. (2003) found that pre-treatment step at 70ºC of primary sludge followed by thermophilic anaerobic digestion is more efficient in terms of methane yield and methane production rate than mesophilic processes, whereas pre-treated WAS has only a positively effect on methane production potential when mesophilic digestion followed. They concluded that the selection of the pre-treatment duration as well as anaerobic digestion temperature should depend on the ratio of primary and secondary sludge.

A few authors studied different temperature conditions over the same sludge (Paul et al. 2008, and Wang et al. 1997). Wang et al. 1997 applied 60, 80, 100 and 120ºC and found that solubilisation increases with temperature.

With ewapect to higher temperature ranges, Valo et al. (2004) found that the degree of WAS solubilization was mostly influenced by the temperature selection rather than time at temperature at ranges of 130-170ºC. Only 15 min was enough for most of the solubilization during thermal hydrolysis being the optimal at 170ºC. Most common treatment time values are in the range 30-60 min.

Most of the anaerobic biodegradability performances of thermally pre-treated sludge have been studied in mesophilic conditions. Earlier studies over thermophilic ranges were described by Stuckey and MacCarthy (1984), obtaining the best performance with thickened WAS pretreated at 175ºC for 1 h, where biogas generated increased from 42% to 51%, then at higher temperatures biodegradability declined which was endorsed to the formation of toxic compounds. This was attributed to the occurrence of Maillard reactions (Bougrier et al. 2008 and Dwyer et al. 2008), which is a reaction between aminoacids and carbohydrates (sugars) at high temperatures, that generate melanoidins known to be difficult to degrade and adding colour to the effluent (Dwyer et al. 2008). Other studies were performed by Pinnekamp 1989, and lately Gavala et al. (2003), Lu et al. (2007), and Climent et al. (2007) obtaining always a positive effect over biodegradability over pre-treated sludge.

Chemical pretreatment

Addition of chemicals as pre-treatment has mostly focused in alkali and acid treatment in order to increase or decrease the pH of the sludge (Everett 1974, Chen et al. 2007). Table 1.16 presents the major literature found. Also their combination with other sludge disintegration techniques, mainly with thermal treatment (Tanaka and Kamiyama 2002, Kim et al. 2003, Vlyssides and Karlis 2004, Neyens et al. 2004), has been seen to highly improve further hydrolysis. High pH in the medium causes protein to loose their natural shape, saponification of lipids and hydrolysis of RNA. Strong alkali ionizes the hydroxyl groups ($-OH \rightarrow -O^-$) which leads to swelling and solubilisation. Cells cannot keep the turgor pressure and disrupt (Li et al 2008, Neyens et al. 2003), and release of the intracellular material. In fact, some authors measure the efficiency of disintegration methods based on sludge pretreated with NaOH, as it leads to a very high degree of disintegration (Khanal et al. 2007, Schmitz et al. 2000, Tiehm et al. 2001). Acid hydrolysis has also been studied, as it also may cause cell lysis; proteins and plysaccharides are unstable and the links are broken, leading also to high solubilisation levels. However, it has serious dreawbacks such as corrosion or solubilisation of heavy metals and phosphates (Neyens et al. 2004). Improvement of the hydrolysis was following the order: alkaline > acidic > (neutral and blank test) (Chen et al. 2007)]. The principal drawback of acid or alkaline treatment is that a post-neutralization is required prior to anaerobic digestion.

Earlier studies have studied ozone and hydrogen peroxide as sludge hydrolytic promoters, with quite good solubilizating rates. Optimal conditions are reported, as these oxidising chemicals at high dose may destroy (oxidize) organic material at expense of subsequent methane yield, ‘wasting’ the chemical and loosing methane, i.e. energy production, (Yeom et al. 2002, Chu et al. 2009).

Peroxidation of sludge has been mainly studied using Fenton process (Neyens et al. 2004, Dewil et al. 2005, Valo et al. 2004), i.e. in the presence of Fe ions and acidic conditions. Neyens et al. (2004) found that Fenton's peroxidation enhances dewaterability, however no solubilisation effect was reported. Only Camacho et al. (2002) found some correlation but just with the addition of hydrogen peroxide at high temperature and dose. To reduce economic costs related to the use of chemicals, low dose and low temperatures could be of great interest (Cacho Rivero and Suidan 2006).

Wang et al (2006) studied chemical addition combined with microwave of WAS within 60-120ºC range of temperature and 0-3% wt of H_2O_2. They obtained a solubilization of 100% of COD at 80ºC and 3% wt. Cacho Rivero et al, (2006) applied H_2O_2 dosages at 90ºC and 65ºC as a co-treatment with mesophilic anaerobic digestion; they found that the major effect of the thermo-oxidative treatment was the solubilization of the particulate organic matter as increase of soluble COD was observed, although no organic matter removal was seen.

Despite the evaluation of several pre-treatments, there are few studies combining them with thermophilic digestion. Ferrer et al. (2007) studied thermal pre-treatment at 70ºC for 9 h and found a positive effect on biogas production, at 50% increase, however at higher temperatures it was not found any effect. Also Bougrier et al. (2007) pre-treated sludge and found an increase in methane production of 25% at 190ºC. These studies mainly focus in biogas production and sanitary conditions are less extensively investigated.

A combination of thermophilic digestion using a thermally or chemically pre-treated sludge seems to be a viable option for those WWTP with mesophilic digestion implemented as it only would require a minimum re-engineering (Appels 2008).

Some of these pretreatments have been applied in full scale WWTP. Of course, there are a number of industrial applications related to sludge, which are offered at commercial scale The most commonly used in industrial application are reported in table 1.14. For more information about the principles and real application, see annex II. The main drawback of the industrial options is that they are proprietary technologies, some patented, which usually means an extra cost in the application of these solutions, requires major re-engineering of the existing installations, specialised workers for operating the new equipment in safe manner and severe operation conditions with additional measures for safe operation. Instead, the objective of this work package was to demonstrate that the application of freely available technology with minor re-engineering allows easy equipment design and coupling with the existing installations.

Table 1.14. Use of sludge pretreatments in industrial applications

Name	**Company**	**Sludge pretreatment**	**Performance after anaerobic digestion**
Cambi BioThelys	Cambi recycling energy Veolia Water Solutions	Thermal: steam T=165ºC for 20-30 min P=12 bar	50-65% VS reduction Produces Class A biosolids
Microsludge	Paradigm Environmental technologies, Inc	Chemical: NaOH Pressure drop	85% of VS reduction 60% of TS reduction Produces Class A biosolids
Sonix Sonolyzer	Ovivo Sonotronic	Ultrasound F=20 kHz	30% TS reduction 50% biogas production
Biodiet technology	Kankyo Engineering Company, Ltd.	Chemical: a strong oxidizing chemical With CO_2 and water	Not reported
Porteous process	England's Hawker Siddeley corp.	Thermal T=130-200ºC for 30 min	50% TS reduction
Zimpro process	Siemens water Technologies	Wet air oxidation T=250ºC P<35 bar	65% of COD reduction
Synox, Protox and Krepro	-	Combination of chemical (acid or alkaline) and thermal	Not reported
Kady Biolysis	KADY International Inc.	Mechanical treatment	Not reported
Kurita Bioleader	Kurita Water Industries	Chemical: O_3	Not reported

Table 1.15. Literature in thermal sludge treatment

Reference	Type of sludge	Pretreatment	Effect of pretreatment	Anaerobic digestion	Results
Lu et al. 2007	PS, after gravity sedimentation tank	70ºC @2days	$VSS_{reduction}$ =29.4%	CSTR 55ºC, HRT=13 days	Total VSS_{red}=55.3% (12% of increase) Increase in 48% in CH_4, from 13.6 to 20.1mmol CH_4/VS_{in} Better pathogen destruction
Climent et al. 2007	WAS	110-134ºC @20-90min	Disintegration evaluation : %DVS/VS increment = $815.96+225.42 \cdot T+239.53 \cdot t+ 13.83 \cdot T^2 +4.13 \cdot t^2 +149.17 \cdot T \cdot t$ Optimal: 134ºC@90min=915% of increment Dependent on time	Batch, 55ºC	No differences between non treated and treated sludge in biogas production
		70ºC@9, 24, 48 and 72h	Optimal 70ºC@9h At 9h, 24h and 48h same effect At 72h declines, high VFA levels, that may inhibit	Batch, 55ºC	Optimal @70º for 9h pretreatment, best biogas production Increase in 58% in biogas production
		Compare thermal with: Ultrasonic Microwave	The best is thermal 134ºC@90min=915	Batch, 55ºC	The best is 70ºC@9h in biogas production

Gavala et. al 2003	Dewatered PS Dewatered WAS	70ºC@1, 2, 4, 7 days	Not reported	Batch, 55ºC	Thermal pre-treatment more efficient in WAS than PS. Terms of methane production Best results: PS, after 7h pretreatment WAS, after 7h pretreatment
				Batch, 37ºC	PS, after 4h pre-treat WAS, after 7h pre-treat
Wang et. al 1997	WAS	60ºC, 80, 100, 120ºC@ 5, 10, 20, 30, 60 min	Time of treatment Large quantities of soluble organic substrates were eluted within the first 10 min, later increased slightly with time.	CSTR, mesophilic 36 HRT= 10, 8, 6, 4 dies	Higher HRT=higher organic matter destruction At higher pretreatment temperature lower methane content Optimum in methane generation @60ºC HRT=8days: methane +52.1% on increase and 26.6% VS eliminated than untreated
Pinnekamp 1989	Thickened WAS PS thickened	120-220ºC @ 45, 90 and 150min.	$VS_{reduction}$ rises with increasing pretreatment temperature in PS and WAS. PS: $VS_{reduction}$= @135ºC 7%, @220ºC=22% WAS: $VS_{reduction}$=@135ºC 5-23%, 220ºC=22-55% depending on the SRT	33ºC and 55ºC HRT=20day 33ºC and 55ºC HRT=10day 33ºC and 55ºC HRT=7.5	There is a reduction in biogas yield at 220ºC. At HRT=20days mesophilic and thermophillic of WAS pre-treated at 150ºC resulted in the same gas yields (393 ºCL/kg VS_{in}). Other digestion times give poorer biogas yields for thermophilic. Preheating time (45, 90, 150min) does not further improve biogas

Wang et.al 2009	Not specified,	@170ºC for 30min	No change in TS and VS From SS 42.02 to 34.36 g/L From $COD_{soluble}$ 1.82 to 13.77 g/L: From VFA 376 to 2581 mg/L as COD) From 780 mg/L alkalinity to 1580	Compare type of reactors at mesophilic C(35ºC) CSTR and ASBR OLR= 2.71 $kgCOD/m^3day$ HRT=20day 5.42 $kgCOD/m^3day$ HRT=10day	Comparison between CSTR and ASBR, the latest performs better. But problems of solids accumulation CSTR: $VS_{removal}$ 54.32% for HRT=20day, 45.21% for HRT=10day CSTR: $TCOD_{removal}$ 60.25% HRT=20day, 48.20 for HRT=10day Methane content: 63.21% HRT=20day, 62.20% for HRT=10day Gas yield ml $CH_4/gCOD_{in}$= 213 HRT=20day, 175% for HRT=10day
Li and Noike 1992	WAS	@120-175ºC for 15-120min	It solubilises with temperature Best option at 175ºC for 30min with 55.2% of COD solubilization	Mesophilic (35ºC) Batch and Continuous HRT=1.5-10days	Optimal conditions: HRT=5-10 days @170ºC for 60min 60% COD removal efficiency 223-235 ml Biogas prod/gCOD (2 times higher the control)
Paul et al. 2006	Digested sludge (DG) from anaerobic dig. WAS	@95ºC for 10-120min @40-95ºC for 0-7h	Differences in solubilisation behaviour depending on sludge origin DS< AS Released COD in DS=40% and in WAS=15% @95ºC,t=40min The increase in the COD/TKN ratio in the solubilisation fraction suggest preferential solubilisation of proteins over carbohydrates.	-	-

Bougrier et al. 2007	Thickened WAS	@135 and 190ºC for 30min	$COD_{solubilisation}$=34 and 46% after 135 and 190ºC	CSTR 35ºC, HRT=20days OLR= 1 gCOD/day/L	190ºC more efficient in $COD_{removal}$=63% $TS_{removal}$=49% $VS_{removal}$=49% Lipids degradation yield=from 67 to 84% Carbohydrates degradation yield from 56 to 82% Proteins degradation yield from 35 to 46 Methane production increase 25%
Stuckey and McCarty 1984	Thickened WAS	@150-275ºC for 1h	Not reported	Batch 35ºC Batch 55ºC	Evaluate % Bioconvertivity: MESO: From 48% to 61% at 175ºC then decreases with temperature increase THERMO: From 42% to 51% @175ºC, then decreases with temperature increase
Kim et al. 2003	WAS	@121ºC P=1.5atm for 30min	$COD_{soluble}$ =from 8.1% of to 17.6%	Batch 37ºC	Increase of biogas from 3657 to 4843 L/m^3 WAS in (+32%)
Valo et al. 2004	Not reported	@130, 150, 170ºC for 15,30 and 60min	$COD_{soluble}$, and DTS, DVS increase with temperature. First 15min more of the solubilisation $COD_{soluble}$=from 2.7% to 59.5% at 170ºC for 1h $TS_{soluble}$=51% $VS_{soluble}$ =94% (of $TS_{soluble}$) Not dependent on time	Batch, 35ºC CSTR, 35ºC HRT=20days	Increase in biogas +45%, @170 for 60min Increase of biogas +61% from 88 to 142 ml/gCOD_{in} at 170ºC for 60min of pretreated sludge

Bougrier et al. 2006a	WAS	@170ºC for 30min	Not reported	Batch, mesophilic 24days	Increase of CH_4 production from 221 to 333 ml/g COD_{in} (+76%)
Bougrier et al. 2006b	WAS	@170ºC for 30min	Not reported	CSTR mesophilic HRT=20days	Increase of CH_4 production from 145 to 256 ml/g COD_{in} (+51%)
Bougrier et al. 2008	5 different WAS	@90-200ºC for 30min	COD solubilisation: S_{COD} (%)= 0.312*T (ºC)-8.73 R^2=0.81 Solids sol: TSS/TS and VSS/TSS ratio decreased with treatment temperature,	Batch mesophilic 17-24days	Biogas volume enhancement linked with COD solubilisation =2.156+1.155 S_{COD}-2.348 Bo Bo=Sludge initial biodegradability
Eskicioglu et al. 2006	Thickened WAS	@96ºC, for 0min, no holding time Time of heating: Conventional heating(CH) for 80min MicroWave (MW)	$COD_{soluble}$ from 3621 to 16518 mg/L in CH and to 8669 in MW CH is better in COD solubilisation, this is most likely due to extended duration on exposure	Not reported	MW toxicity effect on secondary sludge digestion is expected to increase with MW temperature
Camacho et al. 2002	WAS	Thermal (40-100ºC)	$\%COD_{soluble}$=25% of COD @60ºC for 24h, no mineralisation $\%COD_{soluble}$=30-35% of COD @95ºC for24h, no mineralisatiion $\%COD_{soluble}$=35±7% of COD @ 120ºC for 45min (P=1bar)	-	-

Table 1.16. Literature review in chemical sludge treatment

Reference	Type of sludge	Conditions	Effect of pretreatment	Anaerobic digestion	Results
Yang and Gaudy 1974, Yang and Gaudy 1974,	Not reported	H_2SO_4 @121ºC for 5h	75-80% TSS solubilised	-	-
Singh and Patterson 1974	Not reported	H_2SO_4 @120ºC for 5h	60-70% TSS solubilized	-	-
Everett 1974	Not reported	H_2SO_4 @150-200ºC for 15-40min KOH @150-200ºC for 15-40min	Enhanced conditioning	-	-
Stuckey and McCarty 1979	Not reported	HCl @175-200ºC for 1h NaOH @150-200ºC for 1h $Ca(OH)_2$ @175ºC for 1h	52-54% COD solubilized 54-55% COD solubilized 40% COD solubilized	-	-
Alsop and Conway 1982	Not reported	H_2SO_4 @60-90ºC for 1-20min	Significantly improved dewaterability	-	-
Ray et al. 1990	Not reported	NaOH @20-40ºC for 0.5-24h	45% COD solubilized	Not reported	Gas production increased by 112%

Kovacs 1992	Not reported	H_2SO_4 @165ºC for 75min	Filter cakes <65%DS	-	-
Smith and Göransson 1992	Not reported	H_2SO_4 @150-160ºC for 1h	Significantly improved dewaterability	-	-
Woodard and Wukasch 1994	Not reported	H_2SO_4 @90ºC for 1h	50-60% TSS solubilized Filter cakes>50% DS	-	-
Burghardt et al. 1997	Not reported	NaOH @95ºC for 1h	55-65% VS solubilized Filter cakes>43% DS	-	-
Tanaka and Kamiyama 2002	WAS	NaOH @130ºC for 5min	53% of COD solubilised 48% of SS solubilised Lipid and carbohydrate where reduced by 20-30% VFA increased, but was only 3% of the COD	CSTR, 37ºC HRT=2-8days Batch for evaluate, methanogenic activity	Increase in removal COD from 38% to 57% at HRT=8days Specific methane production 3 times higher
Stuckey and McCarty 1984	WAS	NaOH @150-275ºC for 1h		Batch, 35ºC Batch, 55ºC	Evaluate % Bioconvertivity: MESO: From 48% to 58-67% at T>175ºC THERMO: From 42% to 54% at 225ºC
Kim et al. 2003	WAS	NaOH at different concentrations KOH $Mg(OH)_2$ $Ca(OH)_2$ And all of them @121ºC for 30min	Monobasic agents result in higher solubilization percentages. Themochemical give better solubilisation than only chemical The best is NaOH at 7g/L wher solubilisation increase from 17.6 to 86.5%	-	-

Vlyssides and Karlis 2004	WAS	Alkali (lime) @50-90ºC for 1-10h	Linear polynomial hydrosysis model was obtained with good correlation. At pH=11 @90ºC for 10h, VSS red=45% First hydrolysis of carbohydrates>aminoacids>fats>lipids	-	-
Valo et al. 2004 H_2O_2	WAS	KOH (is better than NaOH) Temperatures at room temperature and 130 and 170ºC Fenton: H_2O_2 150 and 300 mmol/l $FeSO_4$ 5mmol/L pH=3 with H_2SO_4 t=1h T=90-130ºC	At room temperature soluble COD=30.7% at pH=12, solubilisation of solids but mainly mineral Thermochemical is higher, CODsoluble=from 30.6% at 130ºC to 63.1% at 130ºC at pH=12 From 59.5% at 170 to 83% at 170 pH=12 Fenton, slight increase in COD solubilisation at 130ºC, (less than 5%) at 90ºC solubilisation is around 30%, however at higher H_2O_2 concentrations oxidation is observed.	Batch, 35ºC, biodegradability test CSTR, 35ºC HRT=20days	Showed that solubilisation lead to better biodegradability @170ºC was more efficient than 130ºC at pH=10
Camacho et al. 2002	WAS	Oxidative with H_2O_2 (@60 and 95ºC) (0-0.6g H_2O_2/gTSS) t=1h Oxidative with O_3 (0-2.5 gO_3/gTSS)	Temperature produces a synergetic effect in H_2O_2 treatment Mineralisation of organic matter was observed beyond 0.34gH_2O_2/g TSS Linear proportion, 60 mg TOC was slubilized/mol O_3 transferred, The oxidative treatment destroy floc structure and disrupted the micro-organisms	-	-

1.3. Thermophilic aerobic digestion (Autothermal digestion)

Currently, the most widely adopted method for stabilising sludge in the European Union is anaerobic digestion. As explained above, significant reduction in sludge is achieved through digestion, which is in line with European Waste Management Policy of Sustainable Development. However, nowadays digestions are carried out at mesophilic conditions (~33ºC) and digested sludge can hardly be reused as biosolids, due to the high content in pathogenic bacteria such as *Escherichia coli* and *Salmonella*. Only a migration to higher temperatures in the thermophilic range can enhance excess sludge reduction, its further reuse as fertiliser accomplishing the sanitary conditions, and sludge energetic revalorisation because of the biogas production.

Obviously, higher temperature requirement for the thermophilic treatments also is a drawback since external heat must be provided in order to achieve thermophilic conditions. The exceeding energy coming from cogeneration systems fed by the methane generated *in-situ* can easily offset this point. However, this is an indirect process with limited heat efficiency. Actual wastewater plants cannot always satisfy this larger energy consumption. A very interesting option is then the autothermal digestion, where an air injection starts an aerobic digestion generating enough heat to bring thermophilic conditions without need of external energy input. Typically 14190-14650 kJ/kg COD oxidised (EPA/625/10-90/007 1990).

Probably, autothermal operation will be the most favourable alternative for the wastewater facilities of small size towns, as they will not have available cogeneration systems that can provide the energy needed. Although the first study focused on Autothermal Thermophilic Aerobic Digestion, (ATAD), is from decades ago, ATAD is in fact a technology relatively new. Its main characteristic is that the reaction itself occurring in an aerobic environment produces the most of the energy required to achieve the thermophilic conditions. This is possible because of the high load of organic matter to be degraded, which generates a high heat power per volume unit.

As counterpart, there is a greater need of dissolved oxygen that only can be met using tailored equipment or pure oxygen. However, in case of low energy availability, implementing thermophilic processes could be a very suitable, e.g. when cogeneration plants are not recommended.

The main advantages of autothermal digestion are (Lampara and Alleman 1999; Csikor et al. 2002):

- Good organic matter removal.

- Fast degradation rates, which require smaller volumes than conventional aerobic and anaerobic digestion, thus solid retention time needed ranges from 5 to 15 days.
- Rapid inactivation of pathogenic microorganisms.
- Low sludge yields, so more substrate is metabolised into carbon dioxide and water instead of cell mass.

For succeeding in autothermal digestion some requirements are reported in some previous wastewater and sludge treatment studies (EPA/625/10-90/007 1990):

- High strength waste is needed; approximately organic feed should ensure a minimum concentration of COD 40000-50000 mg/L and a minimum feed volatile solid content1 of 2.51% w/w.
- Total solids should be below a maximum concentration 4-6% w/w, to allow adequate mixing.
- Air-input value is recommended at 4 $m^3/h/m^3$ active reactor volume, in order to achieve the high oxygen demand for treating organic matter that produces the sufficient energy for self heating.

ATAD has been addressed in a few number of studies reported in the literature (Zupaneie et al., 2008; Bartkowska and Dzienis, 2007; Layden et al., 2007a,b; Kovacs et al., 2007; Gomez et al., 2007), which state to be suitable for rather small WWTP (up to 40000 equivalent inhabitants), where investment to anaerobic processes for generation of biogas are not justified. However, many of these studies assume efficient aeration, which is not guaranteed in large installations (Lapara and Alleman, 1999; Gomez et al., 2007). This point is even more critical when thermophilic conditions are considered as it is the necessity to match the enormous OUR (perhaps as high as 1000-2000 mg L^{-1} h^{-1}) imposed by rapid COD consumption at thermophilic conditions -particularly at high temperatures when the saturation concentration of dissolved oxygen is much lower. The oxygen availability (mass transfer rate) is the key of the process as the temperature potentially achieved is proportional to the COD removed, and this latter to the aeration efficiency (Gomez et al., 2007), which is in the limit of non-mechanical systems for thermophilic conditions.

CHAPTER 2

Hypothesis and objectives

2.1. Hypothesis

Thermophilic process enhances biochemical reactions (Zábranská et al., 2000). Reaction rate increases with temperature in a factor of 2 or 3 in comparison to mesophilic conditions (Metcalf and Eddy, 1987) so that less time is needed to reduce the same amount of organic matter (Zábranská et al., 2000) and the organic load rate can be potentially increased. Additionally, as the same organic matter reduction can be obtained in shorter periods, consequently the reactor volume could be smaller, reducing the investment cost (Romero et al., 1990). Therefore, changes in temperature operation to thermophilic ranges can result in a better exploitation of the existing infrastructures. Pathogenic destruction in anaerobic treatments should also be clearly more efficient in thermophilic ranges (Wantanabe et al., 1997) founding inactivation of pathogenic bacteria at 55ºC and for HRT of 20 days, while at 35ºC was not observed

complete inactivation. Also, it is reported that E. coli is inactivated at temperatures above 60ºC (Middelberg et al., 1995).

Although some literature seems to suggest that thermophilic range should be enough to the full hygienisation of the sludge (Carrington et al., 1982; Wagner et al. 2008), it has been found that some especially reluctant bacteria withstands the typical thermophilic temperature of 55ºC. It is well known that pathogens are inactivated during exposure to heat, which must be above their optimum growth temperature to be effective and relatively fast. The period of exposure is dependent on the temperature and the species of the organism (Feacham et al., 1983). However, depending on the bacteria population, the kind of pathogen and even operating conditions, sometimes they need more drastic conditions to be effectively destroyed. Therefore, heating a higher temperature is needed or exposure to oxidation agents with the objective to eliminate these remaining bacteria, which also helps to improve the digestability of the raw sludge as degradation of organic matter also achieved improves the hydrolysis step.

Also more drastic conditions can promote sludge hydrolysis, which could improve the sludge stabilisation by enhancing its digestion. What is wanted is to make the organic matter present in the sludge more accessible for the microorganisms, thus facilitating its consumption. If the hydrolysis step is optimised, the digestion process could be more efficient.

Disruption of the cell results in the releasing of the organic compounds that are protected by the cell wall therefore promoting liberation of intracellular content (lipids, carbohydrates, proteins and nucleic acids) and letting them more accessible for the anaerobe/aerobe microorganisms in thermophilic conditions.

Several pre-treatment processes, thermal, chemical, biological or mechanical, and their combination are known to improve hydrolysis, by solublilization of sludge solids and disintegration or lysis of the cell walls. Cell lysis could also yield to complete hygienisation of the sludge, making it useful as fertiliser.

Muga et al 2008, by Life Cycle Assessment analysis (LCA) demonstrated that there are different degrees of sustainability in the way a particular treatment technology is selected and then operated, it is very difficult to find the ‘best overall option’ as is not easy to find the technology that satisfies a degree of social acceptance like odourless, visual impact, and employment in the community, space, etc, simultaneously minimizing costs and being best environmental option. However, in most of the studies evaluating sustainability by LCA, there is some step that is subjective to the author, and it implies weighting of the parameters under study, which are decisive to the final conclusion of sustainability assessment and depends on the author. Anyway, there are several indicators in the study of a WWTP

analysis that are decisive in its evaluation, such as biogas production and subsequent composting but with stringent hygienisation requirements.

Concerning sludge studies, there are several authors that include not only sludge management but the overall WWTP process and evaluate how to improve the operational of a municipal wastewater treatment plant using LCA as a decision tool for environmental protection. (Lundin et al. 2002, Suh et al. 2002, Palme et al. 2005, Pasqualino et al. 2009, Peregrina et al. 2006, Hong et al. 2009, Gallego et al. 2008, Houillon et al. 2005)

Suh et al 2002, studied the environmental impact over different sewage sludge treatments in the European context: incineration, agricultural land application or landfill and sludge stabilization processes such as lime stabilization, composting or anaerobic digestion. The project showed that the combination of anaerobic digestion and agricultural land application was the most environmentally friendly process.

Consequently, the hypothesis contrasted is that the application of thermal or peroxidation pre-treatment over a real sludge, followed by thermophilic anaerobic digestion, is able to give Class A biosolid hyginiesed sludge, acceptable for land wide-spreading, and additional enhanced biogas production and solid reduction.

2.2. Objectives

The main objective of this research is finding the better treatment option in order to enhance the stabilisation of the urban sludge and maximize the sub-products generated in this process and its reuse.

Based on this, specific goals were assessed. The objective of chapter 4 was to elucidate the effect that a pre-treatment has over a mixture of thickened primary sludge (PS) and thickened WAS by analysing both chemical and biological parameters in order to decide the better pre-treatment conditions to enhance thermophilic anaerobic digestion and obtain Class A biosolds.

The specific objectives were:

- Test the effect of low (30-80ºC) and high (110-200ºC) temperature pre-treatment over sludge.
- Explore the effect of the addition of hydrogen peroxide over the sludge at different doses.
- Determine the hygienisation of thermally and peroxidated sludge.

- Study the thermophilic anaerobic digestion of both chemically and thermally pre-treated sludge.

Once decided the optimal pre-treament conditions, in chapter 5, its impact on the enhanced thermophilic sludge stabilisation,, and the influence on the pathogen content of the digested sludge are established by using the optimal pre-treatment sludge conditions.

The specific objectives were:

- Build-up an anaerobic digestion pilot plant.
- Analyse the performance at different anaerobic digestion conditions. Specifically, if class A biosolids are obtained after the different anaerobic configurations
    - Thermophilic and mesophilic anaerobic digestion
    - Dual digestion: thermophilic-mesophilic phased reactor.
- Study the thermophilic anaerobic digestion of both chemically and thermally treated sludge

Finally, for small plants, chapter 6 presents the study of thermophilic aerobic sludge stabilisation of the same mixture of PS and WAS and their higienisation after digestion.

The specific objectives were:

- Build-up an aerobic digestion pilot plant.
- Study if class A biosolid are obtained after the thermophilic aerobic performance.

CHAPTER 3

Methodology

3.1. Sewage sludge

Sludge was provided by the Reus WWTP (wastewater treatment plant). The plant gives service to the cities of Reus, Almoster and Castellvell; with a capacity of treating 25000 m^3/day of wastewater, which is equal to a total of 200000 equivalent inhabitants. In figure 3.1 a process flow diagram of the Reus WWTP is presented showing the principal operational units.

The WWTP facilities include a solid matter removal stage and both water and sludge line treatments. The principal facilities of the Reus WWTP plant are:

Water pretreatment:

- 2 Screening fine process with a clear opening of 3 mm
- 2 Sand trap and aerated degreaser chambers

Physico-chemical treatment:	▪ 3 Flocculation and coagulation reactors
	▪ 2 Primary settlers
	▪ 1 Gravity sludge thickener
Biological treatment:	▪ Aerobic biological reactor
	▪ 2 Secondary settlers
Sludge treatment:	▪ Floating sludge thickener
Sludge treatment (cont.):	▪ 2 Heated anaerobic sludge reactors
	▪ 1 Anaerobic sludge reactor (mesophilic)
Sludge dewatering:	▪ 2 Filter press with polymer conditioning
Sludge processing:	▪ 2 Composting reactors

3.1.1. Raw sludge

For this study, it was decided to feed the reactors with a mixture of primary and secondary waste sludge in order to establish the same conditions that Reus WWTP has in the full-scale mesophilic anaerobic reactor. The mixture composition corresponds to the sludge rate produced in the physico-chemical and secondary aerobic treatments of the water process in the WWTP. The reactor feed, hereafter raw sludge, corresponds to 65% of primary sludge previously thickened in the gravity settler and 35% of WAS (waste activated sludge), concentrated in the flotation tank.

After collection, raw sludge was stored at 4ºC until its utilization, being the maximum storage time one week in order to maintain fresh sludge for the experiments.

3.1.2. Anaerobic seed

For the different anaerobic experimental tests, seed was used as a digester precursor, as the use of an inoculum considerably reduces the start-up time of anaerobic reactors (Speecy 1996). In our case, it was taken digested sludge from the mesophilic (~33ºC) anaerobic digester of the Reus WWTP, working with an OLR (organic loading rate) of 1.5 gCOD/gVSS at HRT (hydraulic retention time) of 20 days

The acclimatization of the mesophilic anaerobic sludge into thermophllic temperatures was performed in our laboratory and it will not be included in this study. For the start-up of the aforementioned seed, 10% of the reactor volume was inoculated with a full scale mesophilic anaerobic sludge at 43ºC running in the Reus WWTP, the remaining 90% reactor volume was filled with raw sludge. Reactors were operated in a batch mode until thermophilic sludge was achieved. Initially, three thermophilic reactors were simultaneously operated at 50, 55 and 60ºC.

3.1.3. Aerobic seed

The aerobic inoculum for the autothermal pilot plant was also provided by the Reus WWTP; however the inoculum was at the mesophilic temperature of 30ºC. It was necessary to slowly acclimate these microorganisms into thermophilic range.

The strategy followed to acclimatize the bacteria was increasing the temperature at intervals of 5ºC, starting from 30ºC, each two weeks with intermittent feed.

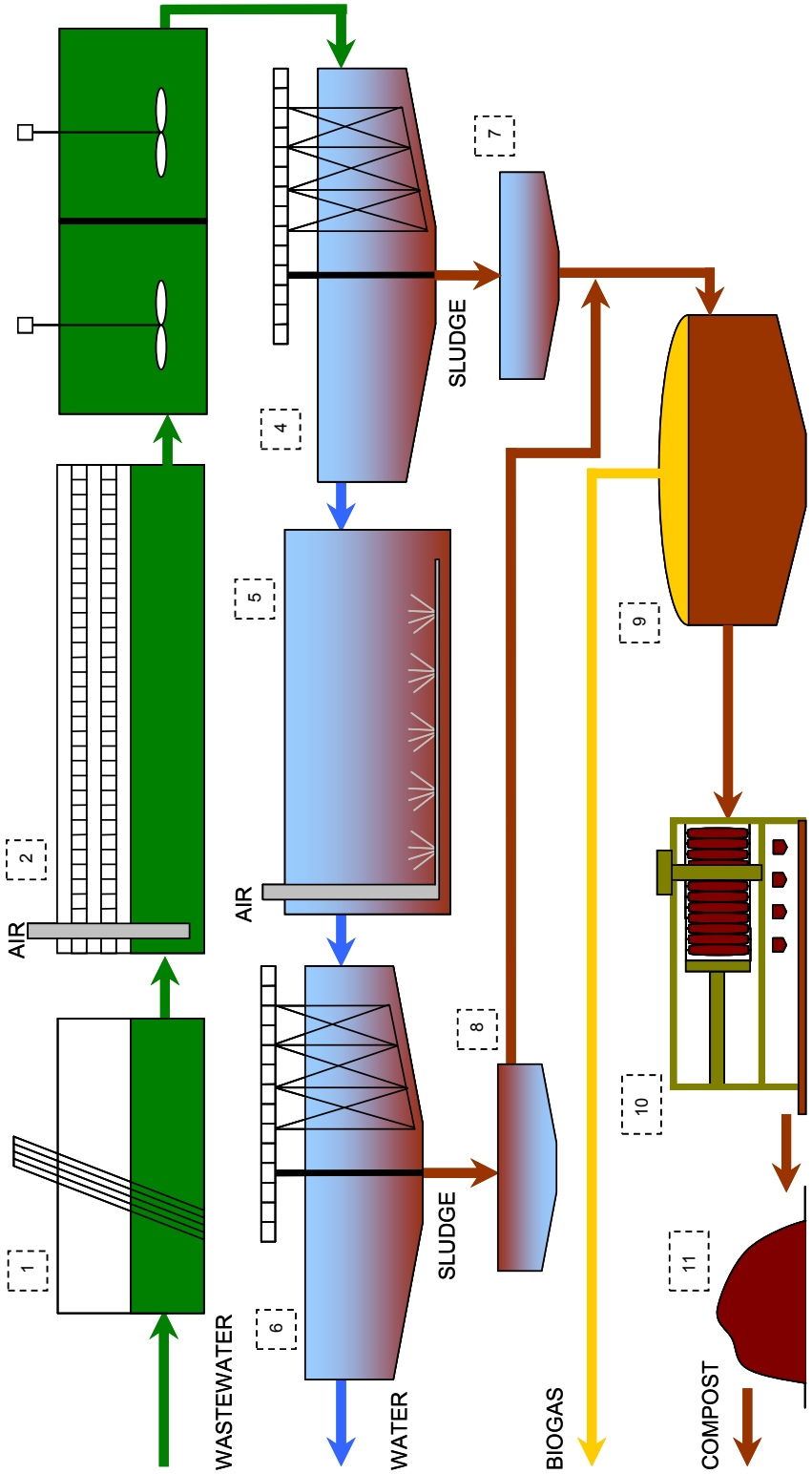

Figure 3.1. Process flow diagram of Reus WWTP. 1) Screening fine, 2) Sand trap and aerated degreaser chamber, 3) Flocculation and coagulation reactor, 4) Primary settler, 5) Aerobic digester, 6) Secondary settler, 7) Gravity sludge thickener, 8) Floating sludge thickener, 9) Anaerobic sludge digester, 10) Filter press, 11) Composting reactor

3.2. Experimental set-up

The experimental procedure was divided in five steps, in order to reach the objectives of the project.

1. Thermophilic anaerobic digestion. Different temperatures and HRT were tested. One reactor was kept at the mesophilic temperature of 33ºC and the other two reactors at two different thermophilic temperatures, initially 50ºC and 60ºC, this latter was decided to change into 55ºC due to its poor results. Also three different hydraulic retention times were studied 15, 20 and 25 days for 33ºC, 50ºC and 55ºC.
2. Two-stage anaerobic digestion. The first stage consisting in an acidogenic step at thermophilic range at 55ºC with and HRT = 5 days followed by a methanogenic step at 33ºC with and HRT = 10 days.
3. Thermophilic aerobic digestion at 55ºC. Study the possibility of autothermal digestion at HRT = 10 and 8 days.
4. Sludge pretreatment (thermal and peroxidation pretreatment). Sludge chracterisation and anaerobic biodegradability through biomethane potential tests (BMP) were assessed over thermal treatment between 30ºC and 200ºC and peroxidation treatment up to 1.0 g H_2O_2/g COD dosages.
5. Anaerobic digestion of pre-treated sludge in a semi-continuous mode (thermal and peroxidated sludge). Fermentation at mesophilic (33ºC) and thermophilic (50, 55ºC) temperatures at an HRT = 20 days was monitored. Also the quality of the thermophilic sludge was determined by activity and kinetic measurements.

3.2.1. Semi-continuous anaerobic digestion plant

A pilot plant with three glass reactors, each one with five litres of effective volume was constructed in order to study three different operation conditions at the same time. In figure 3.2 and figure 3.3 a scheme of each anaerobic reactor and the picture of the anaerobic pilot-plant can be observed.

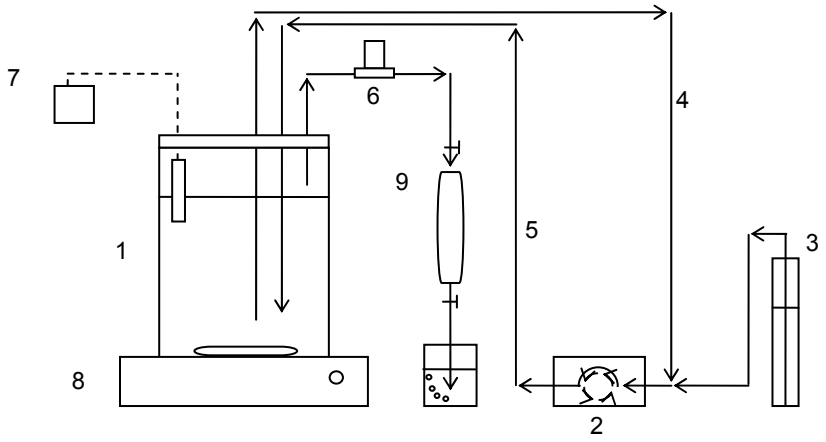

Figure 3.2. Schematic diagram of the anaerobic reactor. 1) semi-continuous stirred tank reactor; 2) feed and extraction pump; 3) feed and extraction volume measurement; 4) extraction line; 5) feed line; 6) gas meter; 7) thermostatic bath; 8) magnetic stirrer; 9) gas container

Figure 3.3: Anaerobic digestion pilot-plant

Maintenance of the reactors up to operation temperature was carried out by introducing the reactor in a thermostatic bath, with a thermostat (Digiterm 100, Selecta), as seen in figure 3.4. This bath was equipped with a water level control due to water loss evaporation caused by high temperatures. This system allowed reducing the costs in the reactor fabrication for not being jacketed. The cap of the reactor had several orifices, for inlet and outlet flux, and exit of the biogas produced. The pilot plant also was provided with a nitrogen inflow that could be use for maintaining oxygen-free conditions with inert atmosphere, specially used at the beginning of the experimentation, or when the reactor was inoculated.

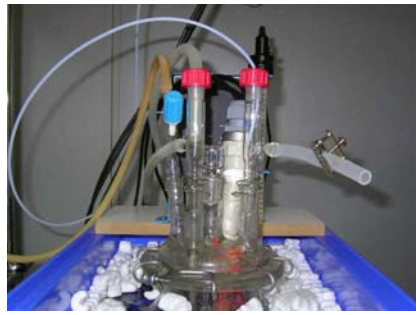

Figure 3.4. Cap reactor detail

A magnetic stirrer provided continuous agitation into the reactor at 120 rpm approximately (Agimatic HS, Selecta). The magnetic stirrer was changed every two years as material loss of the stirrer was observed during experimentation due to the continuous friction. Magnetic stirring was preferred to mechanical to avoid gas leaks in the reactor

Sludge feeding and sample extraction were driven by a peristaltic pump (Watson and Marlow, 323S, see figure 3.4), which drove the sludge without any direct contact with the pump materials, thus eliminating contamination by the operation equipment. Sludge circulated inside plastic tubs, where a three-way valve was installed for feeding and sample extraction. Every six months the reactor sludge lever was checked to assure volume reactor to be constant, and refilled with tap water if needed

Figure 3.5. Sludge feeding and sample extraction

Gas generated in the anaerobic digestion was measured by water displacement, as shown in figure 3.6. In experiments with pretreated sludge, a gas meter was used (MilliGas counter®, Ritter). Then the biogas was collected in a long 1 litre glass tube with three-way glass stopcocks at each for gas composition analysis.

Figure 3.6. Collector gas sampler

During the first experimental start-up, as it might be expected, sludge odour was a problem in the pilot plant. For eliminating this problem in the laboratory, an air extractor was installed and the reactors where isolated with plastic screen.

The three semi continuous anaerobic reactors were operated in a daily semi-continuous (draw-fill) mode operating each one at different conditions in order to study four temperatures and three HRT per each temperature. Temperature tested were the mesophilic temperature of 33ºC, and the thermophilic temperatures of 50ºC, 55ºC and 60ºC. Between 200-333 ml (depending on the operational HRT) of the digested sludge was withdrawn daily in each reactor. Immediately, the same amount of fresh sludge was fed, so that the volume was considered constant and the OLR is the organic matter fed by the fresh sludge.

Sludge was provided by the Reus WWTP, either raw sludge for the anaerobic digestion and the inoculum for starting the reactors, however the sludge treatment line possess only two anaerobic reactors, one operating at the mesophilic temperature of 33ºC and the other at 43ºC. No thermophilic anaerobic digester was operated in full scale in Catalonia when this study was performed, so acclimatization was needed

In order to give an accurate picture of the thermophilic digestion, efficiency and the quality of the end product (biogas), reactor samples were daily withdrawn and analysed as soon as possible, If not, they were stored in the fridge at 4ºC except samples for VFA analysis, which were stored in the freezer at -20ºC to minimize VFA evaporation. Table 3.1. summarises the frequency of the parameter analysed.

Table 3.1. Frequency and responsible of analytic parameters

Variable	Frequency	Responsible
COD	daily	URV
$COD_{soluble}$	daily	URV
pH	daily	URV
ST	2 days/week	URV
SV	2 days/week	URV
Alkalinity	2 days/week	URV
Volatile fatty Acids	2 days/week	URV
Biogas composition	2 days/week	URV
Biogas production	daily	URV
Total Organic Carbon	2 days/week	URV
Total Carbon	2 days/week	URV
BOD_5	1 day/week	External analysis
Ammonia , organic N_2	1 day/week	External analysis
Total Phosphorous	1 day/week	External analysis
Conductivity	1 day/week	External analysis
Salmonella	2 day/month	External analysis
E. coli	2 day/month	External analysis

3.2.2. Semi-continuous thermophilic aerobic digestion plant

3.2.2.1. ATAD reactor design

To succeed in autothermal aerobic digestion, is essential to supply an adequate amount of O_2, so that aerobic microorganisms degrade organic material and the heat released in the reaction is sufficient to maintain thermophilic temperature ranges. The most important parameters when designing an ATAD reactor are oxygen mass transfer, mixing and isolation. Literature reports some design parameters, presented in table 3.2, collected from experience in existing ATAD plants, which were taken into account in our pilot-plant construction.

Table 3.2. Design parameters for ATAD systems (EPA/625/10-90/007 1990)

Reactors:	Daily batch operation
	Two or more stages
Reactor type:	Cylindrical
	Height/Diameter ratio = 0.5-1.0
Sludge type:	Primary (gravity or air flotation thickened)
	WAS (gravity or air flotation thickened)
	Mixture of primary and secondary
	Domestic and industrial origin (manure)
Sludge feed characteristics:	COD > 40000-50000 mg/L
	TS > 40-60 g/L
	VSS ≥ 25 g/L
HRT:	5-6 days (20 h minimum)
Reactor conditions:	Reactor I: 35-50ºC, pH ≥ 7.2
	Reactor II: 50-60ºC, pH ~ 8.0
Air input:	4 $m^3/h/m^3$ active reactor volume
Specific power:	80-105 W/m^3 active reactor volume
Energy requirements:	9-15 kWh/m^3 of sludge
Heat potential for recovery:	20-30 kWh/m^3 of sludge

A pilot plant consisting in a 7 L cylindrical reactor of stainless steel was designed with an active effective volume reaction of 4 L, the scheme of the reactor can be seen in figure 3.7. The reactor was designed to operate in a manual semi-continuous daily-fill mode. The reactor has one orifice at the bottom for purging, and four on the cover of the reactor, for feeding and possibility to introduce on-line monitoring proves.

Foaming layer seems to improve oxygen utilisation with the consequent enhancement of biological activity. The possibility of foaming was taken into account for reactor design and for that approximately one fifth height of the reactor was kept free. Reactor shape in height/diameter ratio of active volume was designed to be 1, as suggested in literature (EPA/625/10-90/007, 1990), to minimize heat loss.

The importance of achieving thermophilic temperature ranges in autothermal digestion relies on taking advantage of the heat released during the oxidation process where organic matter is degraded. The design areas that most affect operating temperature include the efficiency of the aeration system, reactor insulation, foam management reactor, and sludge pre-thickening.

An insulation system was designed to achieve adiabatic conditions in the reactor system and to minimize heat losses caused by convection. Felt wool and elastomer were chosen as insulators in the reactor due to its low thermal conductivity coefficient, 0.071 W/m K (Perry's 1997) for felt wool, and easy availability.

Besides the auto-heating advantage of autothermal digestion, it is also recommendable the use of a double system that can be used either as an auxiliary heating or as a heat recovery device. The acquisition of this auxiliary equipment contributes to have a flexible pilot plant where parameters such as temperature digestion are to be studied. Additionally, in some cases supplementary heat should be provided to maintain thermophilic temperature conditions, especially when the feed sludge has insufficient biodegradable solids to sustain process temperature. Furthermore, safety reasons also suggest that having a cooling system is adequate to prevent an excessive increase in temperature reactor. According to literature (EPA/625/10-90/007, 1990), energy equivalent to 15-30 kWh/m^3 sludge can be recovered. Thus, heating-cooler equipment was installed to measure and control the reactor temperature as desired.

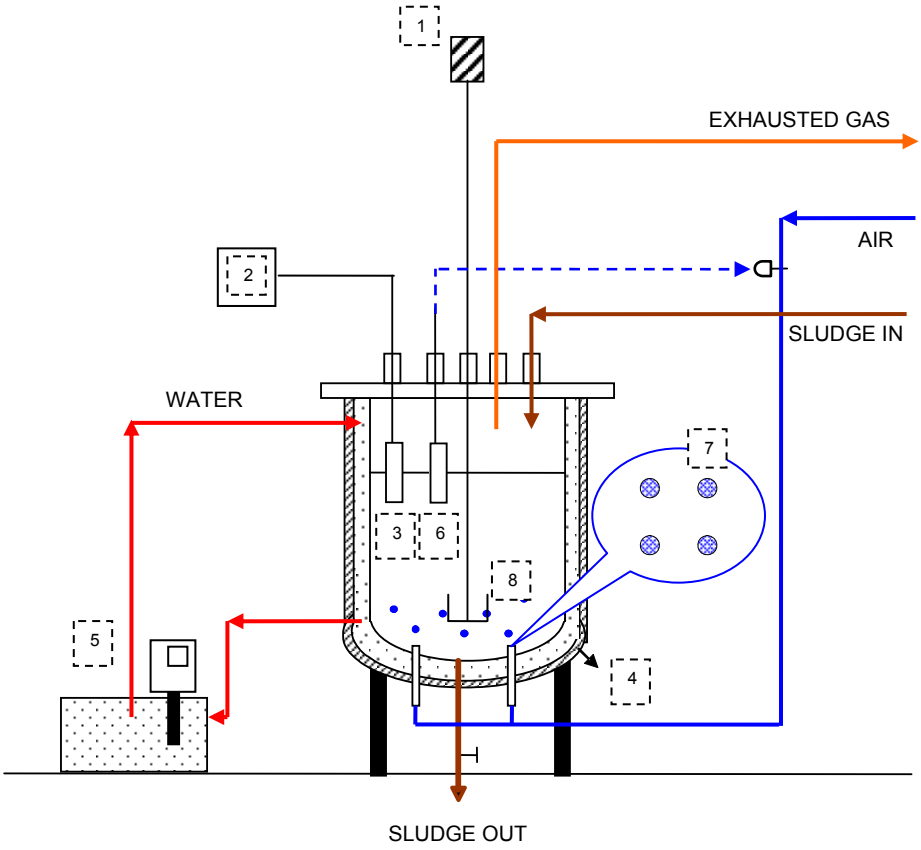

Figure 3.7. Design of the experimental autothermal pilot-plant. 1) Stirrer, 2) Temperature display, 3) Thermocouple, 4) Insulator, 5) Thermostatic bath, 6) Dissolved oxygen prove, 7) Sparger, 8) Impeller

As mentioned above, one of the most important factors for autothermal digestion is aeration and mixing systems. Proper aeration and reactor homogenisation are decisive for leading up the extremely high oxygen demand required in the aerobic process. Availability of oxygen in the liquid phase is controlled by a dissolved oxygen controller. This equipment was designed to regulate, by means of a solenoid valve, the air inflow into the reactor in order to maintain a constant dissolved oxygen value if wanted. For optimising the oxygen transfer efficiency, an aeration device was located in the bottom of the reactor, equipped with a membrane system that provided small air-bubbles in order to maximise the contact area and facilitate oxygen transfer into the sludge. Mixing was provided with an electrical stick stirrer equipped with three intermediate paddle stirrers located at different stick positions.

As nitrification processes in thermophilic range are not expected, process pH does not have generally to be controlled. However, a pH probe was installed in the cap reactor to monitor the pH values for possible outranges. If needed, NaOH and H_2SO_4 solutions were added to maintain pH at the optimal range.

3.2.2.2. ATAD pilot plant

A pilot plant consisting in a 7 L cylindrical reactor of stainless steel were constructed with an active effective volume reaction of 4 L, see figure 3.8. A thermocouple monitors the reactor temperature. Two proves were introduced in the cap in order to measure the pH (pH DULCOTEST®, Prominent) and the dissolved oxygen (InLab®605 O_2 sensor prove, Mettler Toledo). Mixing was provided with an electrical stick stirrer at 400 rpm (RZR2020, Heidolph) equipped with a paddle stirrer located at the end of the stick. Reactor thermophilic temperature was maintained at 55ºC by means of a thermostatic bath (Frigiterm-10, Selecta). Air input value was set at around 16-20 L/h (rotameter, Aalborgh), value suggested in EPA/625/10-90/007 1990. In order to minimise water loss by evaporation, air input was saturated with water at 55ºC before entering the reactor

The reactor was operated in a daily fill mode, samples were withdrawn daily and analysed as soon as possible, and stored if needed at 4ºC.

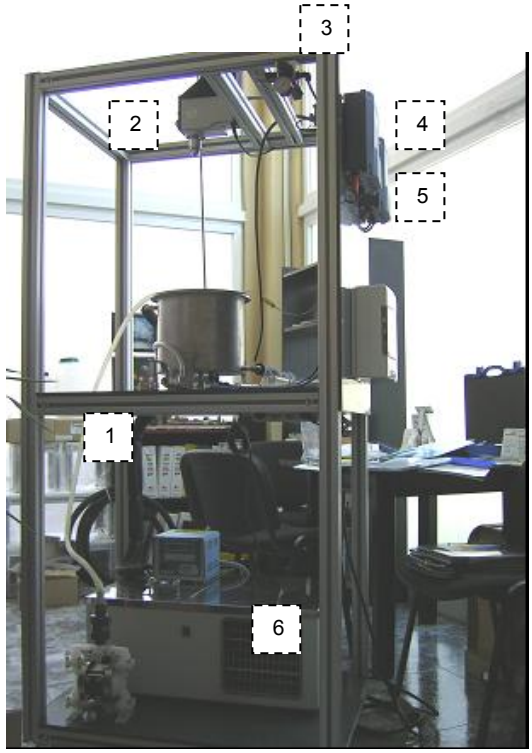

Figure 3.8. Thermophilic aerobic pilot plant. 1) Jacketed stainless steal rector, 2) Stirrer, 3) Automatic air valve, 4) Dissolved oxygen controller 5) Temperature display, 6) Thermostatic bath.

Figure 3.9 shows a detailed view of the reactor cap of the reactor where various orifices holes are located at the top of the cap for placing several measurement and sampling elements. A thermocouple monitors the reactor temperature. Two proves can be inserted in the cap to measure the pH and control the dissolved oxygen concentration. The oxygen prove can be positioned at different locations in order to study the effect of the mixing and aeration on the dissolved oxygen concentration. Reactor feed and outlet exhausted gas extractions are made by different holes in the cap.

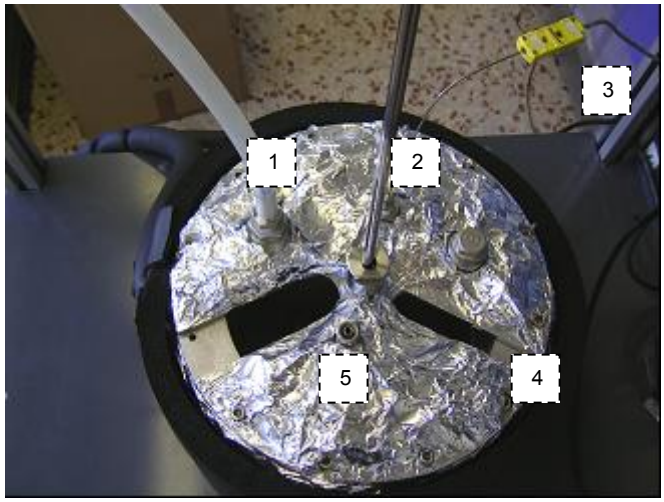

Figure 3.9. Detail of the cap reactor. 1) Exhausted gas, 2) Stirrer, 3) Thermocouple, 4) pH cap orifice, 5) Dissolved oxygen cap orifice

Purge of digested sludge was carried out by the hole placed at the bottom of the reactor, as shown in figure 3.10.

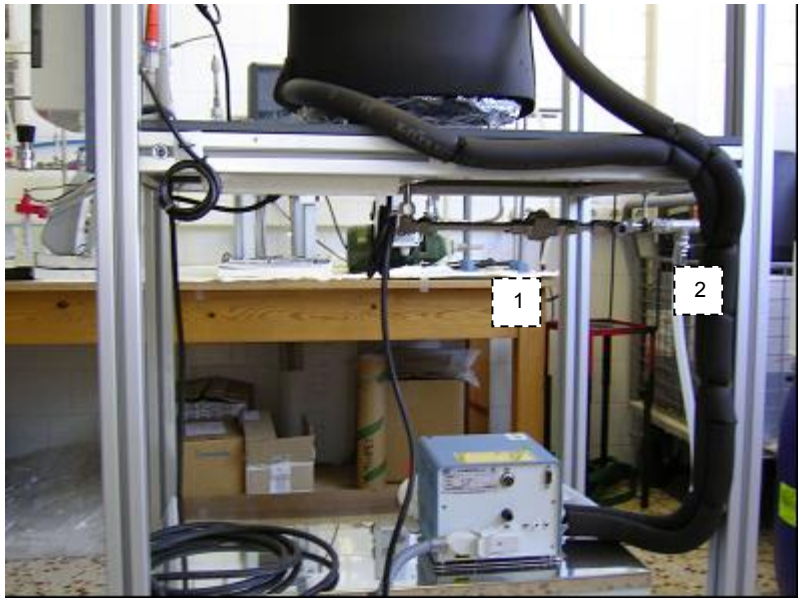

Figure 3.10. Detail of the bottom reactor part. 1) Purge valve, 2) Purge

Figure 3.11 and 3.12 also depict the insulation system to provide nearly adiabatic conditions in the reactor and heating system to minimise heat losses caused by air convection. As stated, the insulation material in the

reactor consisted of felt wool, which was chosen due to its low thermal conductivity coefficient and easy availability. The felt wool layer was then covered by an elastomeric material.

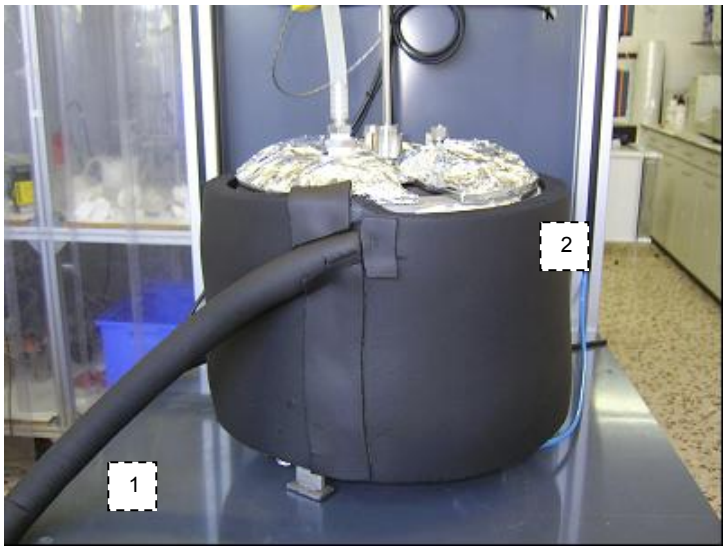

Figure 3.11. Reactor insulation. 1) Heating water circuit insulation, 2) Reactor insulation

The isolation system was improved during operation, because maintenance of the thermophilic temperature range was not possible without external heat. As seen in figure 3.12, an additional polyurethane foam rubber was used specially at the bottom of the reactor, to avoid heat loss through this part.

Figure 3.12. Improvement of the reactor insulation. 1) Polyurethane foam rubber

Finally no glass water cooler to condensate the water loss in the exhausted gas was installed. The water loss due to evaporation was evaluated to be 0.5 litres of water every 2 weeks of continuous operation at 55ºC. To lower the already small error produced due to the reduction of the liquid volume, this was checked weekly and, if needed, tap water was added to maintain an actual active volume of 4 litres.

One of the most important factors for autothermal digestion as abovementioned is aeration and mixing systems. Proper aeration and reactor homogenisation are decisive for leading up the extremely high oxygen demand required in the aerobic process. Availability of oxygen in the liquid phase was controlled by a dissolved oxygen controller (DULCOMETER®, Prominent). This equipment was selected to regulate, by means of a solenoid valve, the air inflow into the reactor in order to maintain a constant dissolved oxygen concentration, if desired. It must be noted that this controller was rarely operative as the dissolved oxygen sensor was not properly functioning at temperatures higher than 45ºC. A new dissolved oxygen sensor was acquired capable of measuring at thermophilic ranges. A portable dissolved oxygen equipment SG6 SevenGo pro™ from Mettler Toledo, equipped with dissolved Oxygen InLab® 605, from Mettler Toledo, for working in extreme conditions between 0-60ºC was finally used for dissolved oxygen monitoring (see figure 3.13).

Figure 3.13. Dissolved oxygen meter

Firstly, the aeration device was located at the reactor bottom (figure 3.14). Air was introduced inside the tank through four nozzles (inner spacing of 120 mm). These spargers were made of stainless steel fibre mesh and had a circular shape with a diameter of 14 mm. Air inflow was controlled by a volumetric flow meter (rotameter, Aalborgh) at 16-20 L/h. This system provided small air-bubbles in order to maximise the contact area and facilitate oxygen transfer into the sludge.

Figure 3.14. Aeration and mixing system in autothermal reactor

Mixing was provided with an electrical stick mixer equipped with an anchor-type paddle stirrer located at the end of the stick. The impeller used is fixed in the shaft (ϕ=10mm). The shape of the impeller is a mixture between a paddle and an anchor (figure 3.14). It has a diameter of 90 mm diameter and a height of 50 mm. The position of the impeller inside the tank can be regulated. The stirring velocity was settled to 400 rpm.

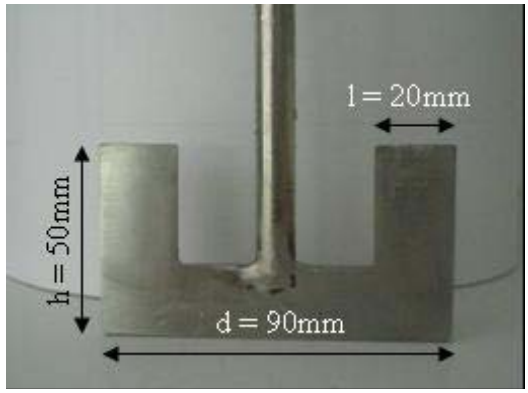

Figure 3.15.Anchor-type paddle stirrer.

Improvement of the mixing were conducted in an identical reactor by University of Nantes, in a cooperative project. Results published by Raouf et al (2009) showed that the initial agitation system (anchor-type paddle, four air nozzles, no baffles) induced, even in water, low gas-liquid mass transfer coefficients and thus small oxygen transfer rates (between 0.01 and 0.09 kg $O_2/m^3/h$) which were insufficient and could be optimised.

A new system was designed, introducing four baffles, an efficient impeller for gas dispersion (a home-made CD6 Chemineer® impeller) and a ring air sparger:

- Baffles (a scheme is shown in figure 3.16). Four baffles (in stainless steel) were added to the tank to prevent the vortex formation at the surface, enabling thus high rotation speeds to be applied. Their dimensions are: 30 cm of total height, 2.1 cm (*T/10*) of width, and 1.0 cm of thickness. They are located at 4 mm (*T/50*) from the tank walls. They were fixed in the cap reactor.
- Impeller. Six-home-made concave-blades disk turbine was used as new impeller, figure 3.17. The dimensions are identical to those of the commercial impeller CD6 Chemineer® 8.5 cm (*D=T/3*) of impeller diameter, 6.4 cm (*3/4D*) of disk diameter, six blades with 2.1 cm of length (*D/4*), 1.7 cm in vertical height (*D/5*), 0.8 cm in horizontal width (*D/10*).
- Air reactor inlet. The 4 air nozzles were replaced by a ring sparger, figure 3.18, with a diameter equal to the impeller diameter and perforated by 20 holes of 0.5 mm of diameter. The air input was saturated with water at 55ºC before entering the reactor in order to minimize water-loss due to evaporation.

Figure 3.16. Baffles

Figure 3.17. Concave-blades disk turbine impeller

Figure 3.18. New air inlet reactor system, Ring sparger.

Although disappearance of organic matter does exist, and COD removal achieved assures (by energy balance) sufficient generated heat for auto-sustained temperature maintenance, autothermal conditions were not achieved due to heat loss, so extra-heating was added to sustain the thermophilic temperature.

This was caused by the still small size of the bench-scale reactor, which leads to excessive heat loss. If a cylindrical reactor is considered, then equations 6.1 and 6.2 gives their volume and area, respectively.

$$V = \pi \cdot \frac{D^2}{4} \cdot H \qquad \textit{Eq. 3.1}$$

$$S = \pi \cdot \frac{D^2}{2} + \pi \cdot D \cdot H \qquad \textit{Eq. 3.2}$$

When the reactor size increases, volume grows faster than surface area does, i.e. the volume (where heat is generated) rises to the cube, while the area (responsible of the heat loss) grows only squared. Therefore, the larger the reactor volume, the higher the possibilities for auto-sustained operation. Figure 3.19 illustrates this idea using calculations based on H/D=1, which is the optimal ratio for minimizing cylindrical area.

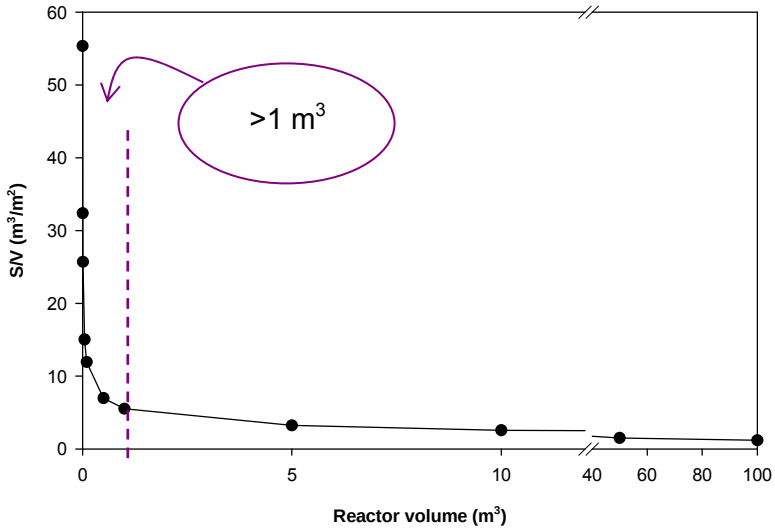

Figure 3.19. Area/volume ratio versus reactor volume in cylindrical reactor.

For the pilot-plant system used, the ratio S/V is almost 30 (V = 7 L), while it is considered, that only S/V ratios lower than 5 can minimize the aforementioned problem of heat loss through the area of reactor, i.e. reactor volumes greater than 1 m^3.

3.2.3. Sludge Pretreatment

A closed jacketed glass reactor with an active volume of 500 ml was used to pre-treat 300 ml of raw sludge at 30, 40, 50, 60, and 80ºC temperatures at free pH. Reactor temperature was maintained with a thermostatic bath (Digiterm 100, Selecta) at the desired set-point (figure 3.20). Pretreatments at higher temperature were performed in a 1000 ml autoclave reactor (Bench ABP-300, Autoclave Engineers) equipped with a magnetically driven stirrer, at a stirring rate of 500 rpm and sludge volume of 300 ml (figure 3.21). Tested temperatures were 110, 140, 170 and 200ºC. These temperatures above boiling water point caused a rise of the system pressure, associated with the evaporation of the liquid phase (autogenous pressure), in this case 1, 3, 6 and 11 bar were the manometric pressures measured in the reactor due to the temperatures of 110, 140, 170 and 200ºC respectively, which is in accordance with the expected water vapour pressure. Treatment time was decided to be 1 hour once the sludge had reached the set point temperature (20-40 min), at free pH. After treatment, the cooling period lasted about 20-40 min.

Figure 3.20: Experimental equipment for low thermal pretreatment over sludge

Figure 3.21. Experimental equipment for high temperatures pretreatment over sludge

For chemical pretreatment with H_2O_2 a closed jacketed glass reactor with a total volume of 500 ml was filled with 300 ml of raw sludge see figure 3.22. Then, hydrogen peroxide was added continuously at the ratio of 0-1 $gH_2O_2/gCOD$ with a peristaltic pump (Watson and Marlow, 323S) at a constant flow range of 1-1.3 ml/min, letting pH free. The temperature reactor was kept constant by passing water at 30ºC through the reactor jacket from a thermostatic bath. Time of reaction was set to one hour. The peroxide doses tested were 0.02, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1 $gH_2O_2/gCOD$.

Figure 3.22. Experimental equipment for peroxidation pretreatment over sludge

Monitored parameters were analysed before and after the pretreatment, as soon as possible in order to determine pretreatment effect, and kept at 4ºC if needed.

3.2.4. Biomethane potential determination (BMP) tests

Biomethane potential determination was carried out in order to evaluate the thermophilic anaerobic biodegradability of the different substrates tested.

Batch tests were carried out in 120 ml serum bottles (see figure 3.23) with a useful volume of 80 ml and in triplicate. The bottles were incubated between 15-35 days in a bacteriological incubator at the thermophilic temperature of 55ºC (Incubat 80L, Selecta).

Figure 3.23 Serum bottles for BMP tests

Buffer and external nutrients were added into the reactors in order to achieve the optimal conditions for anaerobic microorganisms. The medium was prepared from the stock solutions presented in table 3.3.

Table 3.3. Composition of stock solution for basal media preparation (Lu et al, 2007)

Solution A	100 g/L NH_4Cl
	10 g/L NaCl
	10 g/L $MgCl_2 \cdot 6H_2O$
	5 g/L $CaCl_2 \cdot 2H_2O$

Solution B	200 mg/L $K_2HPO_4 \cdot 3H_2O$
Solution C	0,5 g/L resazurin
Solution D	2 g/L $FeCl_2 \cdot 4H_2O$
	0.05 g/L H_3BO_3
	0.05 g/L $ZnCl_2$
	0.038 g/L $CuCl_2 \cdot 2H_2O$
	0.05 g/L $MnCl_2 \cdot 4H_2O$
	0.05 g/L $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$
	0,05 g/L $AlCl_3$
	0.05 g/L $CoCl_2 \cdot 6H_2O$
	0.092 g/L $NiCl_2 \cdot 6H_2O$
	0.5 g/L etylene-di-amine-tetra-acetate
	0.1 $Na_2SeO_3 \cdot 5H_2O$
	1 ml 37% HCl
Solution E	2 mg/L Biotin
	2 mg/L Folic acid
	10 mg/L Pyridoxine hydrochloride
	5 mg/L Riboflavin
	5 mg/L Thiamine
	5 mg/L Nicotinic acid
	5 mg/L Pantothenic acid
	0.1 mg/L vitamin B_{12}
	5 mg/L p-aminobenzoic acid
	5 mg/L thioctic acid
Solution D	52 g/L $NaHCO_3$

The following volumes of the different stock solutions where added to 916 ml of distilled water to prepare the basal media: (A) 10 ml, (B) 2 ml, (C) 1 ml, (D) 1 ml, (E) 10 ml, (D) 50 ml. Then, the solution was gassed with N_2. Before inoculation the medium was reduced with 25 g/L $Na_2S \cdot 9H_2O$ solution to a ratio of 0.1 ml/10 ml of medium (Lu et al, 2007). It is important that when the basal media is prepared, the stock solutions are added to water, to prevent precipitation phenomena.

The inoculum was extracted from the lab-scale reactor operating at 55ºC with an HRT (hydraulic residence time) of 20 days. For batch experiments, the organic loading rate (OLR) was set at 0.3 $gCOD_{added}/gVSS_{inoculum}$. The influence of the inoculum is a key factor in the BMP tests, the ideal inoculum

should have the necessary mircoorganisms for the degradation process, it is ideal also that the inoculum is acclimatized to the substrate (Angelidaki and Sanders 2004), in this case the inoculum was made in our laboratory, fed with raw sludge. Another important factor is the amount of inoculum, because it also contributes to the formation of biogas, thus can blur the results if its biogas production is too high if compared to the other substrates tested; on the other hand, if the inoculum is too low, it can overload the process, with acidification as a result. Here, the inoculum used, produced around endogenous production is between 20-45% of the total biogas produced for the different substances.

Acetate was used as control model substrate to indicate the quality of the inoculum, measuring the methanogenic activity. The inoculum was extracted from a lab-scale reactor operating at 55ºC with an HRT of 20 days.

Bioreactors were filled with 50 ml of inoculum, 10 ml of basal media, and approximately 4 ml of substrate to get an organic loading rate (OLR) of 0.3 gCODadded/gVSSinoculum. Finally, tap water was added to attain a total amount of 80 ml. Then, the digesters where closed with a septum and an aluminium crimp. To eliminate the air and establish anaerobic conditions, the serum bottles were purged with nitrogen, and the free headspace was also filled with nitrogen. The experiment started after pressure and temperature equilibration.

Reactors were carefully stirred before gas measurement. Biogas production was measured from the inoculum without any substrate (endogenous) and from each of the substrates tested including the sludge without any pretreatment (raw sludge). Biogas test was finished when there was no measurable biogas production for a reasonable period (~5 days). Biogas was volumetrically measured at room temperature, as figure 3.24 shows. Biogas produced passed from the headspace of the bioreactor to the graduated glass collecting tube, displacing the barrier solution into the reservoir tank. The starting position ($x=0$) is considered when the pressure compensation reservoir is situated in the same level as the liquid in the volumetric graduated glass (figure 3.24a), then the tube is connected to the reactor vessel, and the liquid of the volumetric graduated glass is displaced. The reading position of the biogas produced corresponds to the value (x) where the surface of the barrier solution in the volumetric graduated glass and the pressure compensation reservoir are at the same level (figure 3.24b).

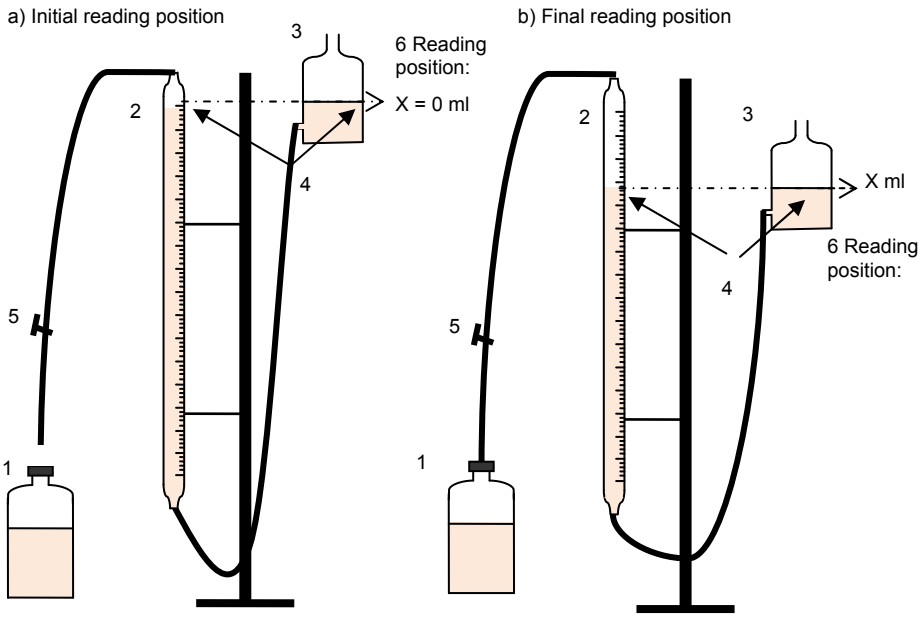

Figure 3.24. Volumetric gas measurement by volume displacement in BMP tests. 1) reactor vessel; 2) volumetric graduated glass; 3) pressure compensation reservoir; 4) barrier solution; 5) valve 6) volumetric reading position

A barrier solution is needed in order to prevent CO_2 solubilisation. Methane is hardly soluble in water, but not CO_2. Solubility of CO_2 in water at 20ºC and atmospheric pressure is 90.1 ml gas in 100 g of water, whereas CH_4 is only 0.4 ml in 100 g of water (Perry and Green 1997), therefore carbon dioxide is more than 225 times soluble than methane.

In case of biogas is to be measured, the barrier solution is generally a highly acid or saline solution in order to try to avoid the diffusion of CO_2 through the liquid phase. When the equilibrium between the liquid and the gaseous phase is achieved, any further dissolution of carbon dioxide is prevented (Rozzi and Remigi 2004). Instead, if only methane production wants to be measured, an alkaline solution is used, which effectively absorbs all the carbon dioxide in the off gas (Guwy 2004). Table 3.4 reports some of the barrier solution found in literature.

Table 3.4. Composition of the barrier solution (Rozzi and Remigi 2004)

Type	Composition
Acidic	▪ H_2SO_4 5% (Schonber et al. 1997 and Sponza 2003) ▪ Na_2SO_4 20% (ISO/DIS 14853 1997)
Saline	▪ NaCl 200 g/l and citric acid 5 g/l
Alkaline	▪ NaOH 2.5% (Vidal et al, 1997) ▪ NaOH 20% (Gonzalez-Gil et al. 2002) ▪ NaOH 1N (Valcke & Verstraete 1983) ▪ NaOH 2N (Sponza 2003)

Finally, the barrier solution used in the BMP tests was an acidified saturated saline solution prepared with NaCl.

Variables used to assess the efficiency of the anaerobic digestion on the BMP tests were TS (total solids), VS (volatile solids), TSS (total suspended solids), VSS (volatile suspended solids), COD (chemical oxygen demand), biogas production and biogas composition.

The biogas produced was almost daily measured, especially at the beginning of the test, its composition was analysed in each reactor once, after 6 days of experiment, and supposed constant during the experimental time. The other variables were analysed at the beginning and end of the BMP test.

3.2.5. VFA kinetic and activity measurement of thermophilic inoculum

The purpose of these measurements is assessing the microbial activity of the digested sludge, which is an indicator of the inherent ability of a microbial population to undertake the degradation of the control material. Model compounds are commonly used for the determination of the different trophic groups; Angelidaki et al. 2009 proposed the substrates listed in table 3.5 to measure the different microbial activity for criteria unification.

For kinetic and activity sludge measurements, it was followed the procedure described in section 3.2.4 describing BMP tests, but using higher volume

reactors, V = 500 ml. In this case, a total volume of 300 ml in the liquid phase was used filled with 100 ml of inoculum, 100 ml of basal media and different substrates, and finally tap water to obtain the final volume of 300 ml. Substrates were, amorphous cellulose to determine hydrolytic activity, glucose for acidogenic population, propionic and n-butyric acid for acetogenic ones and finally acetic acid for acetoclastic bacteria at the final concentration indicated in table 3.5

Table 3.5. Substrate model for determination of activities of different trophic groups in a biogas reactor (Angelidaki et al. 2009)

Population	Initial substrate concentration
Hydrolytic	1 g amorphous cellulose/L
Acidogenic	1 g glucose/L
Proteolytic	1 g casein/L
Acetogenic	0.5 g propionic/L 0.5 g n-butyric/L
Acetoclastic	1 g acetic acid/L
Hydrogenotrophic	Overpressure of 1atm of a mixture of H_2/CO_2 (80/20)

Biogas production and VFA were measured daily and 3 ml/day of sample were withdrawn during the 7 days that the test lasted.

3.3. Analytical methods

In order to give an accurate characterisation of the sludge and performance of digestion, several parameters (see table 3.6) were measured both in the total sludge and on the supernatant after centrifugation in a Digicen20 centrifuge at 10000 rpm for 10 minutes to characterise the soluble/dissolved part.

Table 3.6. Sludge and anaerobic digestion characterisation

Homogeneous sludge	**Soluble part of the sludge (SUPERNATANT)**
TS	TDS
VS	VDS
COD	$COD_{soluble}$
pH	TOC,TC
Carbohydrates	Carbohydrates
E-coli:	VFA
Salmonella:	DBO
	Alkalinity
	H_2O_2
	Total Phosphorous:
	Ammonia and organic nitrogen
	Conductivity
Biogas	
Flow	
CH_4 composition	

The definition and methodology of the different analysis are presented below.

Total Solids (%TS): Total Solids, TS, analysis was determined according to the procedures described in Standard Method 2540B, 17th Ed (APHA 1989). TS determine the solid part left in the vessel after sample evaporation, this is, the solid fraction of the sludge.

Volatile Solids(%VS): Volatile Solids, VS, analysis was determined according to the procedures described in Standard Method 2540G, 17th Ed (APHA 1989). It offers a rough approximation of the amount of organic matter present in the solid fraction of the sludge.

Alkalinity: Alkalinity analysis is determined according to the procedures described in Standard Method 2320A (APHA 1989). Alkalinity indicates the acid-neutralizing capacity of the water and is a function of carbonate, bicarbonate and hydroxide content, being an indicator of the concentration of these constituents. It is normally expressed as milligrams of $CaCO_3$ per litre. The

Automatic titrator 2S2B, Crison was used for this purpose.

Chemical Oxygen Demand: Chemical Oxygen Demand, COD, analysis was determined according to the procedures described in Standard Method 5220D, 17 Ed (APHA 1989). COD is used to measure the content of organic matter of sludge. The COD of a waste is in general higher than the Biological Oxygen Demand, BOD, because more compounds can be chemically oxidized than those that can be biologically oxidized. The digester used was the thermoreactor ECO8, Velp). After letting the tubs to reach ambient temperature, the absorbance at the wavelength of 600 nm was read in the spectrophotometer UV/Vis 8500, Dinko. And compared with the standard Potassium hydrogen phthalate. This analysis was performed either in the homogeneous and soluble part of the sludge.

Biochemical Oxygen Demand: Biochemical Oxygen Demand, BOD_5, was determined by an external laboratory according to the procedures described in UNE 77003:1989 method. It is the measurement of the dissolved oxygen used by microorganisms during the biochemical oxidation of organic matter for 5 days. BOD_5 is the most widely used parameter of organic pollution applied to wastewater.

Total Organic Carbon: Total Organic Carbon, TOC, was measured in a TC Multi Analyser 2100 N/C equipment from Analytic Jena with a non-diffractive IR detector. TOC is performed by chemical oxidation of the sample in a high temperature furnace with the presence of a platinum catalyst. The carbon dioxide produced during the oxidation is measured by means of infrared detector. Sample acidification and aeration prior to analysis eliminates errors due to the presence of inorganic carbon. The standard used has been the potassium hydrogen phthalate.

Total Carbon: Total Carbon, TC, was measured in a TC Multi Analyser 2100 N/C equipment from Analytic Jena with a non-diffractive IR detector. TC is performed with no sample acidification and no aeration for detecting also the inorganic carbon. The analysis performance is the same as in the TOC determination and the standard used is has been the potassium hydrogen phthalate.

Ammonia and organic nitrogen: Ammonia and organic nitrogen was determined by an external laboratory according to the procedures described in UNE-EN 25663:1994 method. Nitrogen data evaluate the treatability of wastewater by biological processes, due to that it is essential to the growth of biomass.

Conductivity: It indicates the ability of an aqueous solution to carry an electric current and depends on the presence of ions and their concentration. It is normally expressed as milisiemens per centimetre. It was measured by an external laboratory.

Total Phosphorous: Total Phosphorous was determined by an external laboratory according to the procedures described in UNE-EN 1189:1996 method. Phosphorous as well as nitrogen is a nutrient of the biomass and is also an indicator of the treatability of wastewater.

Biogas analysis: Gas produced during the anaerobic decomposition contains methane and carbon dioxide as the major components with minor amounts of hydrogen and hydrogen sulphide, saturated with water vapour collected in the sealed containers.

Gas composition was determined by a gas chromatography (6890N Network GC System, Agilent Technologies) using a column packed with Porapack Q 50/80 provided by Tecnokroma with a Thermal Conductivity Detector (TCD). A standard mixture for calibration was provided by Carburos Metalicos SA with the composition (molar %) CH_4, 60%; CO_2, 35%; H_2, 2%, and H_2S, 3%. Gas sample was injected into the GC by liquid displacement which pushed the gas into the automatic injector loop of 1 ml of volume. Fluid displacer was an acidified salt solution, in order to minimize the solubilisation of the gas into the liquid. It was also used manual injection through a syringe; 1 ml of sample was injected in the GC injector.

Volatile Fatty Acids: The measurement of organic acids was tested for controlling the anaerobic digestion. They are normally expressed as milligrams of acetic acid per litre.

Qualitative volatile fatty acids measurement was performed by GC 6890N (Agilent Technologies) equipped with a capillary column (HP FFAP 25 m × 0.32 mm × 0.50 µm) and a flame ionisation detector (FID). Helium was used as carrier gas, with a split ratio

of 20/1. The oven was kept at 80ºC for 1 min, an then the temperature was subsequently increased at a heating rate of 20ºC/min up to 120ºC and later at a heating rate of 6.13 ºC/min up to 205ºC, maintained for 2 min. The temperatures of the injector and detector were both 260ºC. The system was calibrated with solutions of commercial VFA (Sigma Aldrich). Detected acids were acetic, propionic, iso-butyric, n-butyric, iso-valeric and n-valeric acids, from the filtrate supernatant. Samples for VFA analysis were previously acidified and further filtered through a 0.45 µm regenerated cellulose syringe filter.

In order to improve the response in the GC analysis of the different VFA, an inactivated acid is added; specifically 10 µl of phosphoric acid 1:5 was added to1 ml of sample to acidify the samples (Pokorná et al. 2001).

E-coli: The population of E-coli bacteria was externally determined by the *Unitat de Biologia I Microbiologia*, of the *Factultat de Ciències de la Salut* in the *Universitat Rovira i Virgili* following the method ISO/FDIS 9308-3 Cor 1-2000 Water Quality 1998.

Salmonella: The detection of salmonella in sludge was also determined externally by the *Unitat de Biologia I Microbiologia*, of the *Factultat de Ciències de la Salut* in the *Universitat Rovira i Virgili* following an internal protocol based on ALPHA 1998, ISO/DIS 19250-2003 2003, Goosens et al. (1984), and Ewing et al. (1996).

Carbohydrates: Carbohydrates and soluble carbohydrates were measured by the phenol-sulphuric method (Dreywood et al. 1946; Dubois et al. 1956; Bougrier et al. 2007).

H_2O_2 Hydrogen peroxide concentration was measured in the supernatant following the Standard Iodometric Method 4500-Cl B. (APHA 1989).

3.4. Analytic equipment

3.4.1. Reagents

Table 3.7 lists the reagents used, the supplier and/or reference and the experimental part or analysis associated.

Table 3.7. List of reagents

Reagent	Formula	Supplier	Associated with
Mercury (II) sulphate 80g/l,in H_2SO_4,K diCr solution	n.a.	Riedel 34632	COD analysis
Silver sulfate 10g/l in sulfuric acid	$AgSO_4$	Fluka 34629	COD analysis
Potassium hydrogen phthalate	$C_8H_5O_4K$	Sigma P1088	COD and TOC standard
Sulphuric Acid 0.02 N	H_2SO_4	Scharlau AC2083	Alkalinity
Hydrochloric acid · 2N	HCl	Aldrich 653799	TOC analyser
Acetic Acid	$C_2H_4O_2$	Aldrich 10908-8	VFA standard Acetoclastic substrate for BMP
Propionic Acid	$C_3H_6O_2$	Panreac 15A695	VFA standard Acetogenic substrate for BMP
n-Butyric Acid	$C_4H_8O_2$	Acros Organics 108110010	VFA standard Acetogenic substrate for BMP
Phosphoric acid	H_3PO_4	Baker 6055	VFA analysis
Isobutyruc acid	$C_4H_8O_2$	Fluka 58360	VFA standard
Valeric Acid	$C_5H_{10}O_2$	Acros Organics 149570010	VFA standard
Isovaleric Acid	$C_5H_{10}O_2$	Aldrich 12,954-2	VFA standard
Phenol cristalyzed	$C_6H_6O_5$	Panreac 144858	Carbohydrates analysis
Sulphuric Acid	H_2SO_4	Fluka 84720	Carbohydrates analysis
Hydrogen Peroxide 30% w/v	H_2O_2	Panreac 121076	H_2O_2 titration

Potassium Iodide	KI	Riedel de Haen 30315	H_2O_2 titration
Sodium Thiosulphate 5-hydrate	$Na_2S_2O_3 \cdot 5H_2O$	Panreac 131721. 1210	H_2O_2 titration
Ammonium Chloride	NH_4Cl	Sigma A4514	Anaerobic basal media
Sodium chloride	NaCl	Sigma S7653	Anaerobic basal media
Magnesium Chloride hexahydrate	$MgCl_2 \cdot 6H_2O$	Sigma M0250	Anaerobic basal media
Calcium Chloride	$CaCl_2 \cdot 2H_2O$	Sigma C4901	Anaerobic basal media
Potassium phosphate	K_2HPO_4	Sigma P3786	Anaerobic basal media
Resazurin	$C_{12}H_6NNaO_4$	Aldrich 199303	Anaerobic basal media
Iron(II) chloride tetrahydrate	$FeCl_2 \cdot 4H_2O$	Fluka 44939	Anaerobic basal media
Boric Acid	H_3BO_3	Sigma B7660	Anaerobic basal media
Zinc chloride	$ZnCl_2$	Fluka 96468	Anaerobic basal media
Copper (II) chloride dihydrate	$CuCl_2 \cdot 2H_2O$	Sigma 307483	Anaerobic basal media
Manganese (II) chloride tetrahydrate	$MnCl_2 \cdot 4H_2O$	Sigma 221279	Anaerobic basal media
Ammonium molybdate tetrahydrate	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	Panreac 131134	H_2O_2 titration Anaerobic basal media
Aluminium chloride anhydrous	$AlCl_3$;	Fluka 06220	Anaerobic basal media
Cobalt (II) Chloride Hexahydrate	$CoCl_2 \cdot 6H_2O$	Aldrich 25,559-9	Anaerobic basal media
Nickel (II) chloride Hexahydrate	$NiCl_2 \cdot 6H_2O$	Fluka 72247	Anaerobic basal media
Ethylenediamine diacetate	$C_2H_8N_2 \cdot 2(C_2H_4O_2)$	Fluka 03572	Anaerobic basal media
Sodium selenite pentahydrate	$Na_2SeO_3 \cdot 5H_2O$	Fluka 00163	Anaerobic basal media
Hydrochloric Acid 35%	HCl	Panreac 131019	Anaerobic basal media
Biotin	$C_{10}H_{16}N_2O_3S$	Fluka 14400	Anaerobic basal media
Folic Acid	$C_{19}H_{19}N_7O_6$	Sigma-Aldrich	Anaerobic basal media

		F7876	
Pyridoxine hydrochloride	$C_8H_{11}NO_3$	Fluka 95180	Anaerobic basal media
Riboflavin	$C_{17}H_{20}N_4O_6$	Fluka 95170	Anaerobic basal media
Thiamine hydrochloride	$C_{12}H_{17}ClN_4OS{\cdot}HCl$	Sigma T4625	Anaerobic basal media
Nicotinic Acid	$C_6H_5NO_2$	Sigma-Aldrich N4126	Anaerobic basal media
D-Pantothenic acid	$C_{18}H_{32}N_2O_{10}$	Sigma P2280	Anaerobic basal media
Vitamin B_{12}	$C_{63}H_{88}CoN_{14}O_{14}P$	Sigma-Aldrich V2876	Anaerobic basal media
4-Aminobenzoic acid	$C_7H_7NO_2$	Aldrich 429767	Anaerobic basal media
Thioctic or Lipoic acid	$C_8H_{14}O_2S_2$	Sigma T5625	Anaerobic basal media
Sodium bicarbonate	$NaHCO_3$	Sigma S6297	Anaerobic basal media
Sodium sulfide nonahydrate	$Na_2S{\cdot}9H_2O$	Sigma-Aldrich 20,804-3	Anaerobic basal media
Amorphous cellulose	$(C_6H_{10}O_5)_n$	Sigma C8002	Hydrolytic substrate for BMP
Glucose	$C_6H_{12}O_6$	Sigma G8270	Acidogenic substrate for BMP

3.4.2. Equipment

The equipment used in the experimental procedures is listed in table 3.8.

Table 3.8. List of equipment

Apparatus	Model	Associated with
Digital immersion control thermostat	Digiterm 100, Selecta	Anaerobic digestion plant Sludge pretreatments
Digital thermostat	Frigiterm-10	Aerobic thermophilic digestion plant
Gas meter	MilliGas counter®, Ritter	Anaerobic digestion plant
Dissolved oxygen	Dissolved oxygen metter	Aerobic digestion plant

metter	sevengo SG6, Mettler Toledo	
Analytical balance	Electronic Analytical and Precision Balance ED224S, Sartorius	General use
Oven	Digitronic oven, Selecta	Analysis of solids
Automatic titrator	Automatic titrator 2S 2B, Crison	Alkalinity analysis
COD digester	Thermoreactor ECO8, Velp	COD analysis
Spectrophotometer	Spectrophotometer UV/Vis 8500, Dinko	COD analysis Carbohydrates analysis
Total Organic Carbon (TOC) analyser	Multi N/C 2100 analyser, Analytic Jena	TOC and TC analysis
Gas chromatograph (GC)	Agilent 6890N (G1540N), Agilent Technologies S.L.	Biogas analysis VFA analysis
Autoclave	Bench Model ABP-300; MagneDrive Packless Autoclave, Autoclave Engineers	Sludge pretreatment
Centrifuge	ORTO-ALRESA, Digicen 20	Solids analysis
pH-meter	GLP21, Crison	pH measurement
Bacteriological incubator	INCUBAT 80L 2000207, Selecta	BMP analysis
Mechanical agitator	RZR2020, Heidolph	Aerobic thermophilic digestion plant
Magnetic agitator	Agimatic HS, Selecta	Anaerobic digestion plant
Rotameter	CB160, Stuart Aalborg	Sludge pretreatment Aerobic thermophilic digestion plant

3.5. Parameters

In this section, there is a description of the most important parameters commonly used when defining the digestion operation and performance as well as other calculated parameters used in the thesis.

⇒ Hydraulic retention time (HRT)

HRT is the average time that a compound remains in the system (Metcalf and Eddy, 2003). In a complete mixed CSTR bioreactor.

$$HRT = \frac{V}{Q} = SRT \qquad (day) \qquad \textit{Eq. 3.3}$$

$V = \text{Re}\,actor\ volume \quad (m^3)$

$Q = Volumetric\ input\ flow\ rate \left(m^3/day\right)$

⇒ Sludge retention time (SRT)

The SRT is defined as the mass of organisms in the reactor divided by the mass or organisms removed from the system each day (Metcalf and Eddy, 2003).li is the average time that the activated-sludge solids are in the system. In a complete mixed CSTR bioreactor,

$$SRT = HRT = \frac{V}{Q} \qquad (day) \qquad \textit{Eq. 3.4}$$

⇒ Organic loading rate (OLR)

It is the amount of organic matter feed in the bioreactor, expressed as the quantity of COD or VS applied in the bioreactor volume per day.

$$OLR = \frac{Q \cdot S_o}{V} = \frac{S_o}{SRT} \quad \left(\frac{kg \cdot VS}{m^3_{reactor} \cdot day}\right); \left(\frac{kg \cdot COD}{m^3_{reactor} \cdot day}\right) \qquad \textit{Eq. 3.5}$$

$S_o = Feed\ substrate\ \ concentration\ \left(initial\ substrate\ \ concentration\right)$

$\left(gVS/L\right); \left(gCOD/L\right)$

⇒ Organic removal rate (ORR)

It measures the efficiency of the reactor. It is the amount of organic matter removed from the bioreactor.

$$ORR = \frac{Q \cdot (S_o - S)}{V} = \frac{(S_o - S)}{SRT} \quad \left(\frac{kg \cdot VS_{removed}}{m^3_{reactor} \cdot day}\right); \left(\frac{kg \cdot COD_{removed}}{m^3_{reactor} \cdot day}\right) \qquad \textit{Eq. 3.6}$$

$S = Substrate\ concentration \quad \left(gVS/L\right); \left(gCOD/L\right)$

⇒ Solids interrelationships

The solids fractions are related following the scheme presented in figure 3.25. Only TS, TVS (normally written VS), VDS and TDS can be done by direct measurement following the procedures described in section 3.3, the other parameters can be extracted by the scheme using equations 3.7-3.11

$$TS = TVS + TFS \quad \left(g/L\right) \qquad \textit{Eq. 3.7}$$

$$TVS = VSS + VDS \quad \left(g/L\right) \qquad \textit{Eq. 3.8}$$

$$TFS = FSS + FDS \quad \left(g/L\right) \qquad \textit{Eq. 3.9}$$

$$TSS = VSS + FSS \quad \left(g/L\right) \qquad \textit{Eq. 3.10}$$

$$TDS = VDS + FDS \quad \left(g/L\right) \qquad \textit{Eq. 3.11}$$

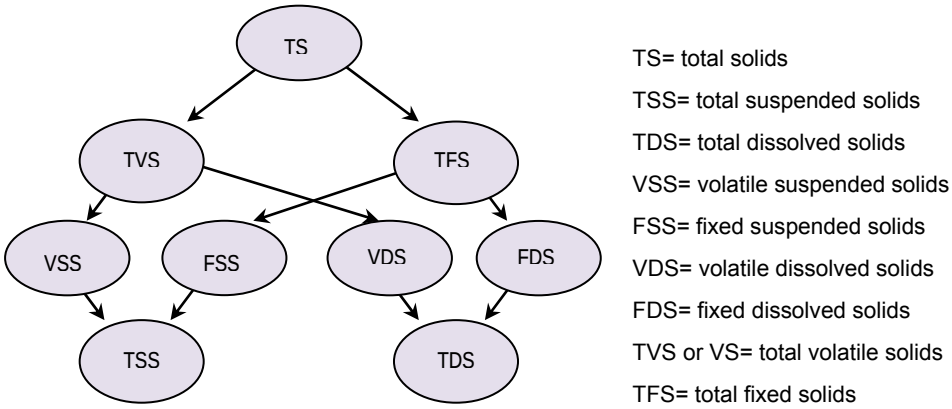

Figure 3.25. Interrelationships of solids (Metcalf & Eddy 2003)

⇒ Biogas yield (Y_{biogas})

This parameter is usually used to describe anaerobic performance; it gives information about the biogas generated from the organic matter. It can be calculated by equations 3.12-3.15, depending on the units wanted.

$$Y_{biogas} = \frac{B}{S_{reactor} \cdot V_{reactor}} \qquad \textit{Eq. 3.12}$$

$$B = Biogas\ production \qquad (L);(g)$$

$$\left(L_{biogas}/g\,VS_{reactor}\right);\left(g_{biogas}/g\,VS_{reactor}\right);\left(L_{biogas}/g\,COD_{reactor}\right);\left(g_{biogas}/g\,COD_{reactor}\right)$$

$$Y_{biogas} = \frac{B}{(S_{feed} - S_{reactor})\cdot V_{reactor}} \qquad \textit{Eq. 3.13}$$

$$\left(L_{biogas}/g\,VS_{removed}\right);\left(g_{biogas}/g\,VS_{removed}\right);\left(L_{biogas}/g\,COD_{removed}\right);\left(g_{biogas}/g\,COD_{removed}\right)$$

$$Y_{biogas} = \frac{B}{S_{feed}\cdot Q} \qquad \textit{Eq. 3.14}$$

$$\left(L_{biogas}/g\,VS_{added}\right);\left(g_{biogas}/g\,VS_{added}\right);\left(L_{biogas}/g\,COD_{added}\right);\left(g_{biogas}/g\,COD_{added}\right)$$

$$Y_{biogas} = \frac{B}{V_{reactor}} \qquad \left(L_{biogas}/m^3_{reactor}\right);\left(g_{biogas}/m^3_{reactor}\right) \qquad \textit{Eq. 3.15}$$

⇒ <u>Methane yield (Y_{CH4})</u>

Methane yield is equivalent to biogas yield, but only in terms of methane production; it can be calculated by equations 3.16-3.19.

$$Y_{CH_4} = \frac{B_{CH_4}}{S_{reactor}\cdot V_{reactor}} \qquad \textit{Eq. 3.16}$$

$$B_{CH_4} = \textit{Methane production} \quad (L);(g)$$

$$\left(L_{CH_4}/g\,VS_{reactor}\right);\left(g_{CH_4}/g\,VS_{reactor}\right);\left(L_{CH_4}/g\,COD_{reactor}\right);\left(g_{CH_4}/g\,COD_{reactor}\right)$$

$$Y_{CH_4} = \frac{B_{CH_4}}{(S_{feed} - S_{reactor})\cdot V_{reactor}} \qquad \textit{Eq. 3.17}$$

$$\left(L_{CH_4}/g\,VS_{removed}\right);\left(g_{CH_4}/g\,VS_{removed}\right);\left(L_{CH_4}/g\,COD_{removed}\right);\left(g_{CH_4}/g\,COD_{removed}\right)$$

$$Y_{CH_4} = \frac{B_{CH_4}}{S_{feed} \cdot Q} \qquad \textit{Eq. 3.18}$$

$$\left(L_{CH_4}/g\,VS_{added}\right);\left(g_{CH_4}/g\,VS_{added}\right);\left(L_{CH_4}/g\,\_COD_{added}\right);\left(g_{CH_4}/g\,COD_{added}\right)$$

$$Y_{CH_4} = \frac{B_{CH_4}}{V_{reactor}} \qquad \left(L_{CH_4}/m^3_{reactor}\right) \qquad \textit{Eq. 3.19}$$

⇒ Theoretical methane yield

The potential anaerobic digestion, expressed as the amount of biogas produced from a substrate, can be defined as the theoretical methane produced, calculated according to the chemical composition and also by digestion batch test.

When elemental composition is known, the methane potential can be calculated using the Buswell formula (Roš and Zupančič 2003) in simplified form disregarding sulphur, equation. 3.20, or extended, including sulphur compounds, equation 3.21.

$$C_aH_bO_cN_d + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3\cdot d}{4}\right)H_2O \rightarrow$$
$$\rightarrow \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3\cdot d}{8}\right)CO_2 + \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3\cdot d}{8}\right)CH_4 + d\,NH_3 \qquad \textit{Eq. 3.20}$$

$$C_aH_bO_cN_dS_e + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3\cdot d}{4} + \frac{e}{2}\right)H_2O \rightarrow$$
$$\rightarrow \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3\cdot d}{8} + \frac{e}{4}\right)CO_2 + \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3\cdot d}{8} - \frac{e}{4}\right)CH_4 + d\,NH_3 + e\,H_2S \qquad \textit{Eq. 3.21}$$

There are other approximations when component composition is approximate. Carbohydrate, fat and protein composition indicate how organic content is distributed. Using an average chemical formula for each component, the theoretical methane potential can be calculated also from the Buswell formula, see table 3.9.

Table 3.9: General theoretical methane potential for fat, protein and carbohydrate calculate using average chemical formulas (Hansen et al. 2003).

Component	Chemical Formula	Theoretical biogas potential (Nm^3 CH_4/ton VS_{in})
Fat	$C_{57}H_{104}O_6$	1014
Protein	$C_5H_7O_2$	496
Carbohydrate	$(C_6H_{10}O_5)_n$	415

If Buswell formula is applied to calculate theoretical methane production of biomass, then

$$B_{th} = 22.4 \cdot \frac{\left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3 \cdot d}{8}\right)}{(12 \cdot a + b + 16 \cdot c + 14 \cdot d)} \left(STP\,L_{CH_4} / gVS\right) \qquad \textit{Eq. 3.22}$$

$$1gVS \rightarrow 0.50\,STP\,L\,CH_4$$

$\Rightarrow$ <u>Biomass formula</u>

$C_5H_7NO_2$

$\Rightarrow$ <u>COD equivalence of methane</u>

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \textit{Eq. 3.23}$$

The COD content can also be used to calculate the theoretical methane potential of a substrate, if COD equivalence of methane is determined. Using equation 3.23, it may be determined that for each mole of methane consumed, two moles of oxygen equivalent are destroyed. This value is normally used for calculating the potential methane production in this study, for its easier calculation.

$$1gCOD \rightarrow 0.35\,STP\,L\,CH_4$$

⇒ COD/VS equivalence

$$\frac{0.35\ STP\,L_{CH_4}/gCOD}{0.50\ STP\,L_{CH_4}/gVS} \equiv 1.42\ gCOD/gVS$$

⇒ Solubilization rate (S).

It is defined as the particulate part of the initial sludge that was solubilized due to the pretreatment. For COD, TOC and carbohydrates, it was calculated according to Bougrier et al. (2008). For instance, for S_{COD}:

$$S_{COD}(\%) = \frac{COD_s - COD_{s_o}}{COD_o - COD_{s_o}} = \frac{COD_s - COD_{s_o}}{COD_{p_o}} \qquad \textit{Eq. 3.24}$$

For the calculation of solubilization rate of TS and VS, the following expressions were used:

$$S_{TS}(\%) = \frac{TDS_s - TDS_{s_o}}{TSS} \qquad \textit{Eq. 3.25}$$

$$S_{VS}(\%) = \frac{VDS_s - VDS_{s_o}}{TSS} \qquad \textit{Eq. 3.26}$$

For the evaluation of the solubilization rate of TOC, an estimation of the homogeneous TOC was used, 1 gCOD/L = (0.67(4-OS)) g C/L (Rittmann and McCarty, 2001), where OS is the oxidation state of the carbon in the organic substrate.

⇒ Specific methanogenic activity (SMA)

To determine this parameter, zero order kinetic model behaviour is usually assumed, so the kinetic equation is independent of the substrate initial concentration. This assumption can be used when the following requirements in the experiment are accomplished (Soto et al. 1993):

$$\frac{dS}{dt} = -k_s \qquad \textit{Eq. 3.27}$$

a) $S >> K_S$, Initial substrate concentration higher than the estimated values of K_S It is reported that K_S values for acetic, propionic and butyric acid range within 0.05-0.2 g/L (Henze and Harresmöes 1983, Soto et al. 1993), however other authors report 2.0, 0.5 and 0.5 g/L

for acetic acid, propionic acid and butyric acid respectively (Soto et al. 1993).

b) $X_o >> Y_{sx}(S_o-S)$. The inoculum concentration (X_o) is higher than the amount of biomass produced during the activity test ($Y_{sx}(S_o-S)$). That is to say that the microbial growth is negligible at these conditions.

c) If a lag phase occurs, the values of methane production after the lag phase should be considered, as long as the conditions for zero order kinetics are accomplished.

The activity is usually expressed as: $gCOD/gVSS \cdot day$.

⇒ Hydrolysis rate

First order kinetics is most commonly selected to describe the hydrolysis for particulate substrates during anaerobic digestion (Pavlostathis and Giraldo-Gomez 1991).

First order hydrolysis model

$$\frac{dS}{dt} = -k_h \cdot S \qquad \textit{Eq. 3.28}$$

If equation 3.28 is solved, using methane production instead of substrate degradation, equation 3.29 is obtained (Angelidaki et al. 2009).

$$\ln\left(\frac{B_\infty - B}{B_\infty}\right) = -k_h \cdot t \qquad \textit{Eq. 3.29}$$

$B_\infty = Ultimate\ methane\ production \quad (g\,CH_4)$

$B = Methane\ production\ at\ a\ given\ time \quad (g\,CH_4)$

$k_= = Hydrolysis\ constant \quad (day)^{-1}$

If a linear plot is represented, then the hydrolysis constant, like in figure 3.26, k_h can be determined as the slope of the straight line obtained.

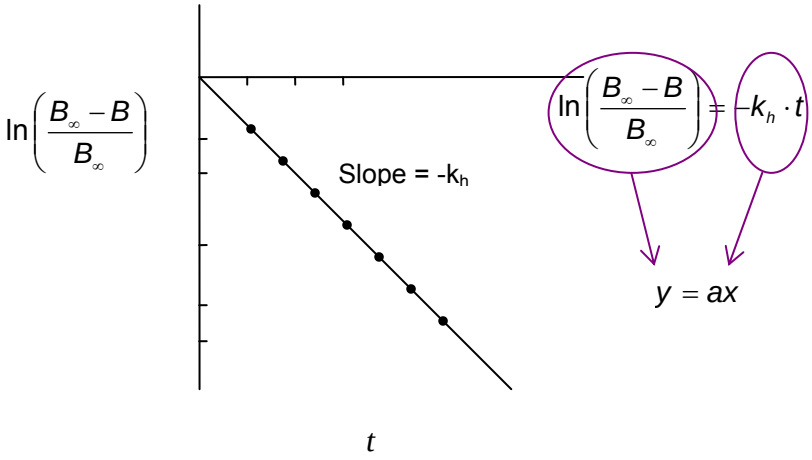

Figure 3.26. Linear plot representing the hydrolysis constant for a first order kinetics

CHAPTER 4

Pre-treatment effect over sludge

4.1. Introductory remarks

This chapter is focused on finding the better thermal and peroxidation pre-treatment conditions in order to maximize thermophilic anaerobic digestion of a mixture of primary and secondary sludge.

Thermal treatment between 30ºC and 200ºC and peroxidation up to 1.0 g H_2O_2/g COD dosages have been applied over raw sludge, which was a mixture of 35% of waste activated sludge and 65% of primary sludge, with the goal of enhancing the thermophilic anaerobic digestion giving class A biosolids.

The objective of this chapter was to elucidate the effect that a pre-treatment has over a mixture of thickened primary sludge (PS) and thickened WAS by analysing both chemical and biological parameters in order to decide the better pre-treatment conditions to enhance thermophilic anaerobic digestion and obtain Class A biosolds.

Pre-treatments considered were firstly thermal (30-200ºC) by changing temperature conditions and contact time, and secondly peroxidation pre-treatment at different doses and reaction temperature.

The specific objectives were:

- Test the effect of low (30-80ºC) and high (110-200ºC) temperature treatment over sludge at 1, 2, 3, 4 and 5 hours of contact time for low temperature, and 0.5, 1.5, 4, 8 and 16 h for high temperature range.
- Establish the effect of the addition of hydrogen peroxide over the sludge, at dosages up to 1.45 g H_2O_2/g COD at the reaction temperatures of 30ºC and 60ºC.
- Determine the hygienisation of thermally and peroxidated sludge.
- Study the thermophilic anaerobic biodegradability of both chemically and thermally treated sludge by means of Biochemical Methane Potential (BMP) tests.

4.2. Influence of the pre-treatments over sludge

4.2.1. Thermal pre-treatment

4.2.1.1. Time and temperature effect of low temperature pre-treatment

Thermal treatment was applied over raw sludge at 30, 40, 50, 60, and 80ºC during 1, 2, 3, 4 and 5 h. Figures 4.1 and 4.2 depict the evolution of COD; TS and VS respectively in front of time. Temperature was applied to sludge and then samples where withdrawn at different times, so initial sludge characteristics of the different set of temperature experiments might be different in some cases Values of the homogeneous COD are not uniform enough due to the high non homogeneity of the sludge; the error due of sampling is estimated to be around 30%. Despite this, a tendency can be extracted from the measured values when analysed with other parameters. Observing figures 4.1 and 4.2, it can be said that neither the temperature treatment nor the reaction times have any significant effect over COD, TS and VS. Thermal pre-treatment at these conditions does not remove organic or solid content of the sludge.

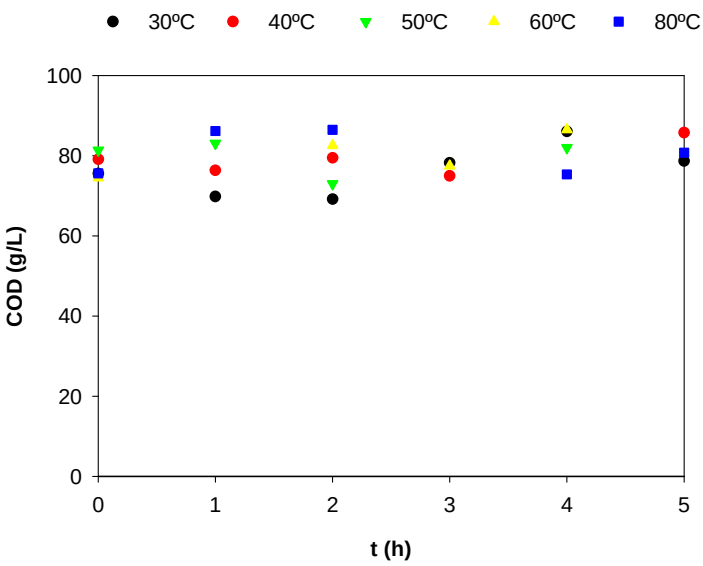

Figure 4.1. Evolution of total COD against time at different thermal conditions

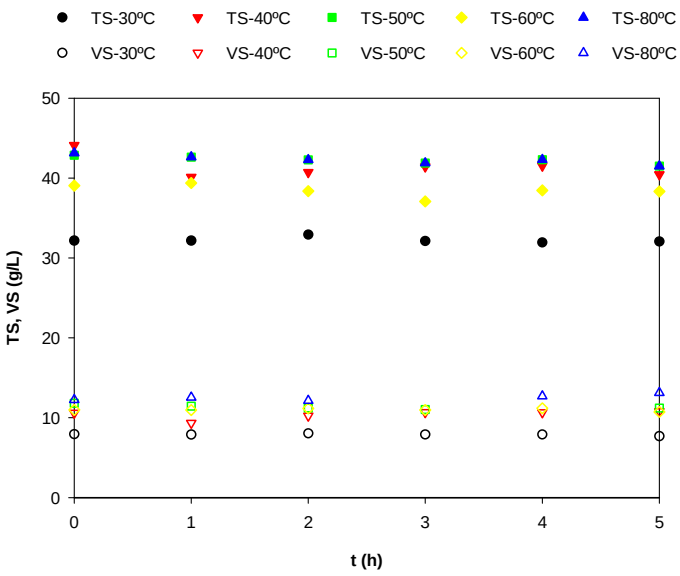

Figure 4.2. Evolution of TS and VS against time at different thermal conditions

Experimental data related to soluble COD concentration is shown in figure 4.3. Higher temperatures lead to an increase of more than 100% in soluble COD content. The soluble COD represents the 2-7% of the total

COD in the raw sludge and it increases up to 9-17% when thermally pretreated, being the optimal at 80ªC where from 8% rises up to 17%. A rapid increase of soluble COD was observed during the first hour of pre-treatment, especially at 60ºC and 80ºC. After this time non-noticeable improvement of the solubilisation is seen.

TDS presented in figure 4.4, is also positively impacted by the pretreatment temperature, as it increases as the temperature does, however small effect can be seen in terms of VDS. This suggests that the major part of solubilised solids are non organic.

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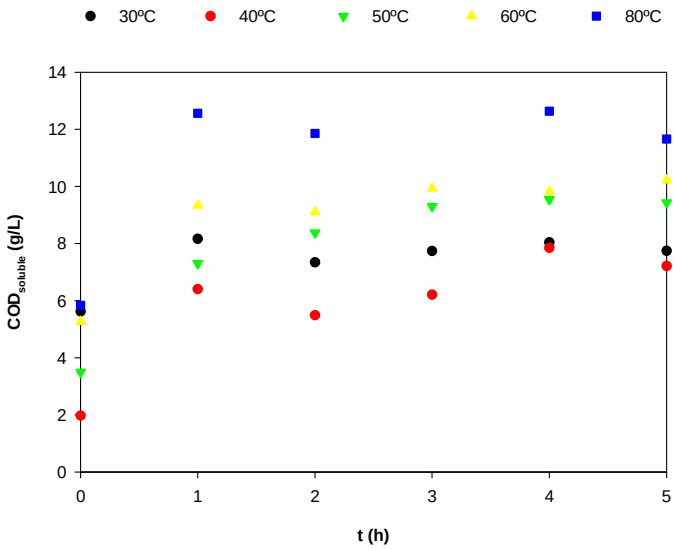

Figure 4.3. Evolution of soluble COD against time at different thermal conditions

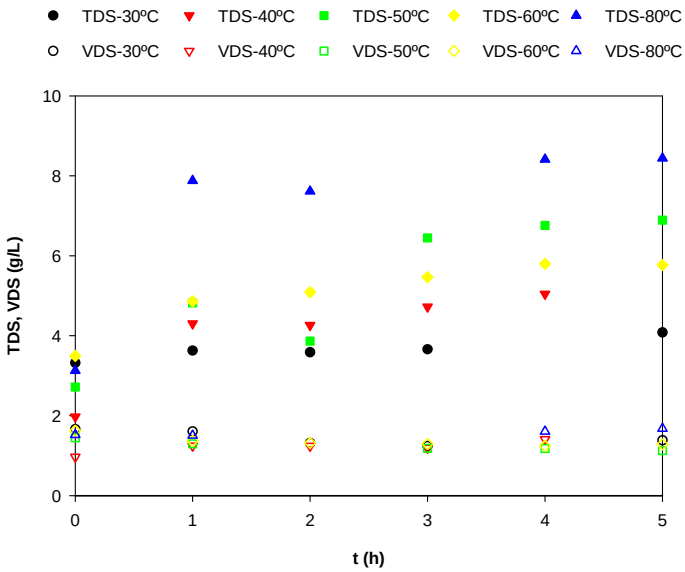

Figure 4.4. Evolution of TDS and VDS against time at different thermal conditions

In figures 4.5-4.10, it can be seen the composition of the sludge treated at the temperatures studied, specially suspended and dissolved (or filtered) fractions and its organic or mineral nature. As observed, the mineral suspended solids decrease as the higher is the temperature treatment, whereas mineral dissolved solids increase, but time has little effect after 1 h of treatment. This suggests that the mineral part of the solids suffers a solubilization process due to the temperature, while no matter is lost as TS do not change weightily. On the other hand, neither volatile suspended solids nor volatile dissolved solids vary significantly with the time or the temperature.

It can be concluded that no noticeable destruction of cells is observed at this mild temperatures tested (30-80ºC). Although there is some solubilisation of organic matter as soluble COD indicates, no membrane lysis occurs at high extent, because the content of biomass, expressed as VSS, does not change significantly.

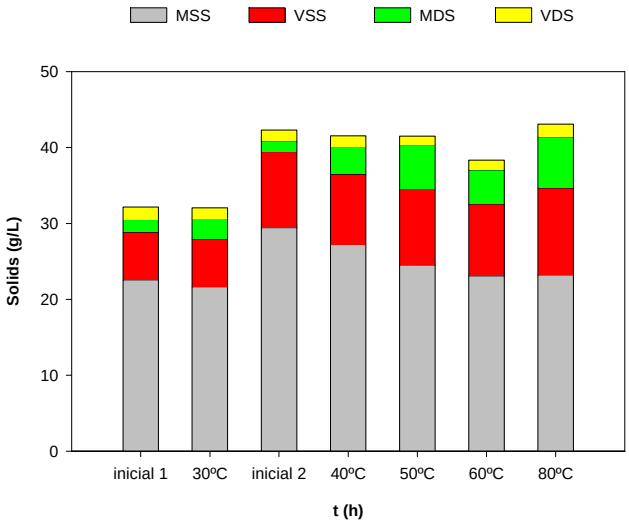

Figure 4.5. Sludge solids composition at 30, 40, 50, 60 and 80ºC after 4 h of treatment

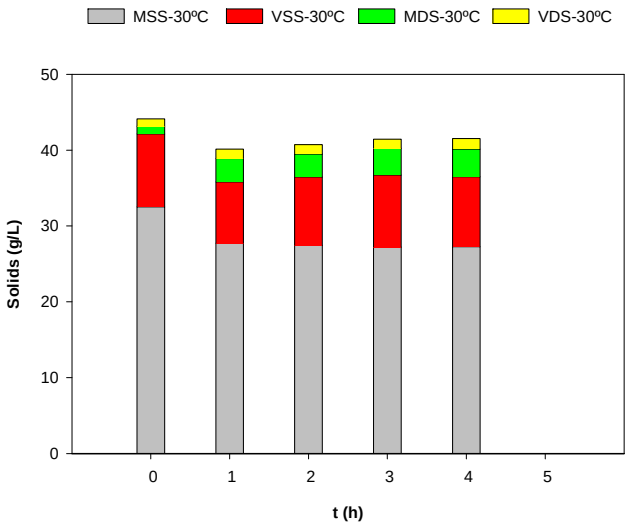

Figure 4.6. Temporary evolution of the sludge solid composition at 30ºC

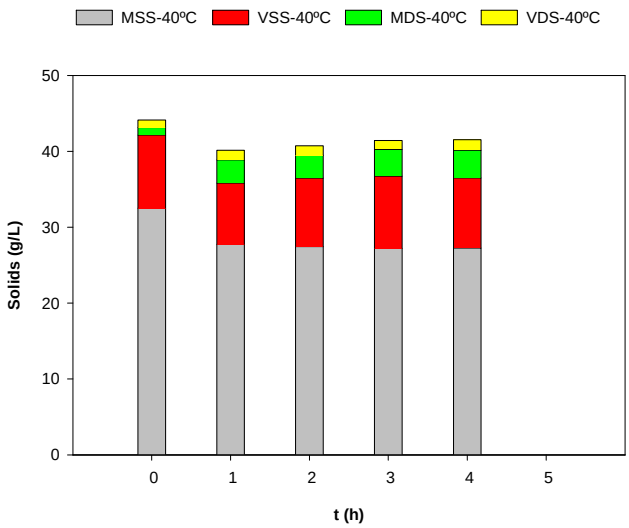

Figure 4.7. Temporary evolution of the sludge composition at 40ºC

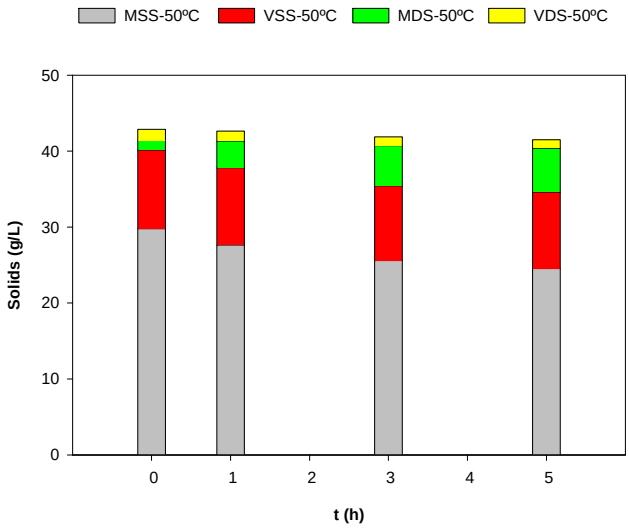

Figure 4.8. Temporary evolution of the sludge composition at 50ºC

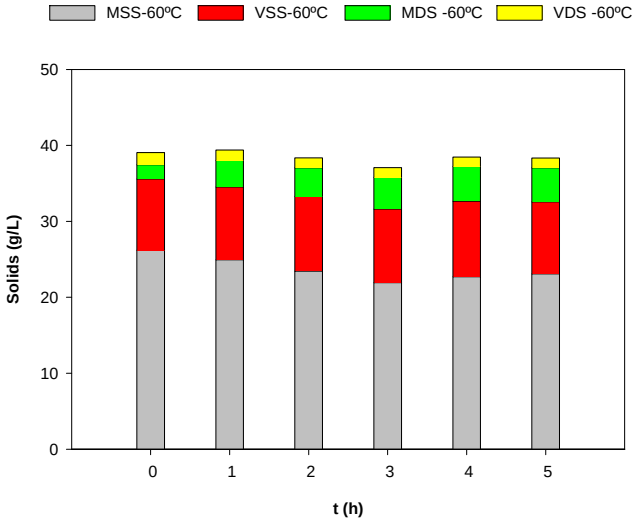

Figure 4.9. Temporary evolution of the sludge composition at 60ºC

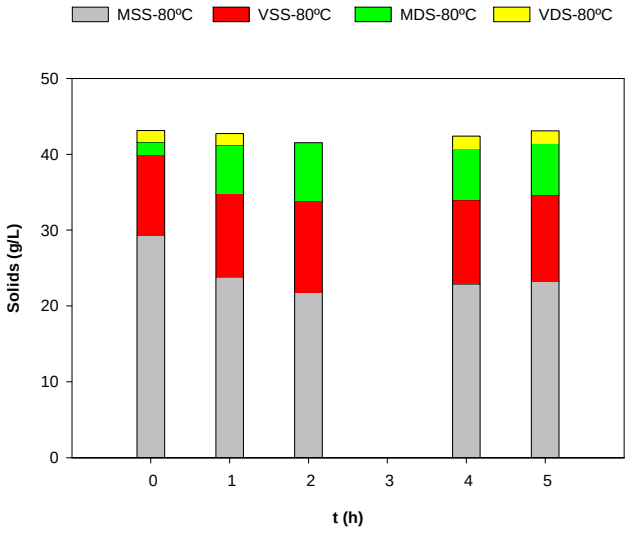

Figure 4.10. Temporary evolution of the sludge composition at 80ºC

4.2.1.2. Time and temperature effect on high temperature pre-treatment

These tests were performed in an autoclave reactor at 110, 140, 170 and 200ºC over raw sludge during 0.5, 1.5, 4, 8 and 16 h. The increase of temperature causes a rise of the system pressure, associated with the

evaporation of the liquid phase. In this case 1, 3, 6 and 14 bar were the working pressures in the reactor due to the vapour pressure of the temperatures of 110, 140, 170 and 200ºC respectively.

The following results are presented as a variation between the properties before and after the pre-treatment. Due to the complexity and non homogeneity nature of the sludge, direct sampling withdrawn in the autoclave reactor was not possible. The experiments at the different times of pre-treatment were started each time with new raw sludge. The different colours in figures 4.11-4.15 correspond to a single temperature experiment, and F-110ºC, F-140ºC, F-170ºC and F-200ºC corresponds to each new feed at the different temperatures.

Figure 4.11 and 4.12 present the time evolution of the variations of the TS and VS after the thermal pre-treatment respectively.

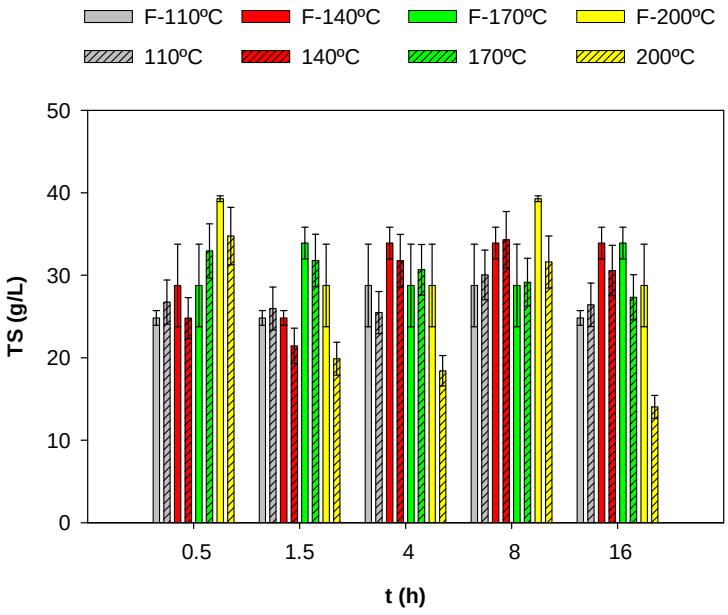

Figure 4.11. Evolution of the TS against time at different thermal conditions

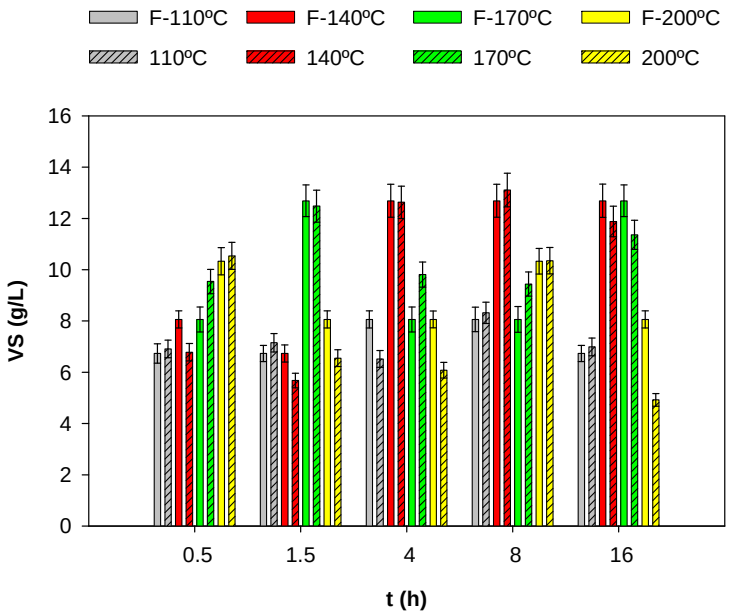

Figure 4.12. Evolution of the VS against time at different thermal conditions

As it is observed in figure 4.11, there are no considerable changes in TS content at temperature treatments lower than 170ºC. Only at times beyond 16 h seems to be a reduction of TS, around 20%, when T = 170ºC. At 200ºC, reduction of matter is observed, 20% of solids reduction within 4 h of treatment, but up to over 40% of elimination with 16 h of treatment.

Concerning VS, no noteworthy organic matter destruction is observed at the conditions studied except for the most critical condition, at 200ºC for 16 h, leading to an elimination in VS content of more than 25% (figure 4.12).

Figure 4.13 presents the progress against time of the soluble TOC in the sludge after the different thermal treatments, which indicates de quantity of organic matter that has been solubilised with the treatment. In general terms, it can be said that the increase in temperature and treatment time promote the solubilisation of the organic matter. However, at 200ºC is observed less expected amount of soluble TOC when times of treatment are 1.5, 4 and 16 h.

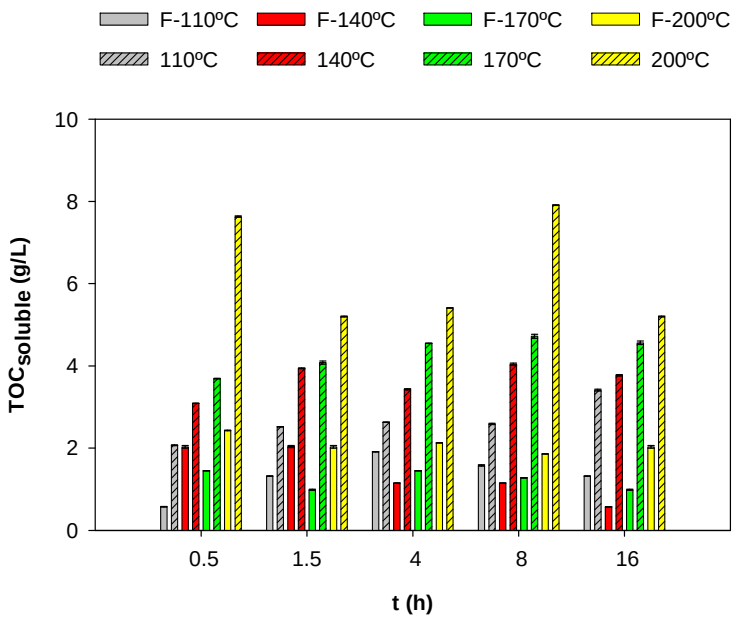

Figure 4.13. Evolution of the soluble TOC against time at different thermal conditions

Analysing the amount of solids in the soluble fraction, figures 4.14 and 4.15, it can be noted that most of the raise of the TDS is due to the solubilisation of the mineral fraction of the sludge, as VDS change is noticeably lower than for TDS.

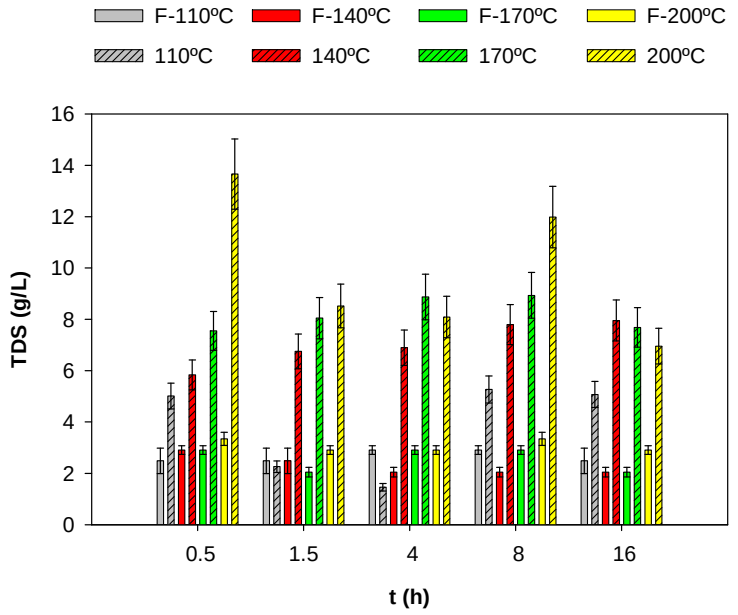

Figure 4.14. Evolution of the TDS against time at different thermal conditions

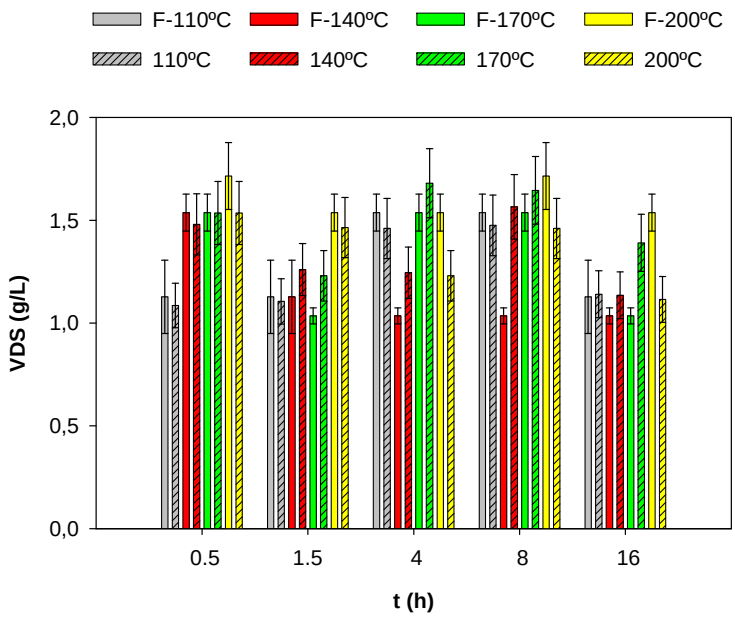

Figure 4.15. Evolution of the VDS against time at different thermal conditions

4.2.1.3. Temperature effect at 1 h of treatment

After evaluating the effect of pre-treatment time at each temperature, it was decided to establish the duration of the thermal pre-treatment at 1 h at the desired temperature, as any further increase of time, especially at temperatures lower than 110ºC, does not improve solubilisation of organic matter. This set of experiments was done using the same sludge, so initial sludge characteristics are the same for all the temperatures tested. Figures 4.16-4.21 show the evolution of several sludge characteristics when the different thermal pre-treatment was applied over the same initial raw sludge. Parameters described are TS, VS, TDS, VDS, VSS, COD, $COD_{soluble}$, $TC_{soluble}$, $TOC_{soluble}$, carbohydrates content (CarbH) and soluble carbohydrates ($CarbH_{sol}$).

As concluded earlier, no significant variation in TS or VS (figure 4.16) is observed, except for the most extreme thermal condition, 200ºC, where 24% of TS and 27% of VS are reduced. What is more noticeable is the progressive increase of the dissolved solids as the temperature raises. For instance, at just 80ºC the TDS and the VDS is over four times higher than the initial content (figure 4.17). The increase is more impressive, for instance, at 170ºC, reaching seven folds the original values. Most of the solids solubilization is due to the organic matter, as more than 75% of the solubilized solids correspond to volatile solids, reaching more than 90% at

pre-treatment temperatures just above 50ºC. These results are not in line in what obtained in previous sections as increment of TDS solubilisation was observed but was attributed to mineral part as VDS changes were not measured. This may be caused by the sludge nature, VS of the sludge used in this experimental set was 83% of the TS, while the mean value of VS of the sludges used in sections 4.2.1.1 and 4.2.1.2 was around 30% of TS.

Biomass destruction in terms of VSS (figure 4.18) was observed at temperatures higher than 140ºC, being around 40% up to 78% at 200ºC.

COD solubilisation (figure 4.19) positively increases with the temperature, from an initial COD_{solube} =21% of the total COD, it increases to 28% at 80ºC (that is 33% of increase respect the initial soluble COD), and up to 51% at 200ºC (this is an increase more than 138% of the initial soluble COD). Soluble TOC also follows the same behaviour, so soluble TOC increases from 1.4 g/L up to 4 g/L at 80ºC (146% of increase), and up to 7.45 g/L at 200ºC (286% higher). Total soluble carbon has increased also but mainly due to organic matter, as soluble TC follows the same correlation as soluble TOC.

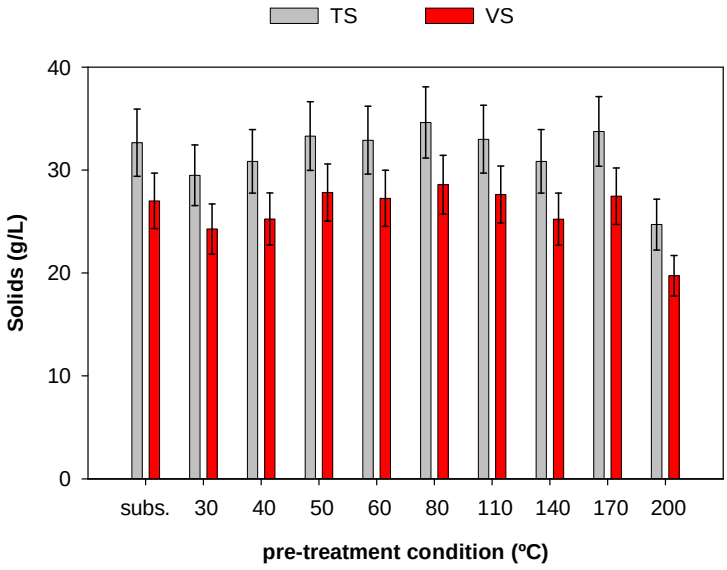

Figure 4.16. TS and VS at different thermal pre-treatment temperatures for 1 h.

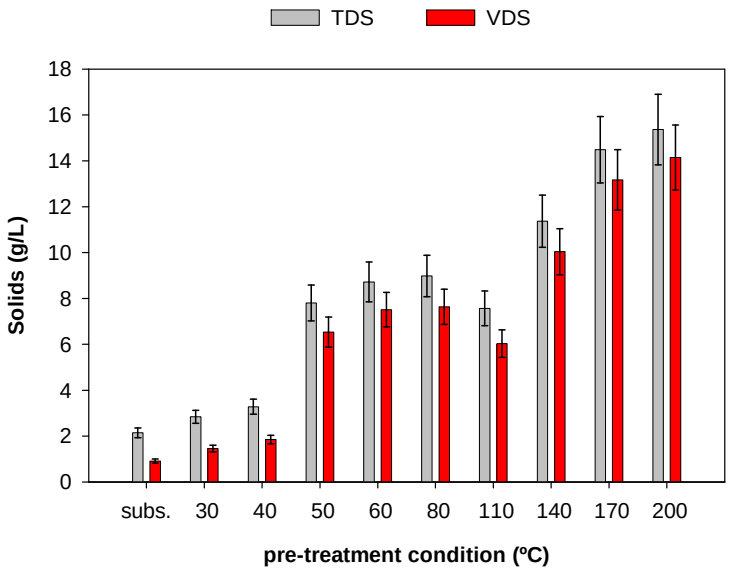

Figure 4.17. TDS and VDS at different thermal pre-treatment temperatures for 1 h.

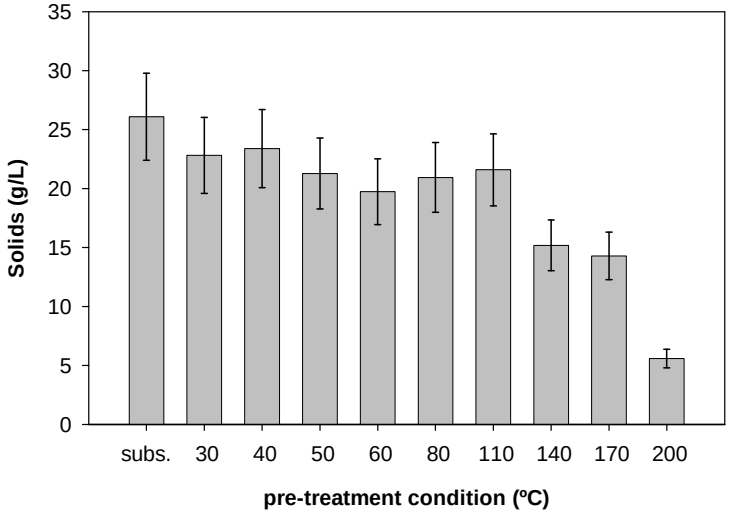

Figure 4.18. VSS at different thermal pre-treatment temperatures for 1 h.

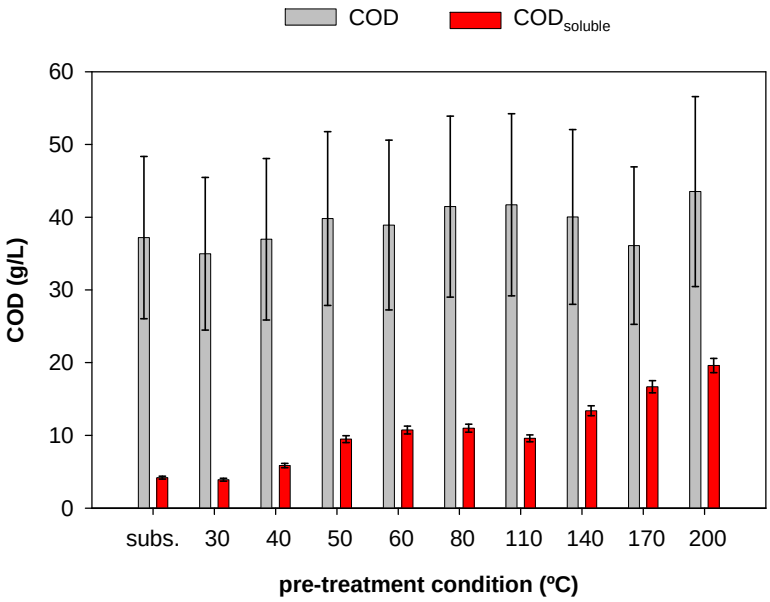

Figure 4.19. COD and soluble COD at different thermal pre-treatment temperatures for 1 h.

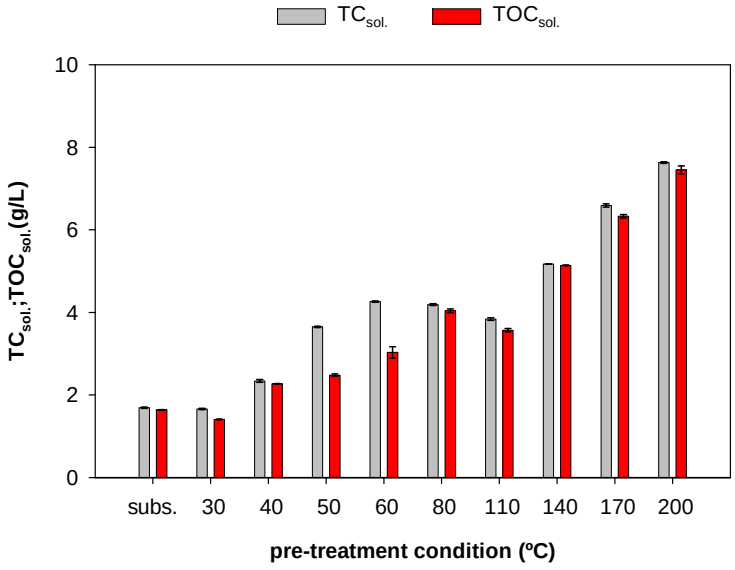

Figure 4.20. Soluble TC and soluble TOC at different thermal pre-treatment temperatures for 1 h.

Solubilisation of organic matter is evident. It can be seen that the higher the temperature treatment, the greater the solubilisation. If a linear fitting is calculated for S_{COD} (COD solubilization rate, using equation 3.22) and S_{TOC} (TOC solubilisation rate, using equation 3.22), a rather good correlation is found, equation 4.1 and equation 4.2. These results are in accordance, especially at temperatures below 80ºC, with other related studies (Bougrier et al. 2008).

$$S_{COD}(\%) = 0.154 \cdot T(^{o}C) - 0.909 \qquad R^2 = 0.87 \qquad \textit{(Eq. 4.1)}$$

$$S_{TOC}(\%) = 0.0156 \cdot T(^{o}C) - 0.363 \qquad R^2 = 0.96 \qquad \textit{(Eq. 4.2)}$$

Soluble carbohydrate concentration, presented in figure 4.21, strongly increased from 0.3 g eqGluc/L for raw sludge to 2.1 g eqGluc/L, for sludge pre-treated at 170ºC. However, this parameter suddenly drops at 200ºC up to only 0.63 g eqGluc/L.

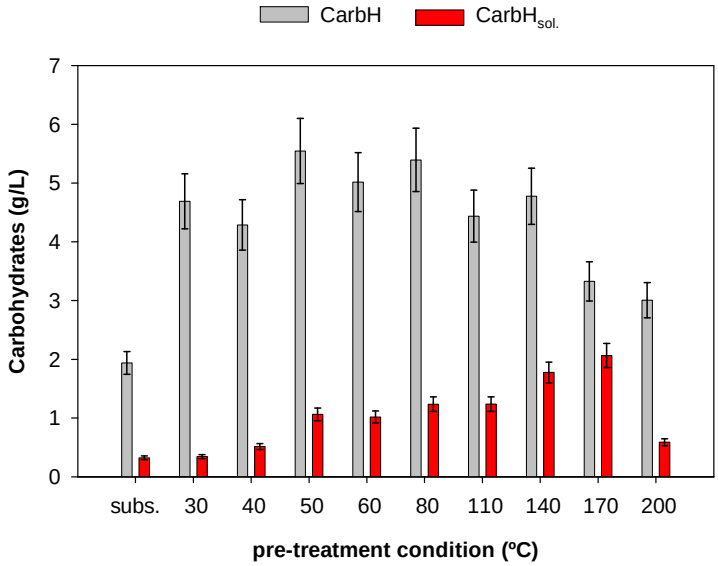

Figure 4.21. Homogeneous and soluble carbohydrates at different thermal pre-treatment temperatures for 1 h.

4.2.1.4. Anaerobic Biodegradability

The anaerobic biodegradability was evaluated by means of the Bio Methane Potential (BMP) test described in Chapter 2, applied to the pre-treated sludge evaluated in the previous section. Batch tests were carried out in triplicate.

The characteristics of the initial sludge used in one full experimental set are shown in table 4.1

Table 4.1. Initial measured conditions of the sludge in thermal pre-treatments.

Type of sludge	CODh (g/L)	CODsol (g/L)	TS (g/L)	VS (g/L)	TSS (g/L)	VSS (g/L)
inoculum	26.15	2.38	31.32	16.63	27.59	14.40
raw	37.20	8.23	32.65	27.00	30.51	26.09
30ºC	34.98	3.91	29.49	24.27	26.65	22.81
40ºC	36.96	5.86	30.84	25.24	27.56	23.39
50ºC	39.82	9.49	33.30	27.81	25.50	21.28
60ºC	38.93	10.76	32.90	27.25	24.18	19.73
80ºC	41.45	11.00	34.62	28.58	25.64	20.94
110ºC	41.71	9.61	32.99	27.62	25.42	21.59
140ºC	40.04	13.39	30.84	25.23	19.48	15.19
170ºC	36.09	16.70	33.75	27.46	19.26	14.29
200ºC	43.53	19.61	24.70	19.73	9.33	5.59

Biogas production was measured from the inoculum without any substrate (endogenous) and from each of the substrates tested including the sludge without any pre-treatment (raw sludge). Biogas test finishes when there was no measurable biogas production for a reasonable period.

Thermal pre-treatment enhances biogas production in all cases, as figure 4.22 shows, i.e. all the pre-treated sludge leads to higher biogas generation than raw sludge. It must be noted that endogenous biogas production represents around 20-43% of the total biogas production reported, whilst the rest owns to the different substrates tested. Higher biogas production is observed as the temperature of the pre-treatment rises, except for 200ºC. Temperatures lower than 80ºC increase less than 50% but at 80ºC biogas production rises up to over 145% in comparison to the biogas formed by substrate without pre-treatment (raw sludge).

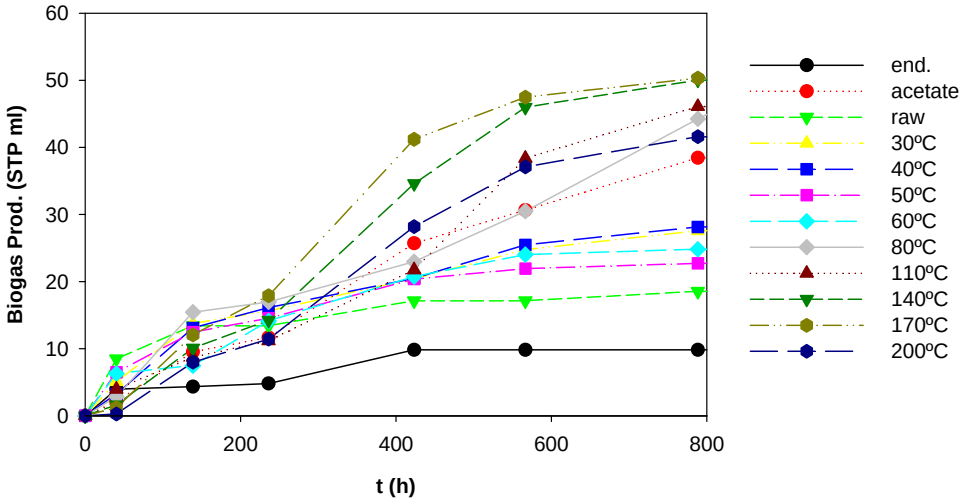

Figure 4.22. Total biogas production of thermal pre-treated sludge in thermophilic batch tests.

Figure 4.23 represents the specific biogas production rate, which is the net biogas production rate. The higher biogas production rate of the low temperature treatment occurs in the first 300 h of the test, and then diminishes, although at higher temperatures it continues having production until 600 h.

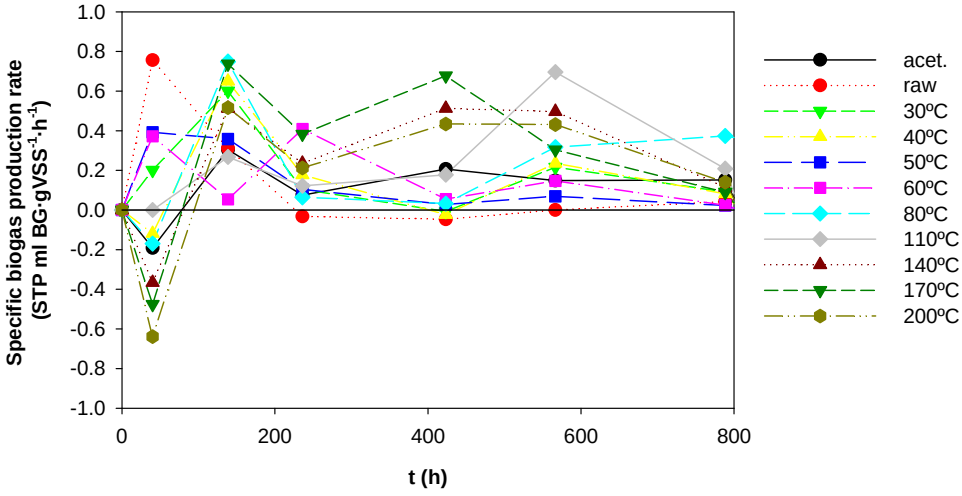

Figure 4.23. Specific biogas production rate of thermal pre-treated sludge in thermophilic tests

Overall results for the tests can be found in table 4.2. The values of the substrate added in the table are direct measurements of the COD that range between 140-174 mg COD, mainly due to the non homogeneity of the sample. For preparing the batch tests the OLR was set to be 0.3 gCOD/gVSS, so the substrate added in the minireactors of the tests is supposed to be the same. However, the basis of the COD measurement was the one measured over the raw sludge, as temperature treatment at 1 h do not affect the homogeneous COD. It can also be found the amount of the substrate added in terms of VS, because it is considered a better variable for evaluating the biodegradability performance, since it has less error associated. Again VS was measured directly over the different samples, it ranges between 97.1-111 mg VS, except for sludge treated at 200ºC when it falls to 78.9 mg VS.

Thermal pre-treatment enhances both the biogas production and the methane fraction obtained in the subsequent thermophilic anaerobic digestion; all minireactors with thermal treatment produce more biogas than sludge with no treatment. Methane quality of the biogas seems to be slightly enhanced but only at high temperature treatment, being around 50% for untreated sludge, then lowering to 30-40% for low pre-treatment temperatures, and finally increasing up again to almost 58% at 170ºC.

Table 4.2 also presents the biogas yield The better yield corresponds to high temperatures, from 0.08 STP L biogas/g VS_{added} yield of raw sludge rises up to 0.31 STP L biogas/g VS_{added} at 80ºC, being the highest 0.40 STP L biogas/g VS_{added} at 200ºC. Theoretical biogas yield, which is calculated from the theoretical biogas production of the organic substrate added (calculated from the Buswell formula, explained in chapter 3, section 3.5) is estimated to be for raw sludge 8.4% and the maximum theoretical yield is at 140ºC with 46.4%.

After thermophilic digestion, degradability was calculated. The maximum in terms of COD corresponds to the sludge pretreated at 80ºC, 50% of the initial COD was eliminated. Nevertheless, as commented before, results in terms of COD are not good enough to take under consideration, for example endogenous biodegradability measurement was around 39% so all other reactors should present at least this biodegradability. If biodegradability is observed in terms of VS, 20-30% of the initial VS are removed, so still 70-80% of VS are no rapidly anaerobically biodegradable.

Table 4.2. Characteristics of BMP test in thermophilic anaerobic digestion over thermal pre-treated sludge

Parameter	End.	Acet.	Raw	P-30	P-40	P-50	P-60	P-80	P-110	P-140	P-170	P-200
Substrate added (mg COD)	0	233	149	140	148	159	156	166	167	160	144	174
Substrate added (mg VS)	0	164*	108	97.1	101	111	109	114	110	100	110	78.9
Total production of biogas (STP ml)	9.82	38.5	18.5	27.6	28.1	22.7	24.8	45.4	46.1	50.0	50.3	41.6
Concentration of methane (%)	16.2	51.4	48.3	54.2	32.4	28.2	38.1	27.0	55.1	54.3	55.8	52.0
Substrate biogas production (STP ml)	-	28.6	8.7	17.8	18.3	12.9	15.0	35.6	36.3	40.2	40.5	31.8
% Theoretical biogas yield # [COD_{added}]	-	18.1	8.1	19.7	11.5	6.5	10.5	16.5	34.2	39	45	27
% Theoretical biogas yield # [VS_{added}]	-	19.3	8.4	21.3	12.6	7.0	11.2	18.0	38.8	46.4	44.1	44.8
Biogas yield (STP L/g)[BP. COD_{added}]	-	0.12	0.06	0.13	0.12	0.08	0.10	0.21	0.22	0.25	0.28	0.18
Biogas yield (STP L/g)[BP. VS_{added}]		0.17	0.08	0.18	0.18	0.12	0.14	0.31	0.33	0.40	0.37	0.40
% Biodegradability [COD]	39.1	32.5	19.1	13.6	28.2	15.5	46.2	50.1	16.6	23.5	28.1	31.0
% Biodegradability [VS]	18.8	14.4	21.7	21.7	23.1	34.3	29.0	19.5	26.1	24.2	13.6	22.6

* 1.42 gCOD/gVSS
# Theoretical calculation of biogas adjusted with the measured methane composition

Figure 4.24 compares biogas enhancement with the increment of solubilisation of the different parameters as temperature increases.

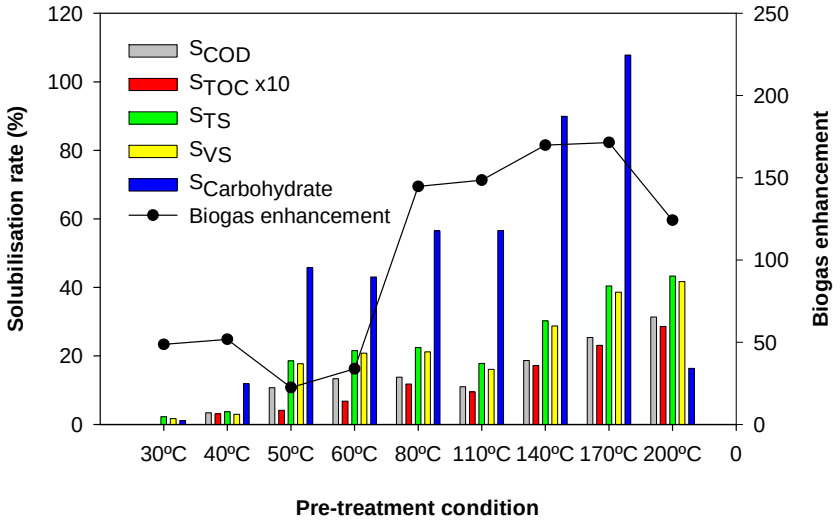

Figure 4.24. COD, TOC, TS, VS and carbohydrate solubilisation rates of thermal pre-treated sludge and biogas enhancement in the subsequent thermophilic anaerobic digestion.

Biogas enhancement is around 150% higher for sludge pre-treated at 80ºC, which corresponds to a biogas yield of 0.31 STP L /g VS_{added}. In contrast, other authors do not report any significant differences (Climent et al., 2007) when compared biogas production for treated sludge at 134ºC for 90 min and untreated sludge. What is also interesting is that a decrease of biogas enhancement is found at the highest temperature of 200ºC. Similar results were reported by Bougrier et al. (2008) for temperatures higher than 190ºC but after mesophilic anaerobic digestion, and also by Pinnekamp (1989) and Stuckey (1984) at mesophilic and thermophilic conditions. This fact was mostly attributed to the products of Maillard reactions (reactive carbonyl group of the sugars that reacts with the nucleophilic amino group of the amino acids).

4.2.1.5. Sludge Hygienisation

To assess the sludge hygienisation, *Escherichia coli* and *Salmonella* were followed as pathogenic content indicators. Faecal coliform density and *Salmonella* concentration for thermally treated sludge are presented in table

4.3 and table 4.4, respectively. Only sludge pre-treated at 110ºC or beyond could be classified as a Class A biosolids, (i.e <1000 MPN Fecal coliform/g TS and <3 MPN/4 g TS). As expected, no *E.coli* neither *Salmonella* microorganisms were found at temperatures near and above sterilisation range. Anyway, it must be noted that a considerable reduction of pathogens is seen at just 50ºC with almost 50% of faecal coliform reduction and null presence of *Salmonella*.

Table 4.3. Faecal coliform concentration (log MPN/g TS) of the sludge at different thermal pre-treatments.

Values	Raw	P-30	P-40	P-50	P-60	P-80	P-110	P-140	P-170	P-200
Mean	9.6	10	10	6.8	5.8	3.7	nd	nd	nd	nd
Min	9.4	10	10	6.6	5.6	3.2	-	-	-	-
Max	9.9	10	10	7.1	6.1	4.2	-	-	-	-

Table 4.4. Salmonella spp. concentration (MPN/4 g TS) of the sludge at different thermal pre-treatments.

Values	Raw	P-30	P-40	P-50	P-60	P-80	P-110	P-140	P-170	P-200
Mean	7.1	8.6	7.1	nd	nd	nd	nd	nd	nd	nd
Min	2.1	2.6	2.1	-	-	-	-	-	-	-
Max	24	28	24	-	-	-	-	-	-	-

4.2.2. Effect of H_2O_2 pre-treatment

4.2.2.1. Hydrogen peroxide dose effect at 30 and 60ºC of reaction

Chemical pre-treatment was performed by the addition of H_2O_2, within a range of 0-1.5 g H_2O_2/ g COD at a constant temperature of 30 and 60ºC. Tables 4.5 and 4.6 show the conditions studied. Notice that the initial concentration of hydrogen peroxide depends on the COD of the sludge and the hydrogen peroxide added.

Table 4.5. Experimental conditions of H_2O_2 pre-treatment over sludge at 30ºC

Hydrogen peroxide dose (w H_2O_2/w COD)	Initial concentration of Hydrogen peroxide (g/L)	% volume added	addition time (min)	Final concentration of Hydrogen peroxide (g/L)
0.00	0.00	0.00	0	n.d.
0.03	2.30	0.80	2	n.d.
0.07	5.80	2.00	5	n.d.
0.14	11.4	3.90	11	n.d.
0.29	21.9	7.90	19	n.d.
0.58	40.8	15.7	43	n.d.
0.87	57.3	23.6	65	n.d.
1.16	71.8	31.5	74	n.d.
1.45	84.7	39.3	93	n.d.

Table 4.6. Experimental conditions of H_2O_2 pre-treatment over sludge at 60ºC

Hydrogen peroxide dose (w H_2O_2/w COD)	Initial concentration of Hydrogen peroxide (g/L)	% volume added	addition time (min)	Concentration of Hydrogen peroxide at 30min (g/L)	Concentration of Hydrogen peroxide at 18h (g/L)
0.00	0.00	0.00	0.00	---	---
0.03	1.30	0.44	1.21	n.d	---
0.07	3.30	1.10	2.60	1.7	---
0.11	8.40	2.27	6.77	---	---
0.22	16.3	5.74	13.6	4.73	---
0.55	24.3	8.81	24,2	18.7	1.73
0.69	29.8	11.0	30.3	32.3	3.74
0.83	35.0	13.2	31.2	31.5	2.72
1.11	44.9	17.6	41.6	38.5	5.09
1.38	54.1	22.0	52.0	51.9	7.65

Figures 4.25 to 4.31 monitor different parameters against the hydrogen peroxide doses studied. The nomenclature –I indicates the initial value before the addition of the hydrogen peroxide but taking into account the dilution effect. In the same way, –C indicates the value of the parameter in the control reactor (for each dose of H_2O_2), again including dilution effect caused by the addition of hydrogen peroxide. And finally, –H_2O_2 is the value

of the parameter measured in the reactor where hydrogen peroxide is added.

As illustrated in figure 4.25, there is no concluding effect over COD for the different hydrogen peroxide doses tested at 30ºC. At the latter two concentrations, hydrogen peroxide was still present in the solution (table 4.5), which can disturb the measurement of COD (U.S. Peroxide, Product information; Yang et al. 1999; Talinli et al. 1992) as interferences with analytical methods overestimate the value.

COD results from sludge pretreated with hydrogen peroxide at 60ºC will not be presented; as table 4.6 indicates, residual H_2O_2 was found even at very low doses, and due to the mentioned interference, the results are not coherent and do not reflect the reality.

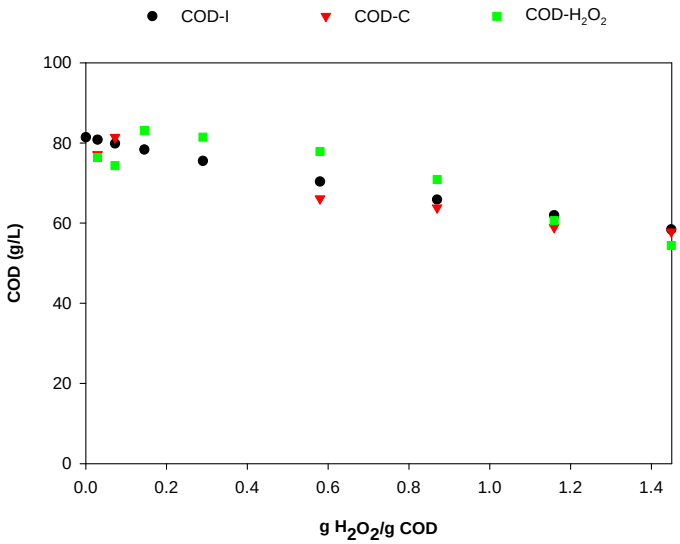

Figure 4.25. COD at different H_2O_2 concentrations at T=30ºC, time of reaction 30 min

Figures 4.26 and 4.29 present the results of the TS and VS of different dosages of H_2O_2 at the two different temperatures studied, for a better discussion of these parameters results are presented in form of total grams.

Figures 4.26 and 4.27 present the results at 30ºC where it is observed the clear decrease in TS and VS at the higher hydrogen peroxide doses. For a relation of hydrogen peroxide added of 1.16 and 1.45 g H_2O_2/g COD, it is obtained an elimination of 22.5 and 14% of TS and a reduction of 35.5 and 31.5% of VS, respectively.

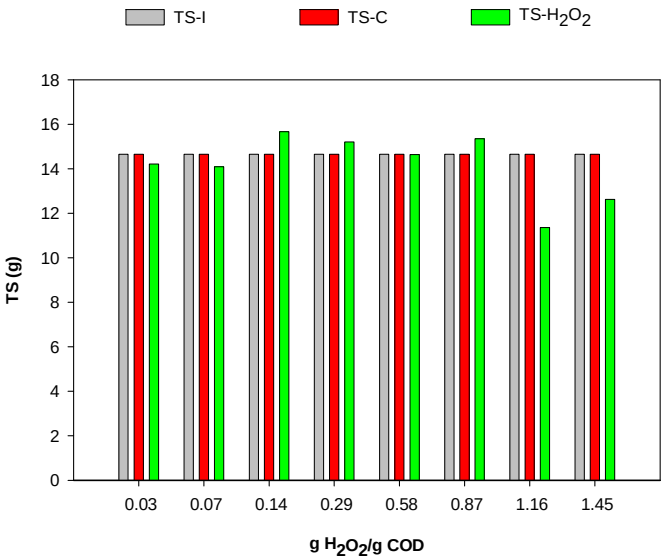

Figure 4.26. Mass TS at different H_2O_2 added concentrations at 30ºC, time reaction of 30 min

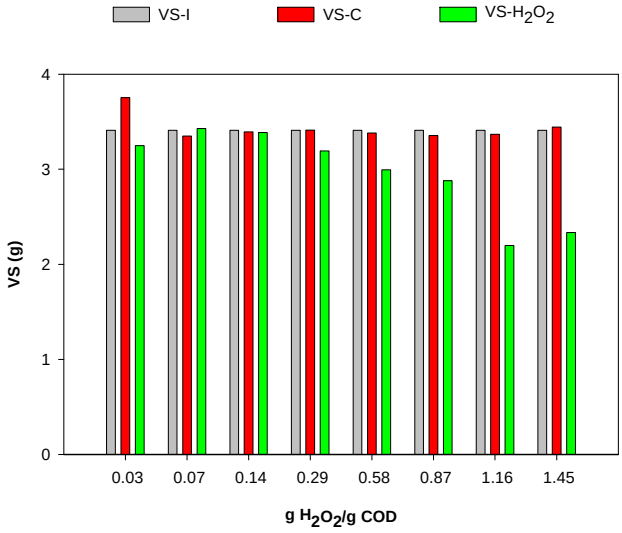

Figure 4.27. Mass VS at different H_2O_2 added concentrations at 30ºC, time reaction of 30 min

At 60ºC, figures 4.28 and 4.29, it can be noted that the increase of temperature promotes elimination of solids at lower doses of hydrogen peroxide, at only 0.55 g H_2O_2/g COD. Results of solid and organic matter removal are presented in table 4.7.

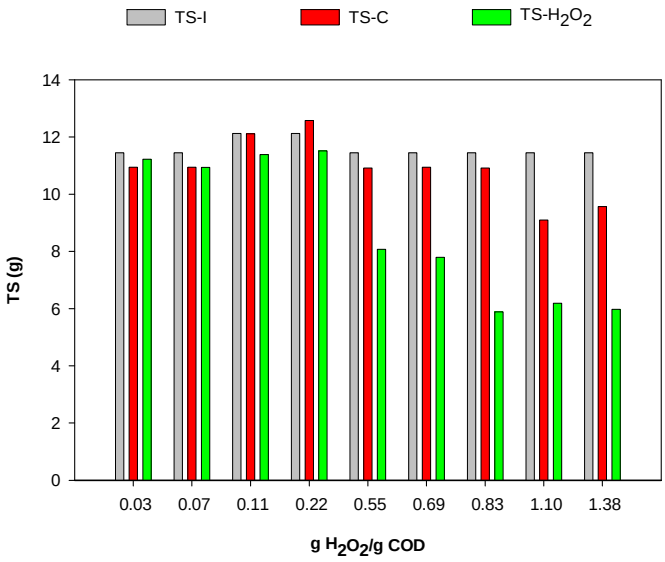

Figure 4.28. Mass TS at different H_2O_2 added concentrations at 60ºC, time reaction of 30 min

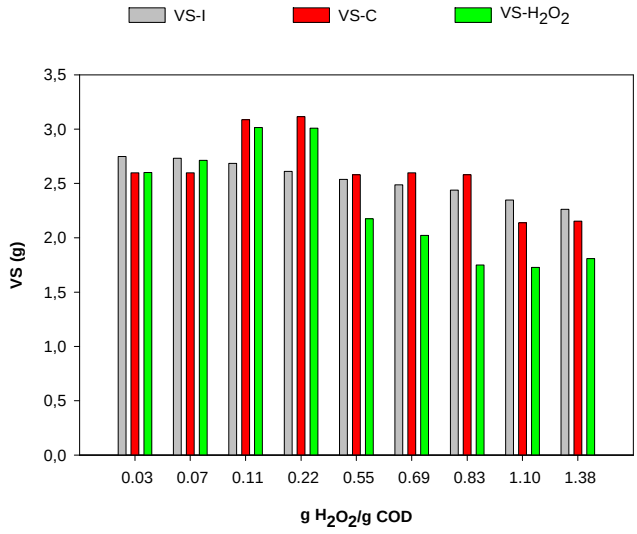

Figure 4.29. Mass VS at different H_2O_2 added concentrations at 60ºC, time reaction of 30 min

Table 4.7. Elimination of TS and VS by the addition of H_2O_2 at T=60ºC

H_2O_2/COD (w/w)	Removal of TS (%)	Removal of VS (%)
0.55	26.0	14.3
0.69	28.8	18.7
0.83	46.1	28.3
1.11	32.0	26.4
1.38	37.5	20.0

Figure 4.30 present the soluble COD at the different H_2O_2 dosages at T=30ºC. Although non relevant organic removal is observed after the addition of hydrogen peroxide at concentrations lower than 0.87 g H_2O_2/g COD, it seems to be a solubilization of the solid part, which becomes in an increase of soluble COD. A relation of 0.03 g H_2O_2/g COD is enough to solubilise more than 70% of the initial COD, that is from 9% to 15% of the total COD.

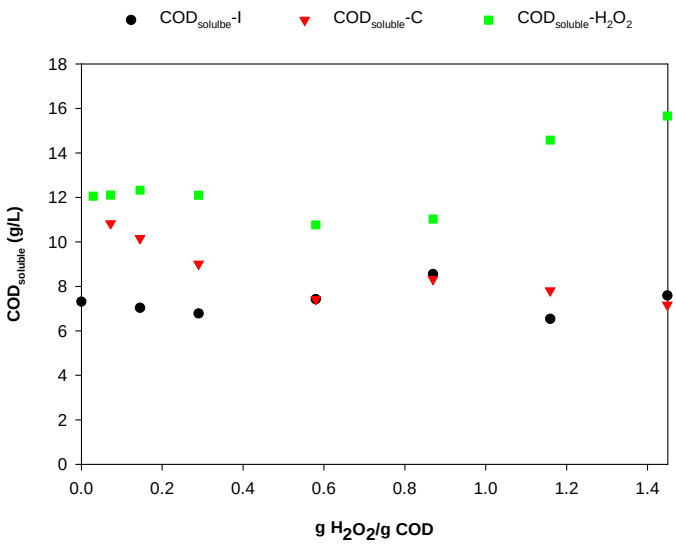

Figure 4.30. Soluble COD at different H_2O_2 concentrations at T=30ºC, time of reaction 30 min

In figure 4.31,is presented the total dissolved solids, in terms of total grams. It is here clearly seen that the addition of H_2O_2 promotes solubilisation. TDS, except for the highest dosage tested of 1.45 g H_2O_2/g COD.

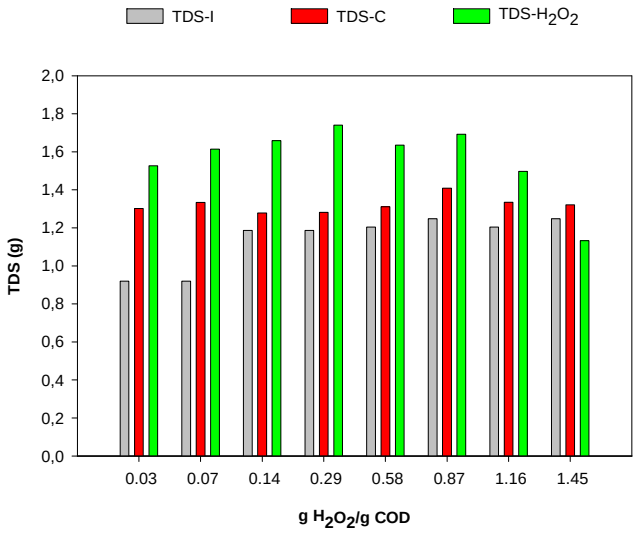

Figure 4.31. Mass TDS at different H_2O_2 concentrations at T=30ºC, time of reaction 30 min

Concerning soluble volatile matter, expressed in VDS in figure 4.32, it is seen that for 0.03 and 0.07 g H_2O_2/g COD dosages, the initial feed is different from the other 6 dosages. In the case of the two lower dosages, the VDS of the control reactor is much higher than the initial, whereas in the others no considerable differences is seen. Despite this difference on the characteristics of the sludge feed, in all cases the addition of H_2O_2, promotes the reduction of the VDS with respect of the control.

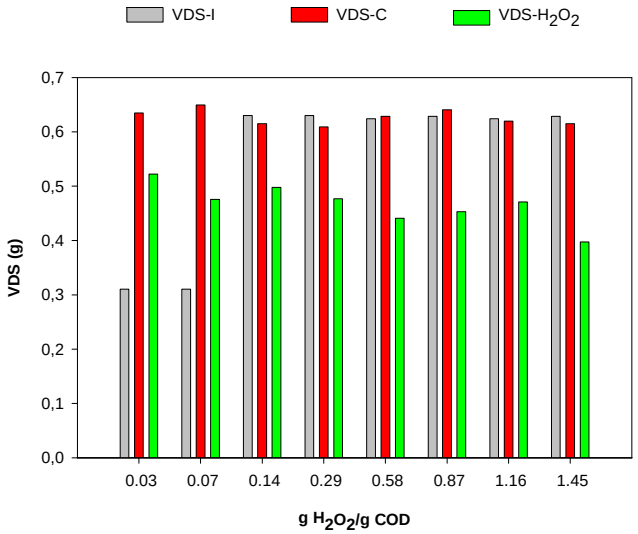

Figure 4.32. Mass VDS at different H_2O_2 concentrations at T=30ºC, time of reaction 30 min

In contrast, experiments at 60ºC, presented in figures 4.33 and 4.34, demonstrate that, at concentrations lower than 0.22 g H_2O_2/g COD, the TDS are higher in the hydrogen peroxide reactor than in the control reactor, while at relations higher than 0.55 g H_2O_2/g COD the TDS are lower. This indicates that at 60ºC there is solubilisation of the solid matter compared with the initial value, as concluded in the previous section. However, at relations above 0.55 g H_2O_2/g COD, elimination of suspended material occurs, mainly mineral, as figure 4.34 suggests. non- remarkable changes in VDS are observed.

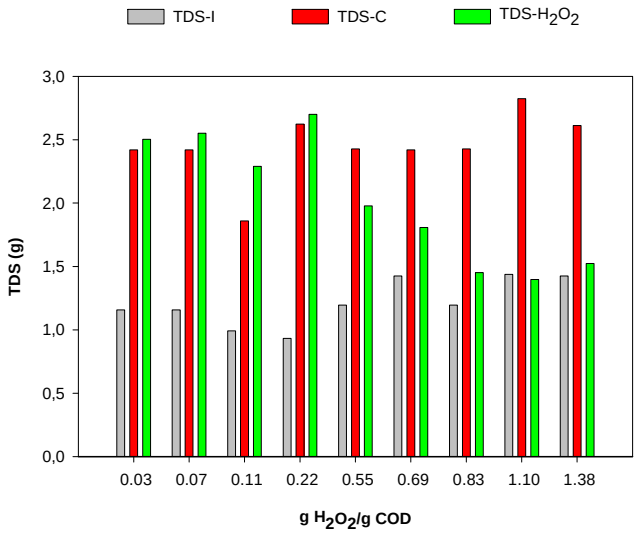

Figure 4.33. Mass TDS at different H_2O_2 concentrations at T=60ºC, time of reaction 30 min

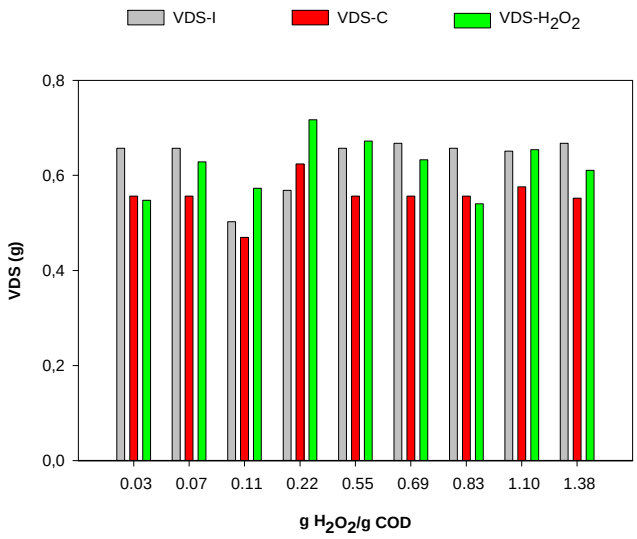

Figure 4.34. Mass VDS at different H_2O_2 concentrations at T=60ºC, time of reaction 30 min

Figures 4.35 and 4.36 present the biomass of the sludge expressed as VSS after the chemical pre-treatment at 30ºC and 60ºC respectively. As observed in figure 4.35, at 30ºC only at the two latter doses studied, 1.16 and 1.45 g H_2O_2/g COD, there is a reduction of biomass, 41 and 34.5% respectively.

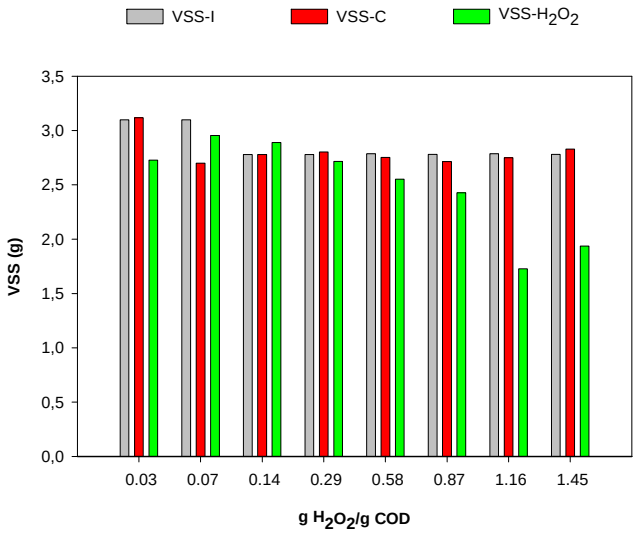

Figure 4.35. Mass VSS at different H_2O_2 concentrations at T=30ºC, time of reaction 30 min

In contrast, at 60ºC, it is already found an elimination of biomass at a dose of 0.55 g H_2O_2/g COD or higher, as observed in figure 4.36. Thus, table 4.8 shows that higher reduction of biomass is obtained as hydrogen peroxide dose increases, except for the highest concentration tested, which maybe is related to a less efficient use of the hydrogen peroxide.

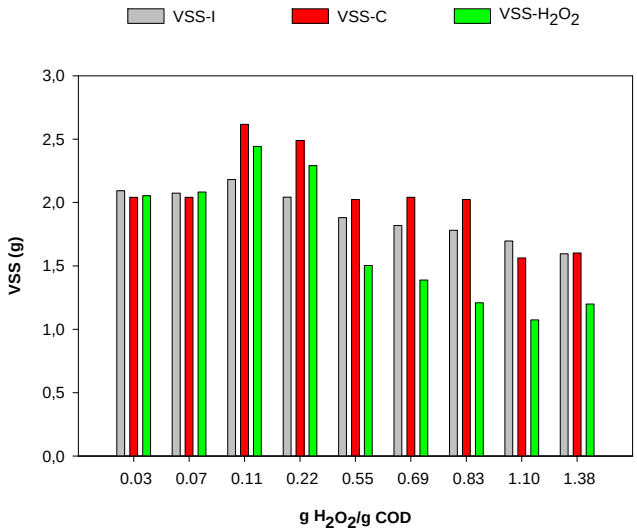

Figure 4.36. Mass VSS at different H_2O_2 concentrations at T=60ºC, time of reaction 30 min

Table 4.8. Biomass elimination by means of chemical pre-treatment with H_2O_2 over sludge at T=60ºC and time of reaction of 30 min

H_2O_2/COD (w/w)	VSS removal (%)
0.55	20.1
0.69	23.7
0.83	32.1
1.11	37.7
1.38	24.9

Similarly, figure 4.37 presents the solids composition of the sludge and the proportion of each fraction after the peroxide pre-treatment at 30ºC in the initial, control and final pre-treated sludges. It can be seen that elimination of cellular mass (VSS) and also mineral suspended material (MSS) is evident in the two latter doses of hydrogen peroxide, 1.16 and 1.45 g H_2O_2/g COD. There are no considerable changes in the composition of the sludge between the initial sludge and the control reactor.

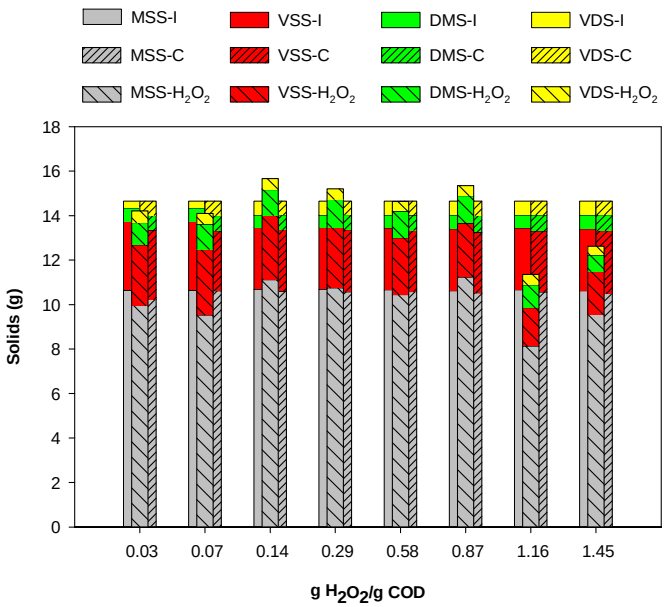

Figure 4.37. Solid sludge composition of the initial (-I), control (-C) and pretreated with H_2O_2 (-H_2O_2) sludge in the chemical pre-treatment against different doses of H_2O_2 at 30ºC and reaction time of 30 min.

Figure 4.38 presents the results of the hydrogen peroxide pre-treatment at 60ºC. Not only elimination of VSS is observed at concentrations higher than 0.55 g H_2O_2/g COD, also reduction of MMS are observed caused by the simultaneous solubilization action of the temperature and the addition of the hydrogen peroxide. As expected, MDS of the control reactor is higher than the initial value, while MSS decreases, principally due to the temperature of 60ºC that causes a solubilisation also of the inorganic matter.

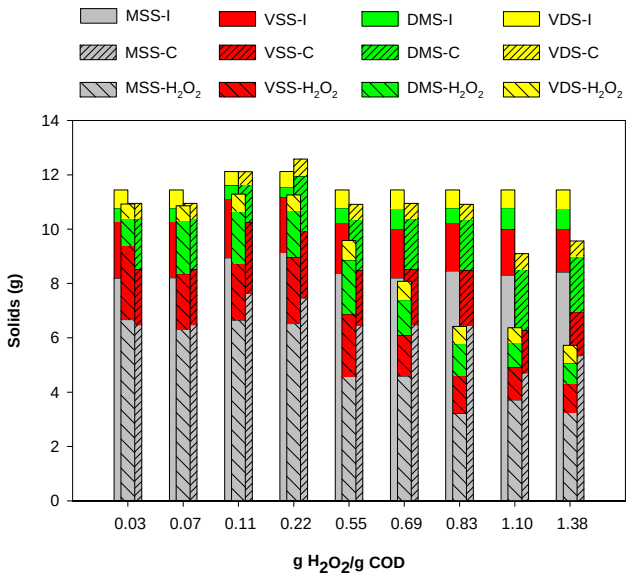

Figure 4.38. Solid sludge composition of the initial (-I), control (-C) and pretreated with H_2O_2 (-H_2O_2) sludge in the chemical pre-treatment against different doses of H_2O_2 at 60ºC and reaction timen 30 min.

Figures 4.39 and 4.40 present the values of the pH of the chemical pretreatmens at 30 and 60ºC respectively. At 30ºC the value of the pH in the hydrogen peroxide reactor is higher than expected, as hydrogen peroxide should acidify the media. It seems that basic substances are released into the media suggesting that hydrogen peroxide reacts with the sludge. In contrast, at 60ºC there is no considerable difference between the initial value and the sludge chemically treated; residual hydrogen peroxide acidifies and the pH does not significantly change.

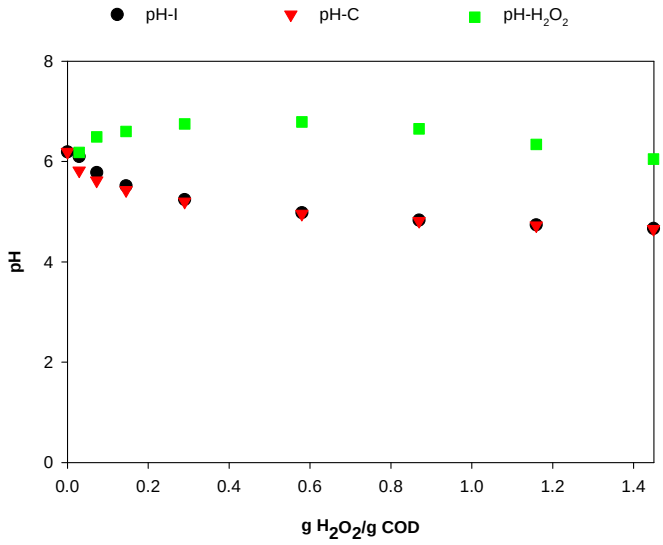

Figure 4.39. pH against different concentrations of H_2O_2 at 30ºC and time of reaction 30 min.

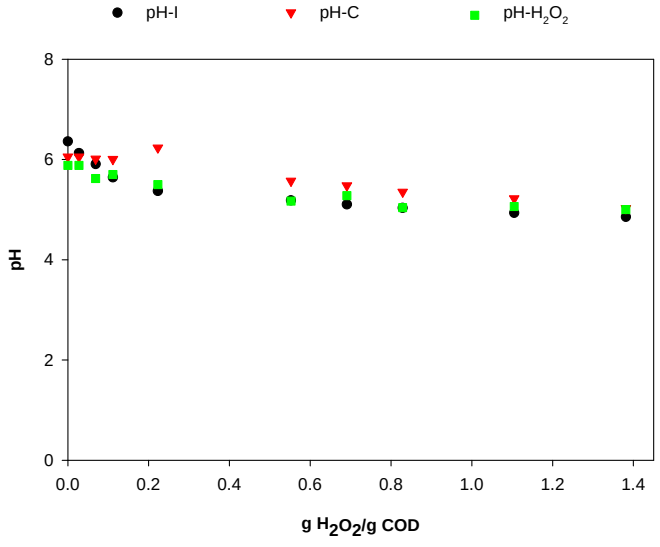

Figure 4.40. pH against different concentrations of H_2O_2 at 60ºC and time of reaction 30 min.

4.2.2.2. Influence of reaction time

It was also studied the importance of time once the hydrogen peroxide was added into the sludge, as residual hydrogen peroxide was found at short times of reaction, especially at 60ºC (see table 4.6). This part was done at 0.55, 0.69, 0.83, 1.11 and 1.38 gH_2O_2/g COD, analysing the samples 18 h after the addition of the H_2O_2 maintaining the reaction temperature at 60ºC.

The nomenclature used in the following discussion is: -I indicates the initial value of the sludge before the addition of the hydrogen peroxide; –C.30min indicates the value of the parameter in the control reactor 30 min after the addition of the H_2O_2; –H_2O_2.30min is the value of the parameter measured after 30 min of reaction in the reactor where hydrogen peroxide is added; -C.18h indicates the value of the parameter in the control reactor at 18 h after the addition of the H_2O_2; and -H_2O_2.18h is the value of the parameter measured after 18 h of reaction in the reactor where hydrogen peroxide is added.

As figure 4.41 indicates, there is no significant variation on the TS against time in the hydrogen peroxide reactor, independently of the dose. However, VS content decreases as figure 4.42 illustrates. Around 20% of the VS was eliminated in the hydrogen peroxide reactor between the two different times tested, 30 min and 18 h.

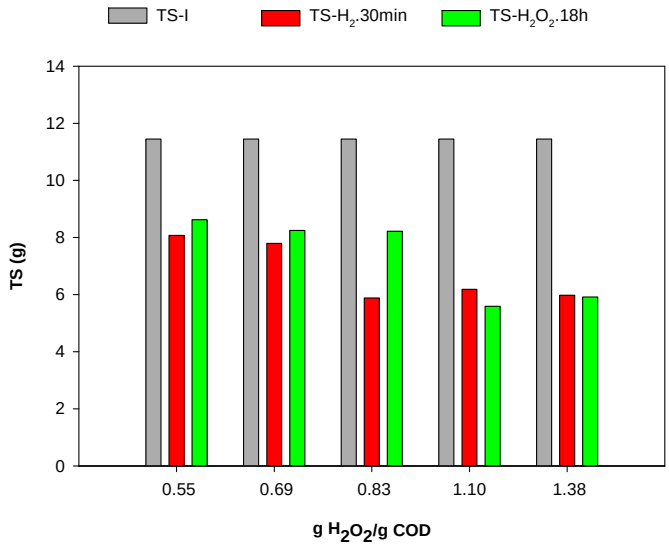

Figure 4.41. TS against different doses of H_2O_2 added at 60ºC and reaction time of 30 min and 18 h.

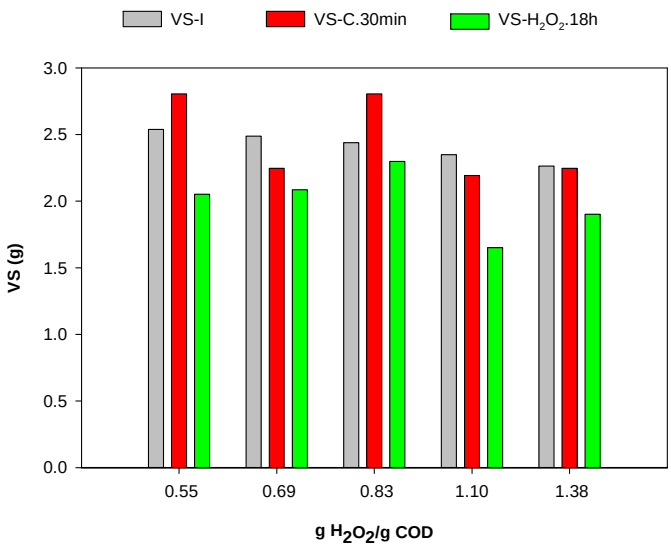

Figure 4.42. VS against different doses of H_2O_2 added at 60ºC and reaction time of 30 min and 18 h.

With respect to the dissolved solids, TDS, figure 4.43 shows the results obtained. With the addition of H_2O_2 and at reaction times of 18 h, the dissolved solids considerably increase when compared with the results obtained at 30 min, especially at the dose of 0.83 gH_2O_2/gCOD, where is observed a 141% raise in terms of TDS if (from 1.45 up to 3.5 g of TDS). Also this tendency is followed by the VDS, as figure 4.44 illustrates.

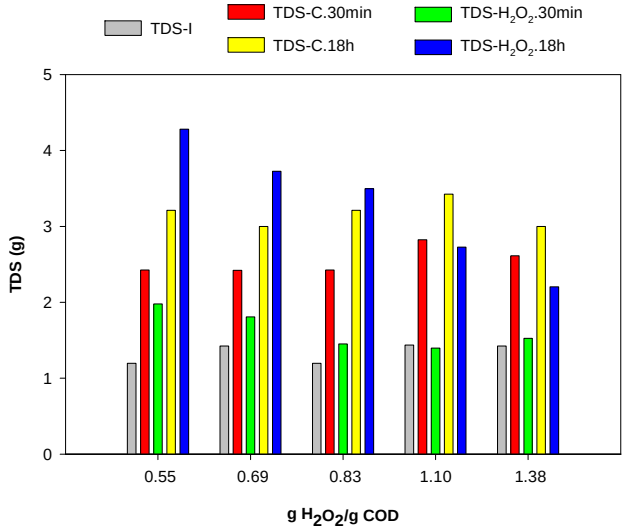

Figure 4.43. TDS against different doses of H_2O_2 added at 60ºC and reaction time of 30 min and 18 h

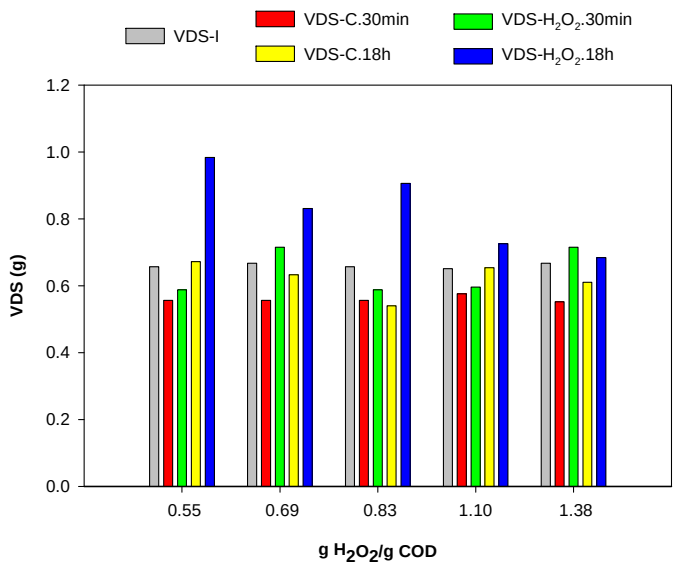

Figure 4.44. VDS against different doses of H_2O_2 added at 60ºC and reaction time of 30 min and 18 h

4.2.2.3. Anaerobic biodegradability

Biodegradability of the different pre-treated sludge was assessed with the BMP tests described in Chapter 2. The characteristics of the initial sludge used in the experimental set are shown in table 4.9.

Pre-treatment with hydrogen peroxide also improves sludge biogas production as figure 4.45 evidences. All peroxidated sludge leads to a biogas production of around 50-60 STP ml not showing a clear advantage as dosages of hydrogen peroxide are incremented. Even the addition of the smallest dose leads to an increase of above 150% when compared to raw sludge. Table 4.10 summarises the main characteristics of the biogas after thermophilic digestion over sludge pre-treated with hydrogen peroxide.

Table 4.9. Initial conditions of the sludge in hydrogen peroxide pre-treatments.

Type of sludge	CODhomog (g/L)	CODsol (g/L)	TS (g/L)	VS (g/L)	TSS (g/L)	VSS (g/L)
inoculum	26.15	2.38	31.32	16.63	27.59	14.40
subs.	37.20	8.23	32.65	27.00	30.51	26.09
P-0.02	58.54	8.23	36.39	29.93	32.17	27.39
P-0.05	57.09	8.09	36.60	30.22	31.84	27.02
P-0.1	53.18	8.34	36.93	30.62	31.14	26.45
P-0.2	52.88	7.91	36.12	29.88	30.45	25.69
P-0.4	48.61	8.08	32.20	26.11	25.79	21.26
P-0.6	68.18	8.44	31.15	25.75	24.24	20.15
P-0.8	61.27	8.58	33.02	27.49	26.36	22.15
P-1.0	62.84	8.38	32.15	26.11	25.73	21.18

As the specific biogas production rate indicates in figure 4.46, most of the biogas production in peroxide pre-treatments starts at 100 h and rate of production is observed up to almost 600 h, then it dismisses, however thermal pre-treatment beyond 110ºC leads to much higher specific biogas rates than the rest of conditions tested.

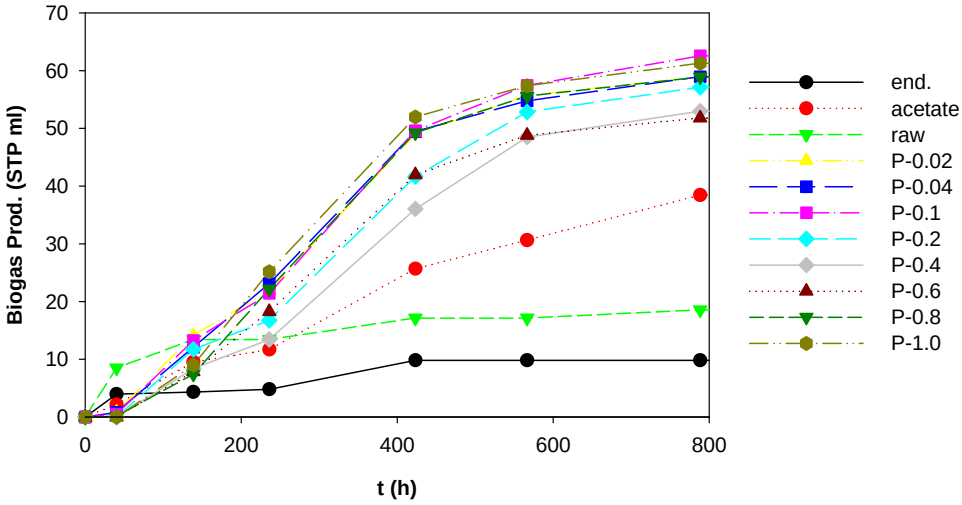

Figure 4.45. Total biogas production of sludge pre-treated with hydrogen peroxide in thermophilic digestion tests.

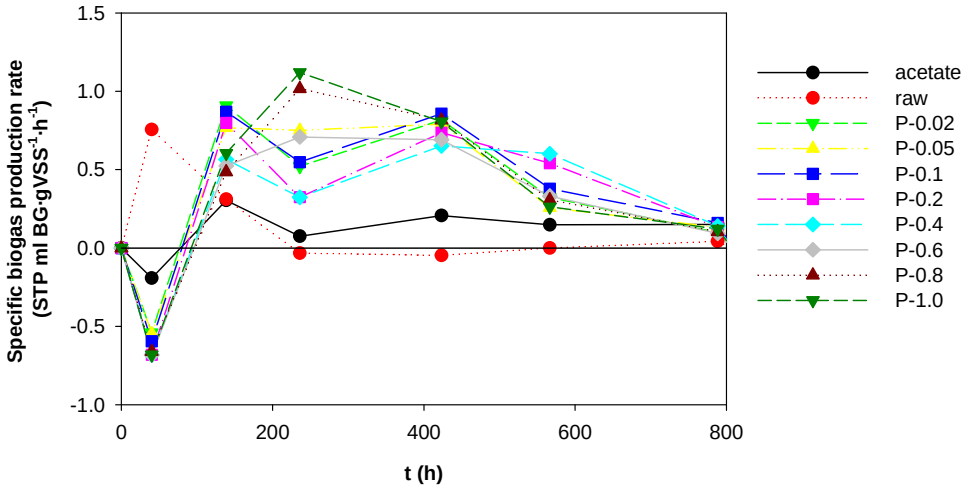

Figure 4.46. Specific biogas production rate of sludge pre-treated with hydrogen peroxide in thermophilic digestion tests.

The quality of the biogas expressed in different terms can be found in table 4.10 for peroxide pre-treatment. It can be seen that peroxidation pre-treatment enhances both the biogas production and the methane fraction obtained in the subsequent thermophilic anaerobic digestion.

COD was not evaluated because the presence of H_2O_2 strongly interferes the measurement of COD (Talinly et al, 1992; Kang et all., 1999) resulting in an overestimation of this parameter. The addition of hydrogen peroxide did not appreciably change the TS or VS concentration of the sludge, i.e. no total mineralization occurred, and the major changes in sludge characteristics dealt with solubilization.

Table 4.10. Characteristics of BMP tests in thermophilic anaerobic digestion over H_2O_2 pre-treated sludge

Parameter	End.	Acet.	Raw	P-0.02	P-0.05	P-0.1	P-0.2	P-0.4	P-0.6	P-0.8	P-1.0
Substrate added (mg COD)	0	233	149	234	228	213	212	194	273	245	251
Substrate added (mg VS)	0	164*	108	120	121	122	120	104	103	110	104
Total production of biogas (STP ml)	9.82	38.5	18.5	58.9	59.0	62.6	57.1	53.0	51.8	58.9	61.3
Concentration of methane (%)	16.2	51.4	48.3	55.7	55.7	56.3	55.5	55.4	54.2	54.1	54.1
Substrate biogas production (STP ml)	-	28.6	8.72	49.0	49.1	52.7	47.3	43.1	42.0	49.1	51.5
% Theoretical biogas yield # [COD_{added}]	-	18.1	8.1	33	34	40	35	35	24	31	32
% Theoretical biogas yield # [VS_{added}]	-	19.3	8.37	49	49	52	47	49	47	52	57
Biogas yield (STP L/g)[BP. COD_{added}]	-	0.12	0.06	0.21	0.22	0.25	0.22	0.22	0.15	0.20	0.20
Biogas yield (STP L/g)[BP. VS_{added}]		0.17	0.08	0.41	0.41	0.43	0.40	0.41	0.41	0.45	0.49
% Biodegradability [COD]	39.1	32.5	19.1	23.2	30.5	30.9	20.8	22.0	34.5	35.3	37.5
% Biodegradability [VS]	18.8	14.4	21.7	19.9	26.3	28.3	32.7	19.7	23.1	25.3	15.4

*1.42 gCOD/gVSS
Biogas adjusted with the measured methane composition

Figure 4.53 summarizes the solubilization rate of TOC, TS, VS and carbohydrates for different doses of H_2O_2. Firstly, it must be noted that its addition implies that the volume significantly changes as H_2O_2 is a liquid solution. Accordingly, the increase of volume was 0.4, 1, 2, 4, 7, 11, 14 and 18%, respectively for each referenced H_2O_2 dose. In order to make a proper discussion, the dilution effect has been eliminated when assessing the impact of the peroxidation

Figure 4.53 evidences that the solubilization is improved by peroxidation, although the linear correlation is weaker in comparison with the thermal pre-treatment, equation 4.3. The hydrogen peroxide addition on sludge does not promote organic destruction being its major effect the solubilization of the particulate organic matter which is in line with other previous findings (Cacho Rivero and Suidan, 2006)

$$S_{TOC}\,(\%) = 0.383 \cdot [H_2O_2]\,(gH_2O\ /\ gCOD) + 0.600 \qquad R^2 = 0.72 \qquad \text{(Eq. 4.3)}$$

Enhancement of biogas, also illustrated in figure 4.49, shows a small dependence on H_2O_2 dosages. Also, methane content, around 54-55%, is improved suggesting that H_2O_2 facilitates the conversion of organic matter into methane.

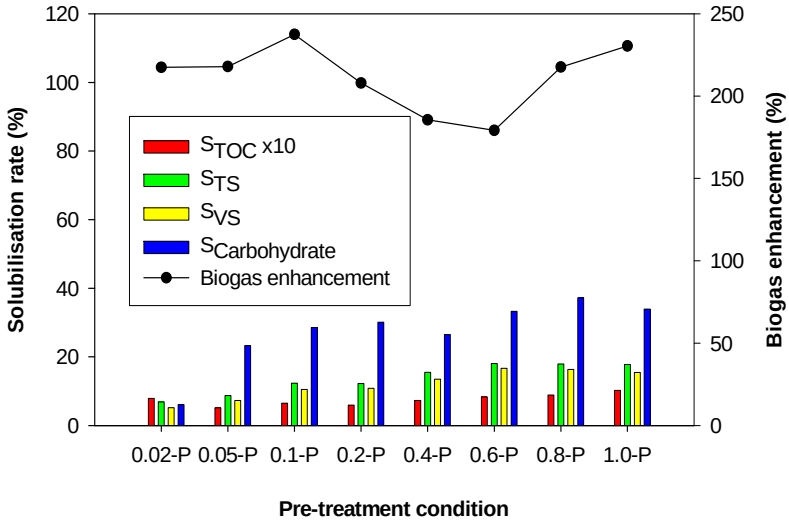

Figure 4.47. TOC, TS, VS and carbohydrate solubilization rate of H_2O_2 pre-treated sludge and biogas enhancement in the subsequent thermophilic anaerobic digestion.

If thermal and peroxidation pre-treatment are compared in terms of biogas production, (figures 4.24 and 4.49), it can be seen that, despite the lower solubilization rates of sludge in peroxide pre-treatments, biogas enhancement is clearly better than for thermal pre-treatment.

4.2.2.4. Hygienisation

Concerning to pathogens, its occurrence is assessed in tables 4.11 and 4.12. It can be seen that H_2O_2 promotes salmonella destruction, but it has practically no effect on faecal coliform densities, even at the higher dose applied, 0.6 g H_2O_2/g COD.

Table 4.11. Faecal coliform concentration (log MPN/g TS) of the sludge at different pre-treatment dosages of H_2O_2 at 30ºC.

H_2O_2 dose	**Raw**	**0.02-P**	**0.05-P**	**0.1-P**	**0.2-P**	**0.4-P**	**0.6-P**
Value	9.8	9.7	9.7	9.4	9.4	8.6	8.4
Min	9.6	9.5	9.4	9.1	9.1	8.3	8.2
Max	10	10	9.9	9.7	9.7	8.8	8.7

Table 4.12. Salmonella spp. concentration (MPN/4 g TS) of the sludge at different pre-treatment dosages of H_2O_2 at 30ºC.

H_2O_2 dose	**Raw**	**0.02-P**	**0.05-P**	**0.1-P**	**0.2-P**	**0.4-P**	**0.6-P**
Value	17	13	8.6	0.4	0.3	0.1	0.1
Min	5.1	3.9	2.6	0.1	0.1	0.0	0.0
Max	57	42	28	1.4	1.0	0.4	0.4

4.3. Conclusions

Thermal pre-treatment within the range of 30-80ºC shows that high temperatures lead to an increase of over 100% in soluble COD content; also TDS depicts the same behaviour. This suggests that part of the homogeneous COD (or TS content) solubilizes but no organic matter is destroyed.

Also a rapid increase of soluble COD was observed during only the first hour of pre-treatment, especially at 60ºC and 80ºC, which also correlates

with the rising in TDS content, after this time non-noticeable improvement of the solubilisation is seen.

At the thermal treatment in the temperature range of 110ºC-200ºC, the tendency is similar. Solubilisation increases as temperature does. Only beyond 170ºC and 8 h of treatment, elimination of TS is observed at significant extent, instead VS only is removed at 200ºC and 16 h.

Although irrelevant organic removal is observed after the addition of hydrogen peroxide at 30ºC at concentration below 0.87 gH_2O_2/gCOD, it seems to be a solubilisation of the solid part, which results in an increase of soluble COD and TDS. A dose of 0.03 g H_2O_2/g COD is enough to solubilize more than 70% of the initial soluble COD, that goes from 9% to 15% of the total COD. At higher concentrations, 1.16 and 1.45 g H_2O_2/g COD, organic destruction is already found. Thus, there is an elimination of biomass expressed as VSS in 41 and 34.5% respectively and also a decrease in the solid fraction, expressed as TS, in 22.5 and 14%. However, the addition of hydrogen peroxide at these two higher doses leads to an undesired increase of the reaction volume, raising the residual volume in 31.5 and 39.5% respectively.

In the addition of hydrogen peroxide at 60ºC, it is observed a higher efficiency than at 30ºC. Up to doses of hydrogen peroxide below 0.55 gH_2O_2/gCOD, it is obtained removal of organic matter up to peak at the ratio 0.88 gH_2O_2/gCOD, where the elimination of TS and VS content is around 46.1 and 28.3% respectively. The maximum removal of VSS, 37.7%, is obtained at 1.11 g H_2O_2/g COD. Higher reactions times at this temperature where evaluated in dosages where hydrogen peroxide was still present in the reactor. It was observed that at higher times improves solubilization either with the organic and mineral matter; however no improvement is seen in the elimination of organic matter.

Only sludge pre-treated above 110ºC can be classified as Class A biosolids, although a considerable reduction of pathogens is already observed at 50ºC with almost 50% of faecal coliform reduction and null presence of *Salmonella*. Hydrogen peroxide promotes *Salmonella* destruction, but does not practically have any effect on faecal coliform densities even at the highest dosage tested, 0.6 g H_2O_2/g COD.

Despite the lower solubilization rates of the sludge in H_2O_2 pre-treatments, biogas enhancement is clearly much higher than for thermal pre-treatment. Enhancement of biogas shows a small dependence on H_2O_2 doses. Also, methane content in the gas, around 54-55%, is improved.

After these evaluations it was decided to select for studies at lab-plant scale for the semi-CSTR thermophilic anaerobic digestion, thermal pre-treatment at 80ºC and peroxidation with a dose of 0.2 g H_2O_2/g COD. Despite higher temperatures leads to higher biogas production, the temperature of 80ºC is preferred as is below the boiling point of water. Equipment that would be

required beyond this point is much more expensive and critical. Moreover, at 80ºC class A biosolids are obtained so sanitary conditions for fertilize use is presumably acceptable. Concerning dosages of hydrogen peroxide, the most decisive parameter have been the pathogen content, specifically the *Salmonella*, dosage of 0.2 g H_2O_2/g COD clearly promotes the reduction of *Salmonella*, within an acceptable addition of chemical.

CHAPTER 5

Enhancement of thermophilic anaerobic digestion using pre-treated sludge

5.1. Introductory remarks

A pilot plant with three identical glass reactors was constructed in order to simultaneously study three different operation conditions in a semi-CSTR mode with daily draw-fill mode. Each reactor had 5 litres of effective volume. The reactor temperature was maintained with a thermostatic bath at the desired temperature equipped with a water level control for balancing water loss evaporation. A magnetic stirrer was preferred for continuous agitation of the reactor to prevent gas leak. A peristaltic pump was used for sludge feeding and sample extraction. Gas generated during the anaerobic digestion was continuously measured with a mass flow meter and then collected in a long 1 litre glass tube with three-way glass stopcocks at each for gas composition analysis.

The objective of this chapter was to establish the fundamentals of thermophilic sludge stabilisation and its enhancement by using the optimal pre-treatment sludge condition suggested in Chapter 4, thermal

pretreatment at 80ºc for 1 h, and chemical treatment with H_2O_2 at a dosage of 0.2 g H_2O_2/g COD at 30ºC

Again the raw and the pre-treated sludge examined is a mixture of thickened primary sludge (PS) and thickened secondary sludge (WAS). Among others, the main objective was the evaluation of the pathogen sludge content.

The specific objectives were:

- Build-up an anaerobic digestion pilot plant.
- Analyse the biological performance at different anaerobic digestion conditions. Specifically if class A biosolids are obtained after the different anaerobic configurations:
    - Temperature (33, 50, 55 and 60ºC)
    - HRT (15, 20 and 25 days)
    - Dual digestion: thermophilic (55ºC)-mesophilic (33ºC) phased reactor.
- Study the thermophilic anaerobic digestion of both chemically and thermally pre-treated sludge

5.2. Thermophilic anaerobic digestion

5.2.1. Raw sludge heterogeneity

The sludge used for feeding the reactors comes directly from the operative WWTP. This implies several fluctuations in its characteristics, due to some inherent changing conditions when using real wastes. Climate changes and variety of population, especially in weekends and holidays may highly alter the composition of the sludge. Also the sludge, specially the raw sludge, is a non-homogeneous fluid and the analysis highly differs in the same sample, especially when homogeneous characteristics are given. In figures 5.6 and 5.7, the total COD, the TS and VS can be seen, corresponding to the feed sludge used in an experimental period of 7 months. As it can be seen, COD ranges from 24000-75000 mg O_2/L being the average around 45000 mg O_2/L. Also solid content and volatile solids give similar fluctuations; an average of 33 and 25 g/L were measured respectively.

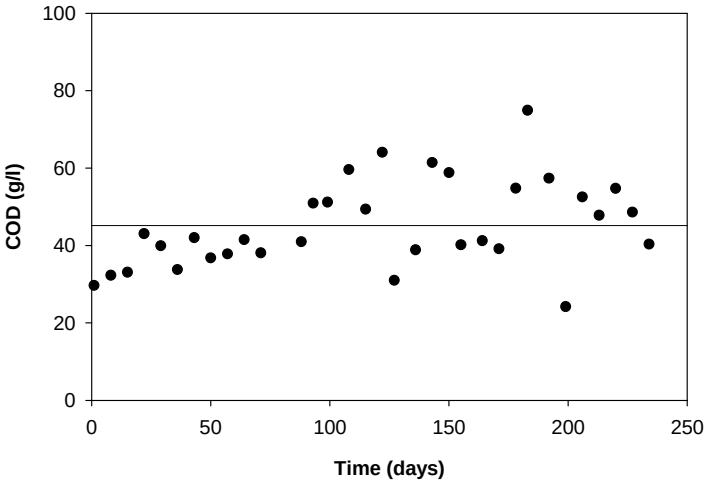

Figure 5.1. Chemical Oxygen Demand of raw sludge.

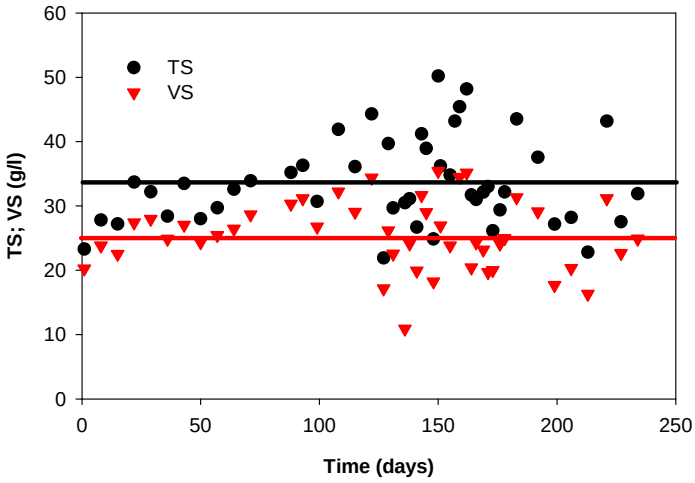

Figure 5.2. Total Solids and Volatile Solids of raw sludge.

5.2.2. Effect of the temperature digestion in anaerobic conditions

In order to establish the baseline information about the anaerobic sludge stabilisation of the sludge provided, four different digestion temperatures were tested, one at the mesophilic condition of 33ºC and three different thermophilic temperatures, i.e. 50, 55 and 60ºC.

It was used the anaerobic digestion pilot-plant with three identical reactors. One reactor was always kept in the mesophilic temperature of 33ºC and the other two reactors at different thermophilic temperatures, initially 50ºC, and 60ºC. Later, it was decided to change the highest temperature into 55ºC due to poor results.

In figures 5.8-5.16, it is shown the acclimatization period for changing the conditions in the thermophilic reactor at 60ºC into 55ºC at a TRH=20 days for the principal parameters in anaerobic process: COD, soluble COD, TS and VS. As seen, the time needed to reach stable conditions in the anaerobic digestion was 100 days, 5 times the HRT. The time needed to acclimatise the bacterial population into this new thermophilic temperature was longer than expected, as three times the HRT is the value generally reported (De la Rubia et al. 2005; Bouškova et al. 2005). This may be caused due to the bad performance of the 60ºC thermophilic sludge and the unbalanced bacterial population, which needed to be recovered at the new conditions.

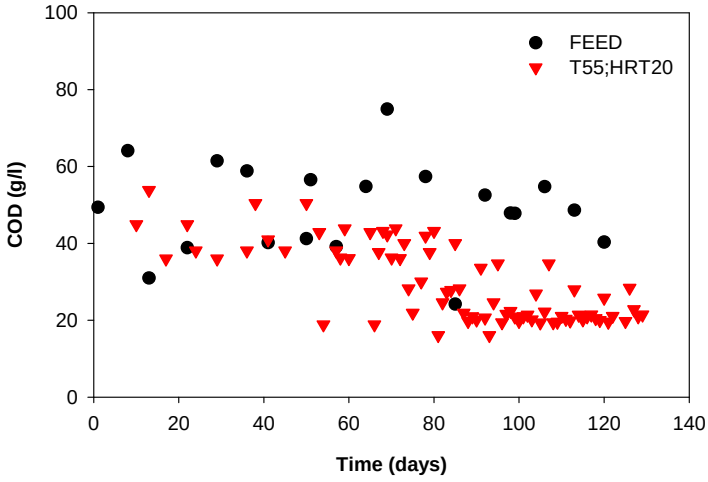

Figure 5.3. Evolution of COD in the acclimatization from 60ºC to 55ºC at a HRT=20 days

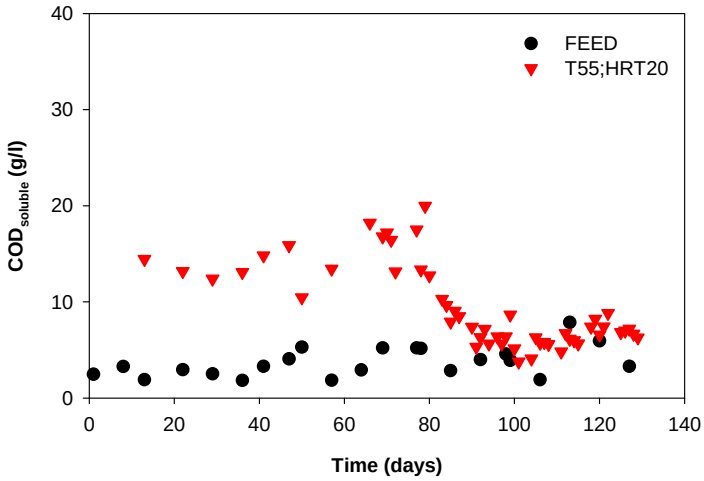

Figure 5.4. Evolution of soluble COD in the acclimatization from 60ºC to 55ºC at a HRT=20 days

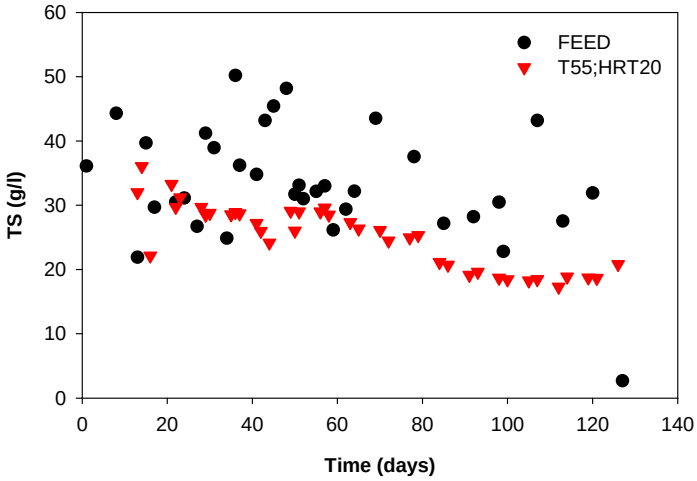

Figure 5.5. Evolution of TS in the acclimatization from 60ºC to 55ºC at a HRT=20 days

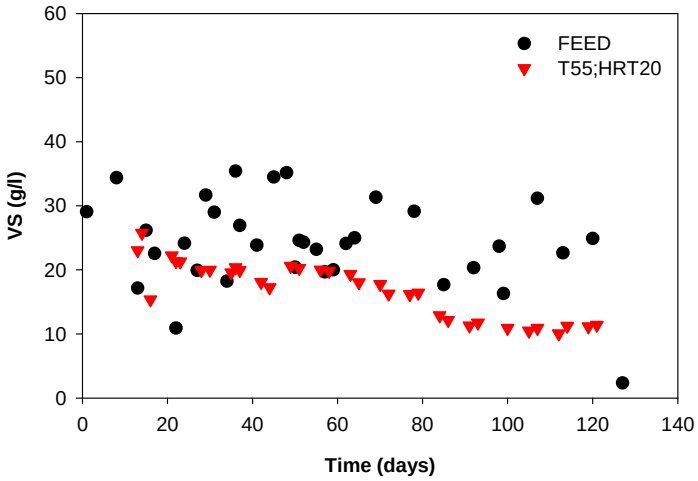

Figure 5.6. Evolution of VS in the acclimatization from 60ºC to 55ºC at a HRT=20 days

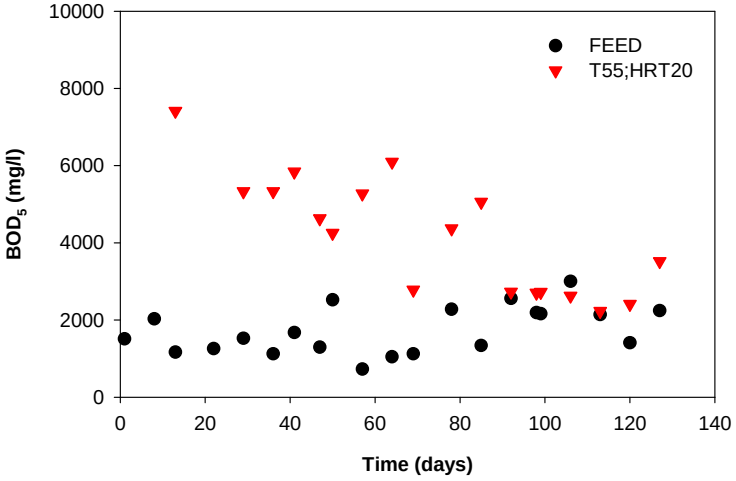

Figure 5.7. Evolution of BOD in the acclimatization from 60ºC to 55ºC at a HRT=20 days

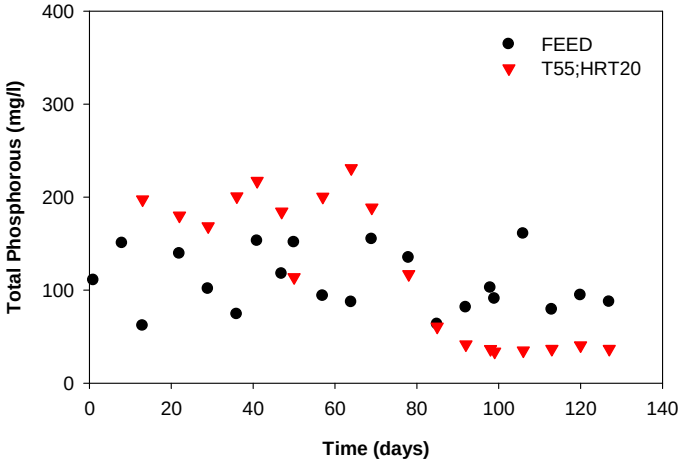

Figure 5.8. Evolution of Total Phosphorous in the acclimatization from 60ºC to 55ºC at a HRT=20 days

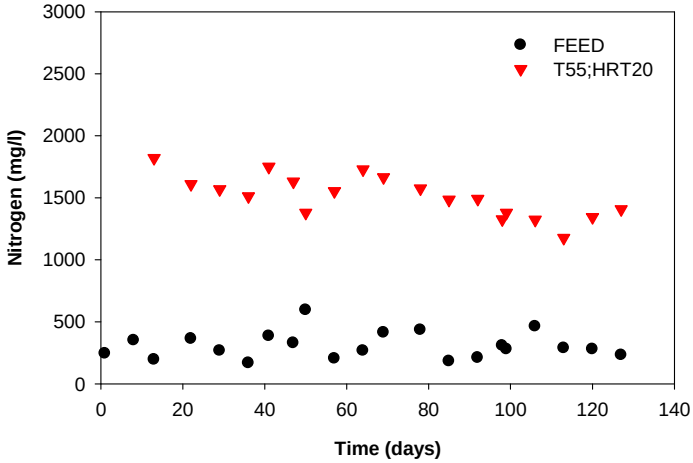

Figure 5.9. Evolution of Nitrogen in the acclimatization from 60ºC to 55ºC at a HRT=20 days

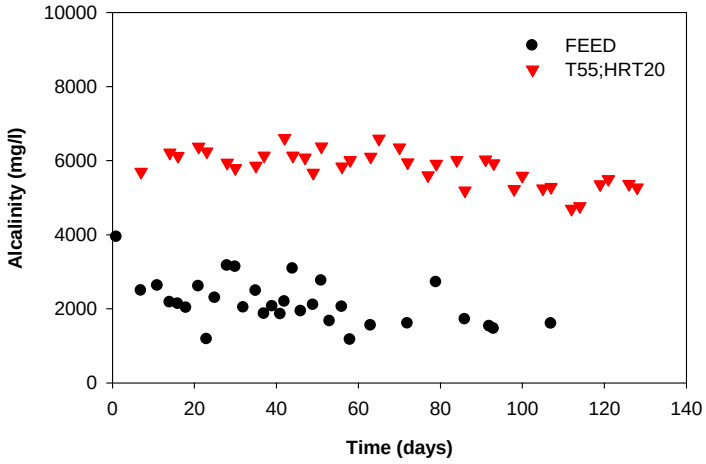

Figure 5.10. Evolution of Alkalinity in the acclimatization from 60ºC to 55ºC at a HRT=20 days

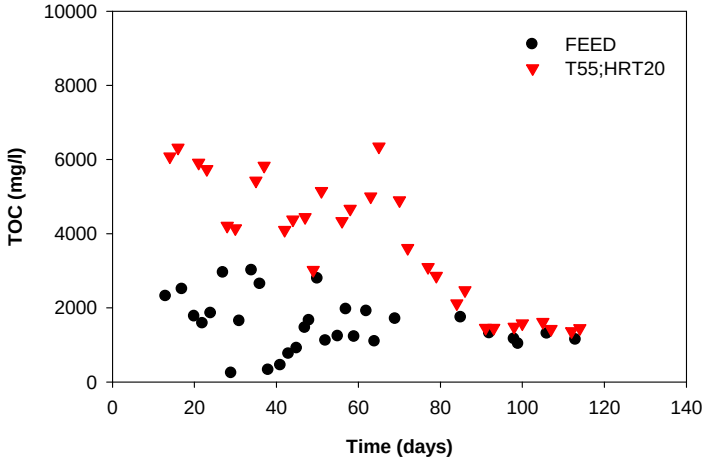

Figure 5.11. Evolution of soluble TOC in the acclimatization from 60ºC to 55ºC at a HRT=20 days

Table 5.2 collects the results exploring the influence of 33ºC, 50ºC, 55ºC, and 60ºC in anaerobic digestion.

Table 5.1. Effect of the temperature in anaerobic digestion at a HRT=20 days

PARAMETER	FEED	DIGESTER TEMPERATURE			
		33ºC	50ºC	55ºC	60ºC
$COD_{reduction}$ (%)	-	59	58	52	33
$TS_{reduction}$ (%)	-	42	48	41	41
$VS_{reduction}$ (%)	-	57	59	54	49
pH	6.2	7.3	7.8	7.2	7.15
Alkalinity (g/L)	1.6	3.5	3.9	6.1	4.3
E. Coli (NMP/g)	$6.0 \cdot 10^5$	$3.6 \cdot 10^2$	$1.2 \cdot 10^2$	$2.5 \cdot 10^2$	$3.2 \cdot 10^2$
Salmonella (NMP/g)	Presence	Presence	Presence	Sometimes	Sometimes
$COD_{soluble}$ (g/L)	3.6	3.5	6.8	7.2	11
$BOD_{5\ soluble}$ (g/L)	0.7	0.4	1.4	4.6	5.7
$TOC_{soluble}$ (g/L)	1.7	0.4	1.0	4.4	4.9
$TC_{soluble}$ (g/L)	3.4	2.0	3.0	5.1	6.7
Total $Phosphorous_{soluble}$ (mg/L)	100	48	42	180	130
Ammonical and organic $N_{2\ soluble}$ (g/L)	0.2	1.0	1.4	1.6	1.6
Conductivity (mS/cm 20ºC)	2.7	6.8	8.2	8.8	14
VFA (g eq Acetic/L)	3.0	1.2	4.1	4.2	6.6
Biogas composition ($\%CH_4$)[#]	-	76	73	79	72
Biogas production (STP L/kg $VS_{destroyed}$)	-	712	197	935	36

[#] normalized composition

The values presented in table 5.2 are an average of approximately one month at stable conditions. The reactors were considered stable approximately between two and three HRT, and when COD, TS and VS values were maintained constant.

Considering the elimination of organic matter present in the sludge, expressed either in terms of homogeneous COD elimination or VS removal, it can be seen that there is not a significant improvement in thermophilic temperatures over mesophilic condition, around 52-59% of COD removal and 54-69% of VS removal is observed in all reactors, except for 60ºC,

where organic efficiency is much lower, only 33% and 49% of COD and VS removal respectively. Total solids removal was measured to be around 41-48%, no effect is observed at the different temperature digestions

In view of the pH, it can be observed that in general thermophilic digestion is slightly more alkali than mesophilic, except for 60ºC. In this latter case, the more acidic value and the lower biogas production indicates that methanogenic bacteria seem to be inhibited. As a consequence, the reactor undergoes an accumulation of VFA and consequently a decrease in pH is expected. VFA content corroborates that at 60ºC the concentration is higher, however pH value is not as lower as can be expected; probably the high intrinsic alkalinity in the reactor smoothes the pH change by buffering the system.

Regarding the sludge analysis of the supernatant composition of the sludge, the quantity of organic matter is much higher in thermophilic than in mesophilic temperature, as $COD_{soluble}$ and $TOC_{soluble}$ indicates, from values of 3.5 and 0.4 g/L respectively for 33ºC, at thermophilic temperatures they raise a minimum of two times those values. Also biodegradability of the liquid part of the sludge increases, from a BOD_5 of 3.5 g/L for mesophilic digestion it enhances up to 6.8 g/L for 50ºC and the maximum is obtained at 60ºC being 11 g/L. It seems that hydrolytic and acetogenic bacteria are more active at higher temperatures, or that methanogenic microorganisms are less effective.

The maximum biogas production is observed at 55ºC, 935 STP L/kg $VS_{destroyed}$, 30% of improvement if compared with mesophilic. In this line, some authors have also reported this improvement in thermophilic biogas production (Zábranská et al. 2000, De la Rubia et al. 2006). At 60ºC, the lower biogas production 36 STP L/kg $VS_{destroyed}$ seems to suggest that methanogens are not very effective, despite the high values of VFA (6.6 g eq Acetic/L), indicating that acidogenesis takes place.

Pathogenic content of *E-coli* and *Salmonella* have not been good enough to obtain class A biosolids at any of the conditions studied. All reactors have accomplish *E-Coli* conditions (less than 1000 MNP), but concerning *Salmonella*, only 55ºC and 60ºC in two of 5 analysis have not been found any colony. More strong operational conditions are needed in order to assure sanitary conditions for fertilise use.

Conductivity also increases with temperature, probably because of the different ionic components produced in the degradation of the organic matter during the digestion, like hydroxides, carbonates, bicarbonates, phosphates, calcium ions, magnesium ions, ammonia, ammonium, nitrites, nitrates, acids, sulphates, etc.

Overall, only thermophilic digestion at 55ºC compares well with mesophilic conditions in terms of biogas produced per unit of VS eliminated, from 712 STP L/kg $VS_{destroyed}$ at 33ºC to 935 STP L/kg $VS_{destroyed}$ at 55ºC. Neither

thermophilic digestion at 50ºC (with a biogas production of 197 STP L/kg $VS_{destroyed}$) nor at 60ºC (biogas production of 36 STP L/kg $VS_{destroyed}$) reach biogas productivity better than in mesophillic conditions. Probably, the population of thermophiles is not large enough at 50ºC or 60ºC, or these temperatures are too low or too high for this type of bacteria. Therefore, it is evidenced that 55ºC is the best temperature for thermophilic digestion as it yields high biogas production and advantageous quality in terms of methane content, around 79% of methane is found in the biogas, enough quality for convert the biogas into energy. Methane quality of biogas produced in mesophlic digestion is also of good quality, around 76%, was measured, and comparable content is given by 50ºC and 60ºC, with 73% and 72% respectively.

5.2.3. Effect on HRT

In contrast to the acclimatising time needed to obtain stabilised sludge when changing temperature conditions, the effect when HRT time is modified is not so intense. As example, figures 5.17-5.25 present the temporary evolution of several monitored parameters at the thermophilic temperature of 50ºC when changing from an HRT time of 20 days into 15 days. As seen there, it is not a significant change within these values.

In tables 5.3 and 5.4, are presented the results of different HRT, for mesophilic temperature of 33ºC and thermophilic temperature of 50ºC respectively.

No noticeable COD removal differences were observed during the operation period of the different HRT of 15, 20 and 25 days neither in mesophilic nor in thermophilic range, around 55-59% of COD removal was obtained at 33ºC and for 50ºC it was between 56-59%.

Nonetheless, concerning solids reductions, it can be noted a slightly difference specially if HRT = 15 days and 20 days are compared, less HRT leads to less material removed at both temperatures. At 33ºC and HRT=15 days, TS reduction is 44% and, at HRT=20 days, it increases up to 57%, similar tendency is noticed at 55ºC where from 33% of TS removal at HRT=15 days rises to 59%. Likewise, VS reduction at the mesophilic reactor and HRT= 15days, VS removal is 44% and at HRT=20 days is 57%, and for the thermophilic reactor from 44% at HRT=15 days, increases to 59% at HRT=20 days.

Pathogenic removal improves as HRT increases, at HRT=15 days mean *E-coli* population was measured to be 630 NMP/g, at HRT=20 days was 360 NMP/g except for the highest HRT of 25 days, where was measured to

be 1800 NMP/g. It was expected that pathogenic destruction should increase as HRT increases since bacteria stay for more time at high temperature and less amount of microorganisms to be destructed are added, however values measured for the HRT of 25 days do not show this tendency. This may be explained because the concentration of *E-coli* of the feed raw sludge of that period was much higher in comparison, 8300000 NPM/g during that period, and between 171000-723000 NPM/g in the rest. Anyway, Class A biosolids are not obtained, since some reactors still present *Salmonella* population

Biogas production increased with the decrease of HRT except for the HRT of 20 days. Since more organic loading rate is added into the reactor at lower HRT, more absolute VS is removed (de la Rubia et al. 2006) so more biogas is produced. Probably, to elucidate clearly the effect on HRT, a more stable feed is needed, as in this lab-scale reactor the changing inputs may affect the results of the digestion more than those produced by the changes in HRT. Methane composition is in all cases good enough for co-generation use as energy producer.

Neither pH nor alkalinity is affected by the HRT in mesophilic or thermophilic temperatures. Normal values are measured in all HRT, a mean pH around 7.4 and alkalinity in the range 3.5-4.1 g/L for 33 ºC and a pH of 7.9 and an alkalinity of 3.9-5.21 g/ for 50ºC.

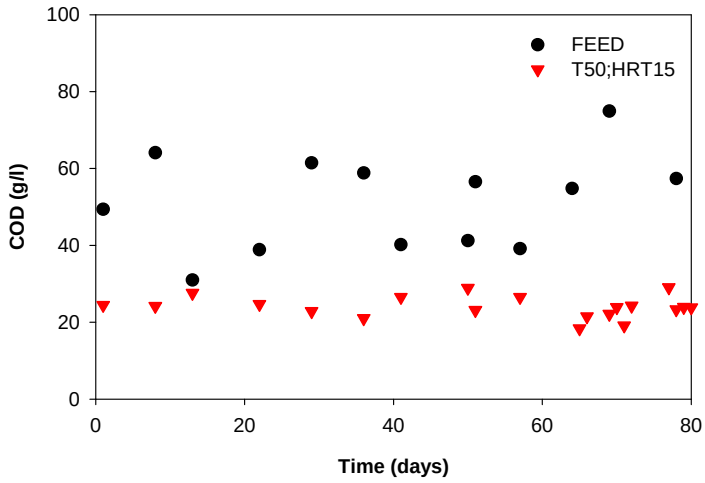

Figure 5.12. Evolution of COD in the acclimatization from HRT of 20 to 15 days at T=50ºC

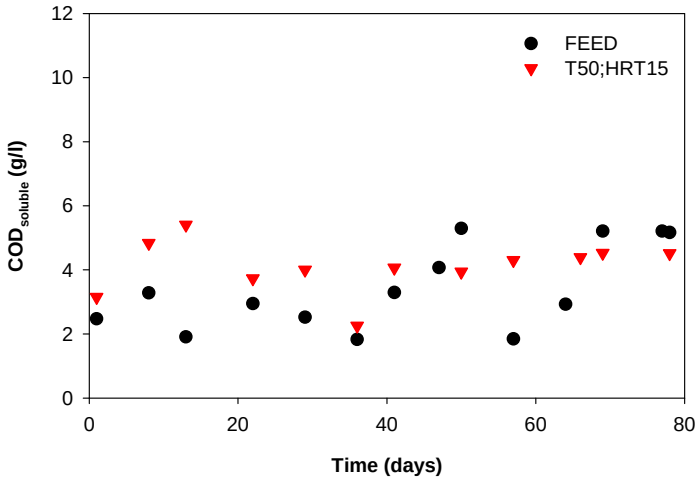

Figure 5.13. Evolution of soluble COD in the acclimatization from HRT of 20 to 15 days at T=50ºC

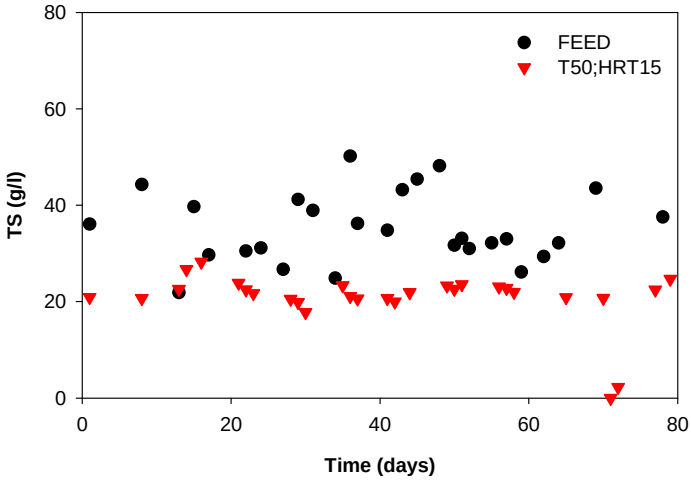

Figure 5.14. Evolution of TS in the acclimatization from HRT of 20 to 15 days at T=50ºC

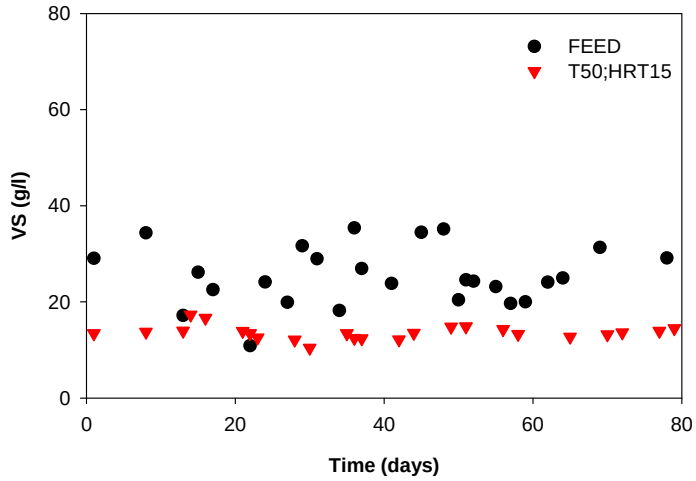

Figure 5.15. Evolution of VS in the acclimatization from HRT of 20 to 15 days at T=50ºC

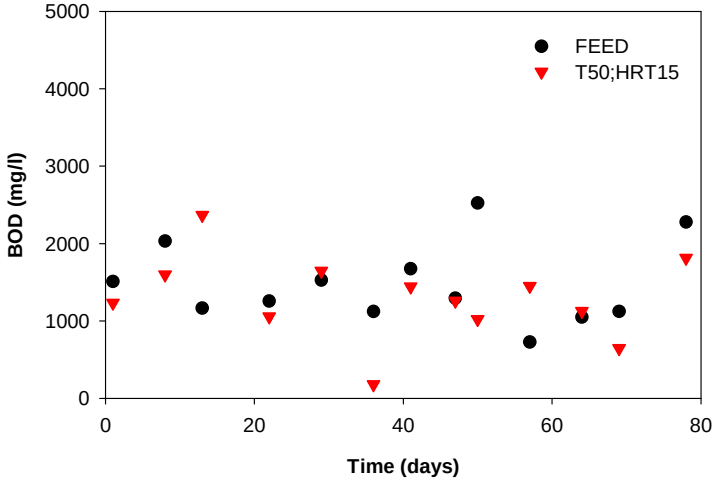

Figure 5.16 Evolution of BOD in the acclimatization from HRT of 20 to 15 days at T=50ºC

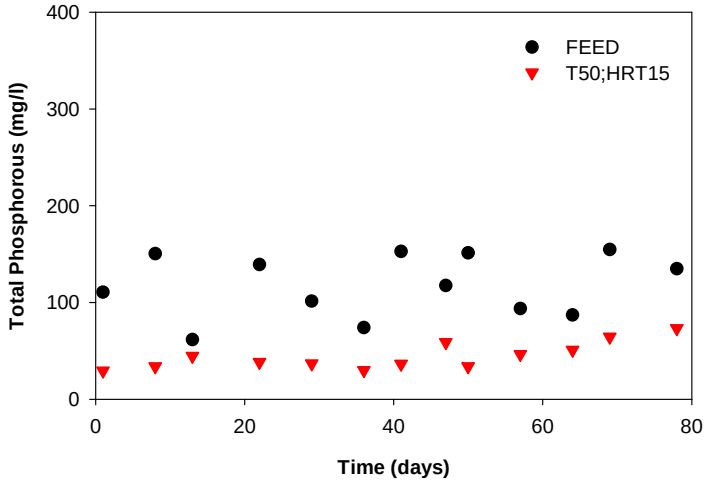

Figure 5.17. Evolution of Total Phosphorous in the acclimatization from HRT of 20 to 15 days at T=50ºC

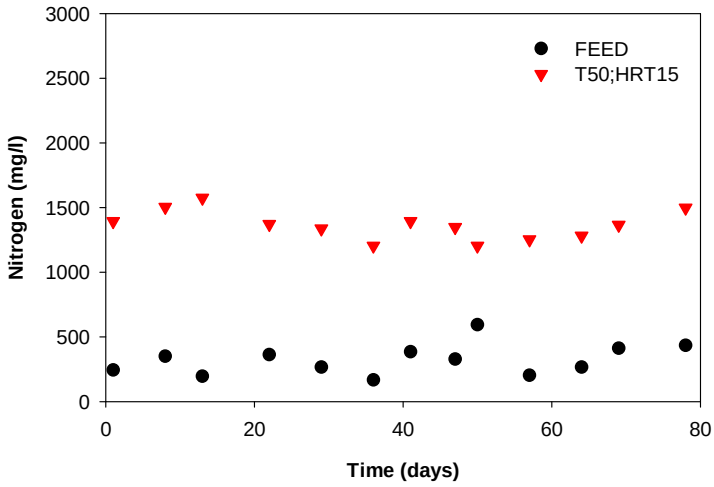

Figure 5.18. Evolution of Nitrogen in the acclimatization from HRT of 20 to 15 days at T=50ºC

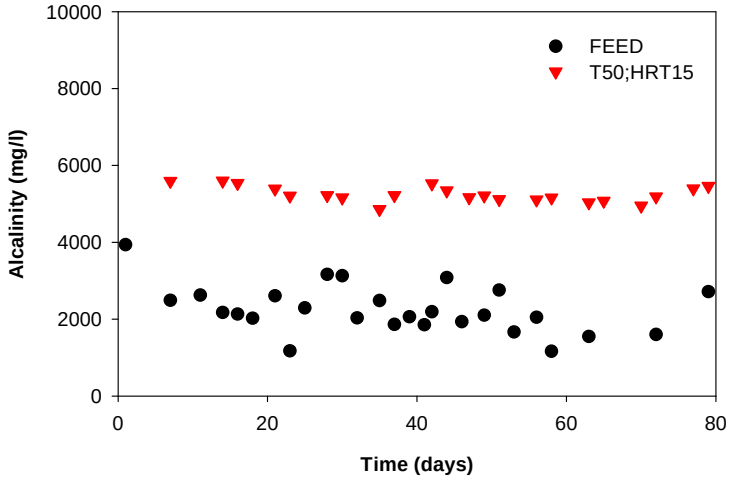

Figure 5.19. Evolution of Alkalinity in the acclimatization from HRT of 20 to 15 days at T=50ºC

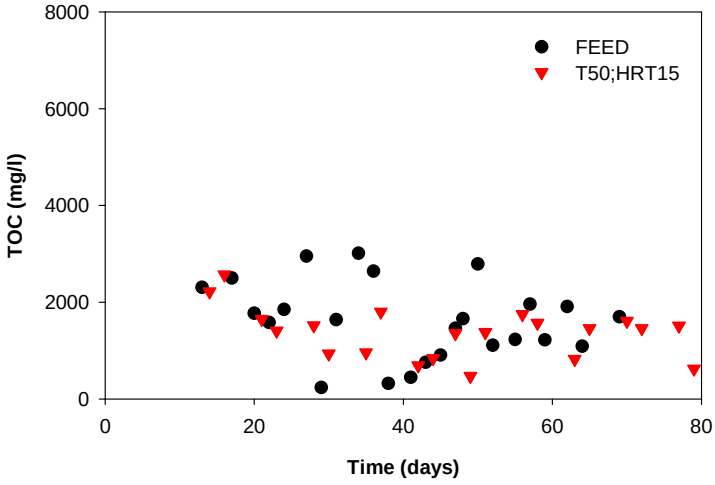

Figure 5.20. Evolution of soluble TOC in the acclimatization from HRT of 20 to 15 days at T=50ºC

Table 5.2. Effect of the HRT in anaerobic digestion at mesophilic temperature of 33ºC

PARAMETER	HYDRAULIC RETENTION TIME		
	15 days	20 days	25 days
$COD_{reduction}$ (%)	58	59	55
$TS_{reduction}$ (%)	33	42	37
$VS_{reduction}$ (%)	44	57	53
pH	7.4	7.3	7.5
Alkalinity (g/L)	4.1	3.5	3.9
E. Coli (NMP/g)	$6.3 \cdot 10^2$	$3.6 \cdot 10^2$	$1.8 \cdot 10^3$
Salmonella (NMP/g)	Presence	Sometimes	Sometimes
$COD_{soluble}$ (g/L)	2.0	3.5	4.1
$BOD_{5\ soluble}$ (mg/L)	310	420	370
$TOC_{soluble}$ (mg/L)	580	430	360
$TC_{soluble}$ (g/L)	1.4	2.0	1.0
Total $Phosphorous_{soluble}$ (mg/L)	68	48	32
Ammonical and organic $N_{2\ soluble}$ (g/L)	1.0	1.0	0.9
Conductivity (mS/cm 20ºC)	7.0	6.8	6.1
VFA (g eq Acetic/L)	1.1	1.2	1.0
Biogas composition ($\%CH_4$)[#]	76	75	82
Biogas production (STP L/kg $VS_{removed}$)	1978	712	1603

[#] normalized composition

Table 5.3. Effect of the HRT in anaerobic digestion at thermophilic temperature of 50ºC

PARAMETER	HYDRAULIC RETENTION TIME		
	15 days	20 days	25 days
$COD_{reduction}$ (%)	59	58	56
$TS_{reduction}$ (%)	33	48	35
$VS_{reduction}$ (%)	44	59	52
pH	7.9	7.8	8.0
Alkalinity (g/L)	5.2	3.9	5.2
E. Coli (NMP/g)	280	120	740
Salmonella (NMP/g)	Sometimes	Presence	Sometimes
$COD_{soluble}$ (g/L)	5.3	6.8	4.2
$BOD_{5\ soluble}$ (g/L)	1.3	1.4	1.4
$TOC_{soluble}$ (g/L)	1.4	1.0	1.1

$TC_{soluble}$ (g/L)	3.2	4.1	3.6
Total $Phosphorous_{soluble}$ (mg/L)	59	42	33
Ammonical and organic $N_{2\ soluble}$ (g/L)	1.3	1.4	1.4
Conductivity (mS/cm 20ºC)	7.9	8.1	8.2
VFA (g eq Acetic Ac./L)	4.3	4.9	5.0
Biogas composition ($\%CH_4$)#	76	73	83
Biogas production (STP L/kg $VS_{removed}$)	1464	197	1086

normalized composition

5.2.4. Dual treatment, thermo phased thermophilic (55ºC) - mesophilic (33ºC) anaerobic reactor

It was also studied the anaerobic performance in a dual stage digestion consisting in an acidogenic step operating at the thermophilic temperature of 55ºC with an HRT = 5 days, followed by an enhanced methanogenic stage at the mesophilic temperature of 33ºC and an HRT = 15 days.

Figures 5.26-5.33 depict the evolution of several parameters of both steps to reach stable conditions. Figure 5.26 presents the evolution of the homogeneous COD. Results indicate that the first thermophilic reactor is more sensitive to the organic loading rate changes; instead, the second step reactor practically is not affected by changes. In the same way, evolution of TS and VS presented in figures 5.27 and 5.28 shows the same tendency.

If the evolution of soluble COD is analysed, figure 5.29, one can observe that in the first reactor, thermophlic, the concentration of soluble organic matter raises reaching a value of 11 g/L, whereas in the second reactor, mesophilic, the soluble organic content is very low 0.6 g/L. Higher values of organic matter in the first step reactor may be due the higher solubilisation rates obtained when working in thermophilic environment, and the high increase of the VFA concentration up to 6.8 g eq Acetic/L, as figure 5.32 shows. This high VFA concentration indicates that the acidogenic step is actually achieved in the first thermophilic step.

Inspecting results from the second stage, one can see that the effluent has very low content in soluble organic matter, and no presence of VFA was detected, which results in less odour problems and produces a high-quality stable final effluent, as usually this liquid part of the solid is again re-introduced in the water depuration system.

Data of pH showed in figure 5.30 is practically constant during the period of acclimatation, being for the termophilic first step around 7.3 and for the

mesophilc step 7.6. It is reported that pH range of 4.0-6.5 is the optimum for the acid formation step in the first part of a two phase configuration, while a pH range of 6.5 to 8.2 is the best for the subsequent methane production phase (Speecy 1996). However, the continuous high alkalinity in both reactors 3.6 g/L, presented in figure 5.31, especially in the acidogenic one seems to buffer this acidic pH tendency and prevents the reactor from a pH drop due to the formation of organic acids.

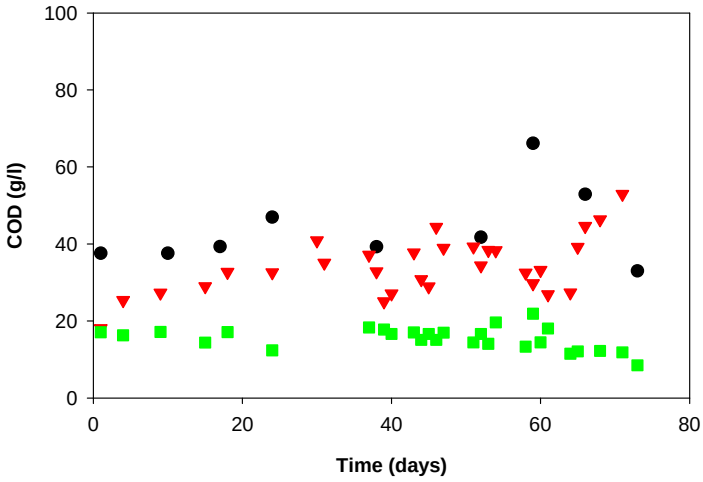

Figure 5.21. Evolution of COD in the acclimatization into dual system thermo-meso anaerobic digestion

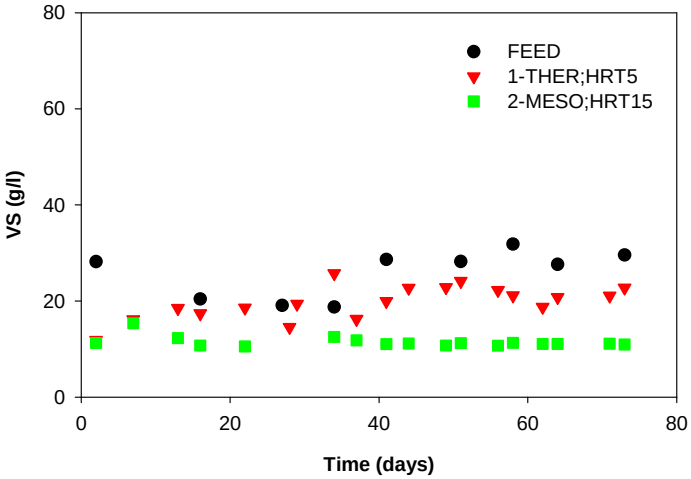

Figure 5.22. Evolution of the VS in the acclimatization into dual system thermo-meso anaerobic digestion

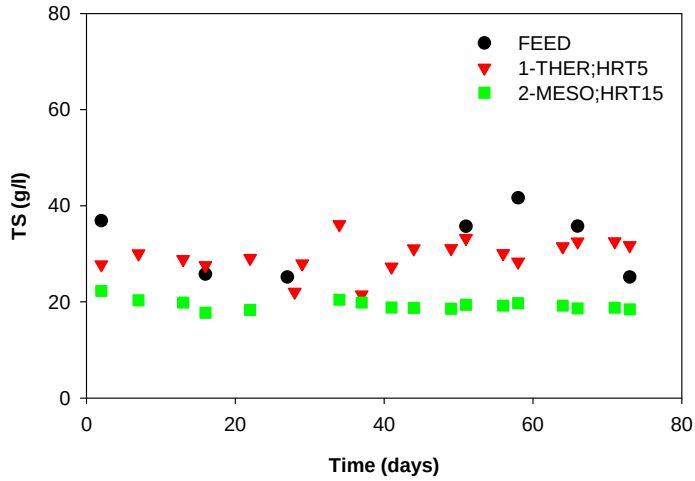

Figure 5.23. Evolution of the TS in the acclimatization into dual system thermo-meso anaerobic digestion

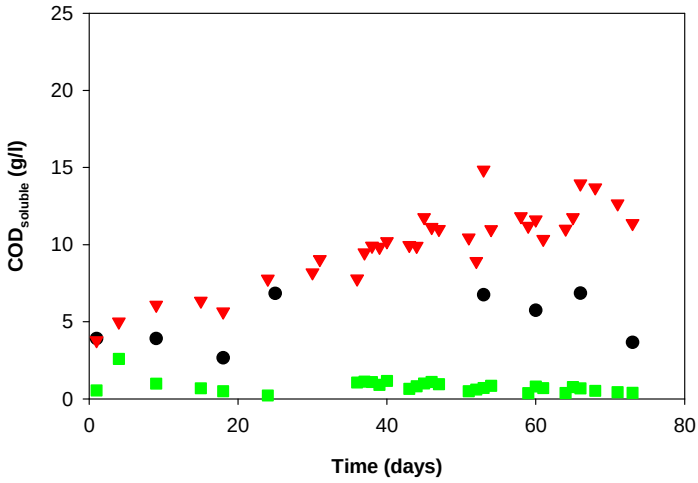

Figure 5.24. Evolution of soluble COD in the acclimatization into dual system thermo-meso anaerobic digestion

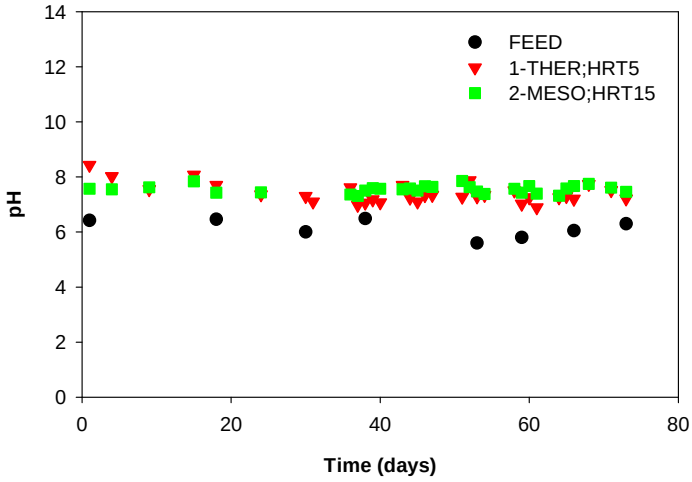

Figure 5.25.Evolution of pH in the acclimatization into dual system thermo-meso anaerobic digestion

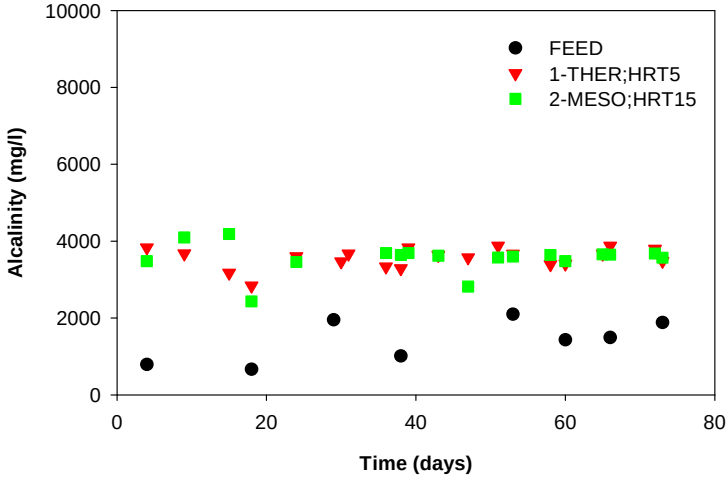

Figure 5.26.Evolution of the alkalinity in the acclimatization into dual system thermo-meso anaerobic digestion

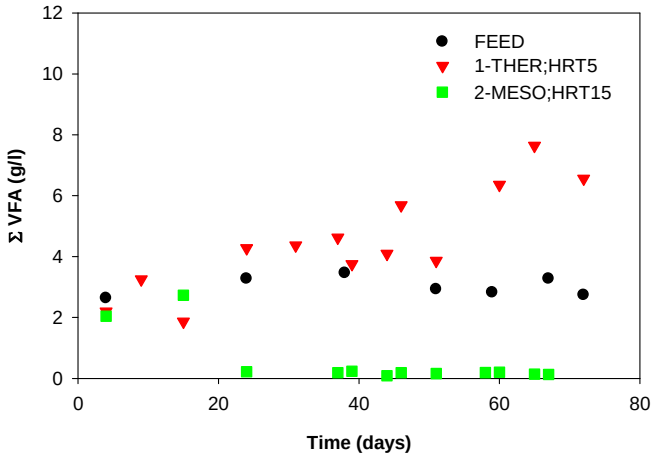

Figure 5.27 Evolution of the VFA in the acclimatization into dual system thermo-meso anaerobic digestion

Individual VFA was also evaluated; figure 5.33 exhibits the evolution of acetic, propionic, n-butyric, i-butyric, i-valeric and n-valeric acid. All individual VFA concentrations increase in the first stage of the dual digestion, except acetic acid that remains close to the values as the thermophilic single stage reactor. At the final of the dual stage (mesophilic step) all individual VFA considerably decrease in the final effluent. It was measured 57 mg/L of acetic acid, 32 mg/L of butyric acid, 10 mg/L of n-butyric acid and finally 36 mg/L of i-butyric acid, valeric acid was not detected.

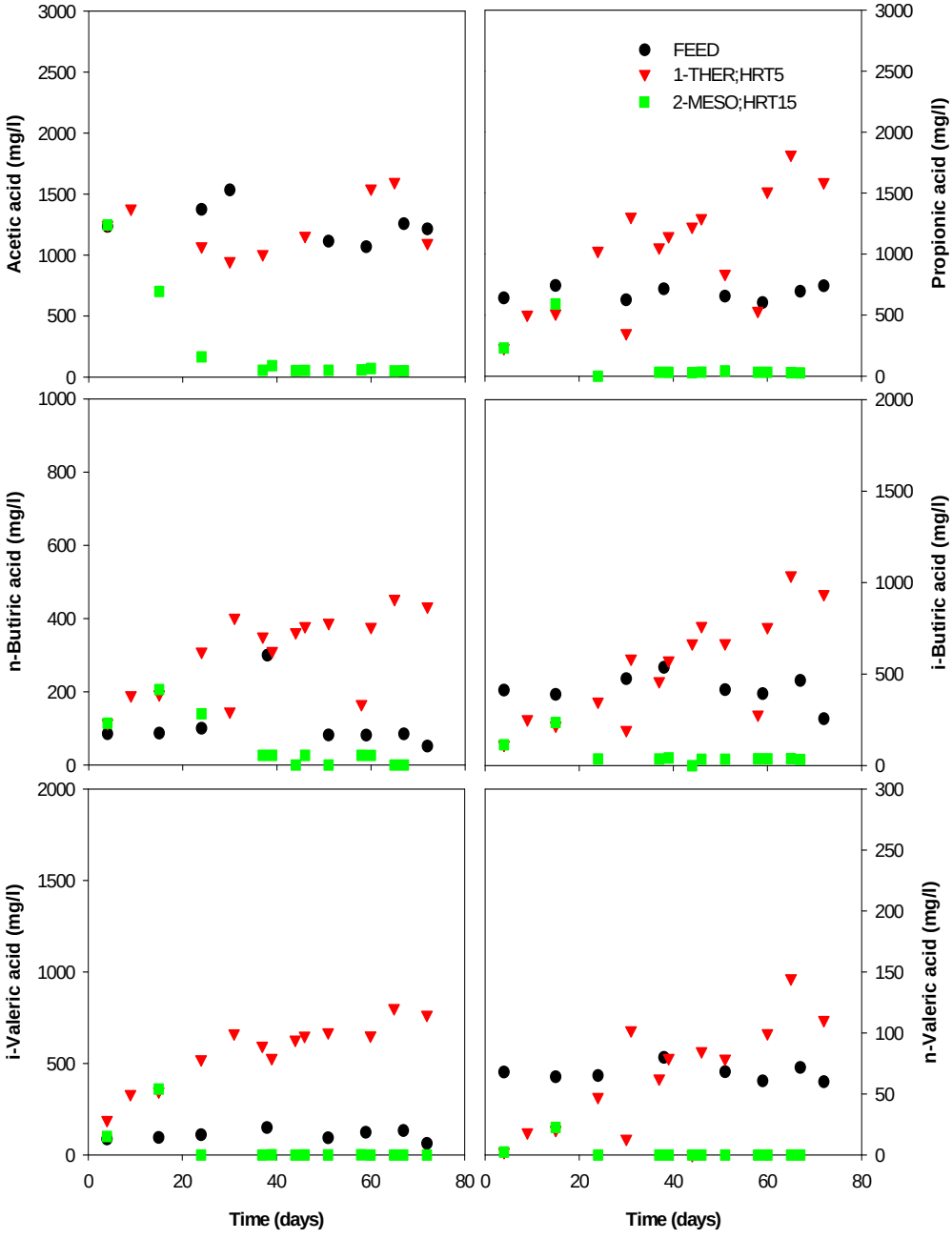

Figure 5.28.Evolution of individual VFA in the acclimatization into dual system thermo-meso anaerobic digestion

Table 5.5 shows the results at steady state of TPAD system thermophilic-mesophilic with an HRT of 5/15 days compared to single thermophilic and mesophilic at HRT of 20 days. The results from the dual digestion are presented in two columns, the first corresponds to the thermophilic step, 1-THER-55. The second column corresponds to the results of the overall dual process, after the mesophilic step, indicated as 2-MESO-33.

The best results were obtained at TPAD systems. They showed better performance in terms of COD, TS and VS destruction, 66%, 48% and 63% respectively. Process stability is highly enhanced as the final effluent has much lower soluble organic matter; around 600 mg/L of soluble COD is found in the final effluent whereas in mesophilic and thermophilic single stage is almost 6 times and 12 times higher respectively. Furthermore, the low VFA amount brings the opportunity of minimizing odour problems in the final effluent. Only the TPAD seems to be efficient enough to obtain Class A biosolids, *E-coli* population after the dual digestion was measured to be 150 NPM/g, and null presence of *Salmonella*. However, this result must be taken with care as the analysis of the pathogens in the dual digestion could be made only once, while results from single anaerobic digestion corresponds to an average of a minimum of 4 different sample measurements.

These results are in line with some other studies with comparable operational conditions. It is reported the obtention of class A biosolids, and 61% of VS reduction for a semi-continuous thermophilic 2 days - mesophilic 10 days dual system of a mixture sludge 60/40 PS-WAS (Huyard et al. 2000). Other authors report 52% in VS reduction (Riau et al. 2010) in batch mode in thermophilic 6 day-mesophilic 15 day and also pathogen reduction into class A biosolids.

Biogas production in the acidogenic stage was not completely eliminated 313 STP L/kg $VS_{destroyed}$; however methane content is very poor, only 48% of methane was measured. Thus, this first acidogenic stage could still be operated at lower HRT such as between 2 h–2 days, which is reported to almost eliminate the production of biogas, as methanogens find difficulties to proliferate (Speecy 1996). Nonetheless, Riau et al. 2010, Cheunbarn and Pagilla 2000 and Han et al. 1997 report that for eliminating more pathogens higher retention times (more than 4 days) should be used. Overall, biogas production is slightly lower than in the single stage thermophilic reactor but higher than for mesophilic. For the dual digestion, it is obtained 692 STP L/kg $VS_{destroyed,}$ whereas for mesophilic digestion at HRT=20 days, it is 647 STP L/kg $VS_{destroyed,}$ and for thermophilic is 857 STP L/kg $VS_{destroyed}$.

Table 5.4. Anaerobic performance of dual thermophilic-mesophilic process

PARAMETER	DUAL DIGESTION		SINGLE	SINGLE
	1-THER-55 5 days	2-MESO-33 15 days	MESO-33 20 days	THER-55 20days
$COD_{reduction}$ (%)	24	66	59	52
$TS_{reduction}$ (%)	19	48	42	41
$VS_{reduction}$ (%)	24	63	57	54
$COD_{soluble}$ (g/L)	11	0.6	3.5	7.2
pH	7.3	7.6	7.3	7.8
Alkalinity (g/L)	3.6	3.6	3.5	6.1
E. Coli (NMP/g)	280	150	362	252
Salmonella (NMP/g)	NP	NP	Presence	Sometimes
VFA (g/l)	0.8	nd	1.20	4.2
Biogas composition ($\%CH_4$)[#]	48	73	76	79
Biogas production (STP L/kg $VS_{destroyed}$)	313	(378)[§] 692	647	857

[#] normalized composition.
[§] biogas production of the single reactor

5.2.5. Anaerobic digestion of pre-treated sludge at mesophlic (33ºC), and thermophilic (50 and 55ºC) conditions in a semi-continuous reactors mode

5.2.5.1. Hydrolysis evaluation of the feed

The aim of this section was to evaluate the auto-hydrolysis capacity of the different sludges used to feed the semi-continuous reactors: raw sludge, thermal pre-treated sludge at 80ºC during 1 h and peroxidated sludge pre-treated with 0.2 g H_2O_2/g COD at 30ºC. The auto-hydolysis was evaluated at 4ºC, 50ºC and 55ºC, which are the storage temperature and the two different temperatures in the anaerobic reactor. Results are presented in figure 5.34. Soluble TOC measurements were performed at room temperature.

In this case, hydrolysis was evaluated using soluble TOC, as this parameter indicates the quantity of organic matter present in the soluble part, so if

auto-hydrolytic bacteria are present they might solubilize this organic material.

Concerning to the sludge kept at 4ºC, a general tendency can be drawn. Thus, no significant change in soluble TOC was seen during the 5 day analysis test. However, if longer periods are tested (>15 days) soluble organic matter may increase, up to 2 times the initial value.

If the sludge is kept at 50 and 55ºC, solubilisation TOC slightly increases reaching 27% and 11% for raw sludge, respectively Although the increment at 50ºC is higher, the maximum soluble TOC is measured at 55ºC where, 4.8 g/L is obtained. For thermal pre-treated sludge no influence was observed at 50ºC, but an increment of the solubilisation of 27% at 55ºC. Concerning peroxidated sludge increments of 16% and 10% of solubilisation where obtained at 50ºC and 55ºC, respectively.

The increment is progressive day to day, so this may indicates the presence of auto-hydrolytic bacteria that have been released and are operative solubilising material, especially at 50ºC and 55ºC.

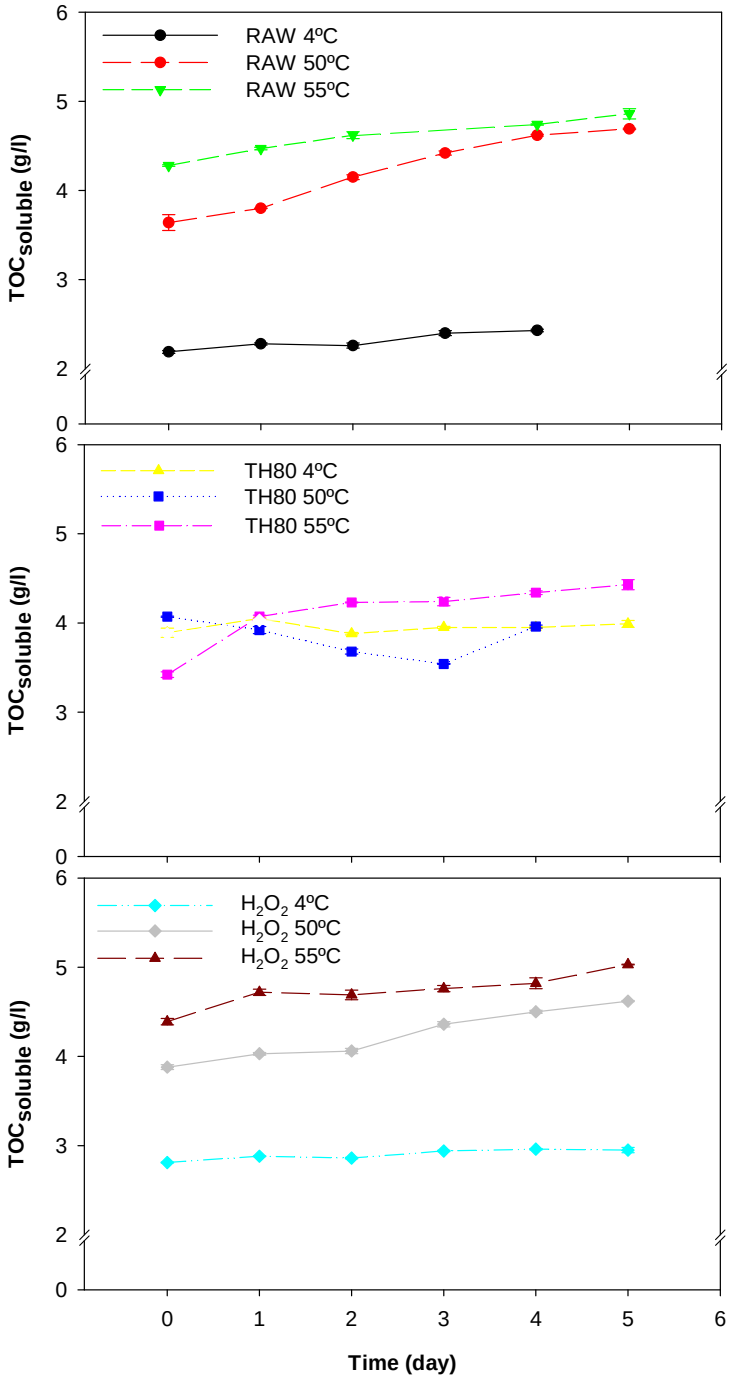

Figure 5.29. Auto-hydrolysis capacity of different feed sludge

5.2.5.2. Thermophilic Anaerobic digestion of pre-treated sludge in semi-continuous reactor

This section shows the results obtained for the anaerobic digestion in a semi-continuous reactor. It was studied the effect of the thermal pre-treatment at 80ºC for 1 h and also the effect of the chemical pre-treatment with hydrogen peroxide at a dose of 0.2 g H_2O_2/g COD at 30ºC in combination with the anaerobic digestion at three different temperatures, 33ºC (mesophilic range), and two different thermophilic temperatures 50ºC and 55ºC with an hydraulic retention time set at 20 days.

Figure 5.35 depicts the evolution of the homogeneous COD of the sludge at the conditions studied. As it can be seen, concerning thermal pre-treatment, 40 days were necessary to acclimate the digester at the new feed conditions, starting from raw sludge alone (without any pre-treatment) until only thermal pre-treated sludge. This period owns to change in the composition of the dissolved fraction of the sludge, as pre-treated sludge has more organic matter solubilised than sludge without pre-treatment. This is not observed in the subsequent change from thermal to peroxidised pre-treated sludge because now there was no drastic change in the characteristics of the influent.

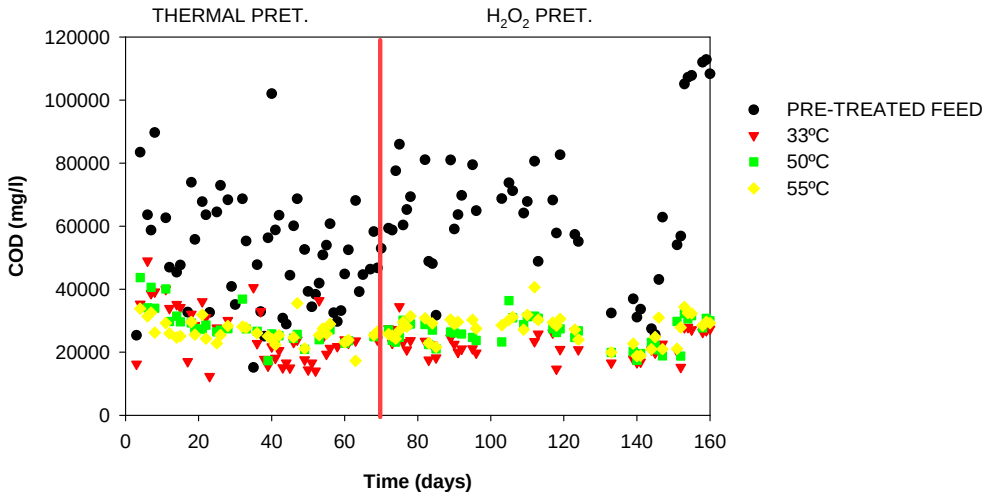

Figure 5.30. *Evolution of the homogeneous COD in the semi-continuous anaerobic digestion of pre-treated sludge at a HRT=20dys.*

In figure 5.36, the data of the total solids and volatile solids for the different reactors are presented. Total solids and volatile solids reduction in the

reactors is similar for the three temperature conditions. However, sludge pre-treated with hydrogen peroxide shows poorer results when compared with thermal pre-treatment and sludge without pre-treatment.

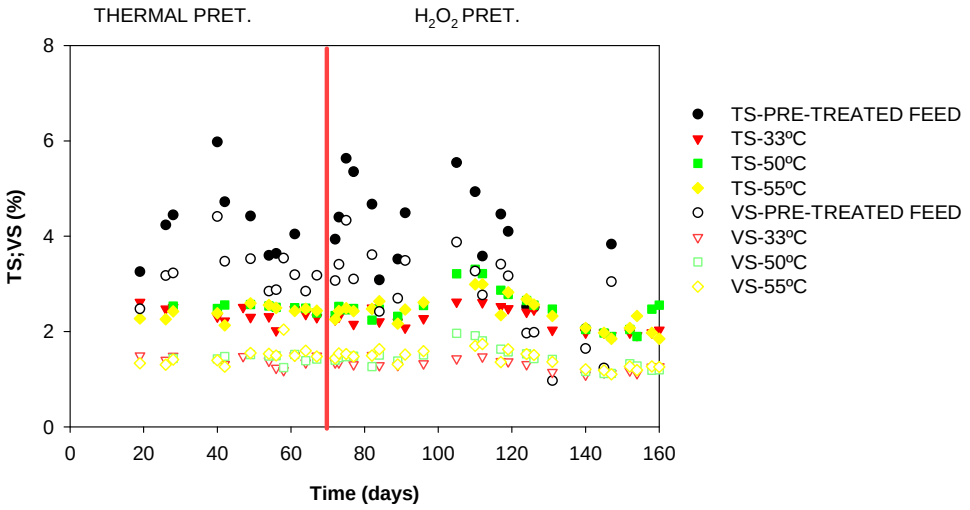

Figure 5.31. Evolution of the TS and VS in the semi-continuous anaerobic digestion of pre-treated sludge at a HRT=20days.

Table 5.6 summarises the results of the main parameters in the anaerobic digestion for the three types of feed studied: sludge without pre-treatment, sludge thermally pre-treated and chemically pre-treated.

It has not been seen a positive effect, in terms of COD, TS or VS removal, on the anaerobic digestion of thermal pretreated sludge over digestion of sludge without pretreatment neither in mesophilic or thermophilic range, values around 60% for COD removal at 33ºC, 59% at 50ºC and 59% for 55ºC were obtained. Values for TS removal were, 45% at 33ºC, 45% at 50ºC and 43% at 55ºC, and finally for VS removal 59% at 33ºC, 58% at 50ºC and 55% at 55ºC. However when peroxidated sludge is feed, the TS and VS removal tended to decrease at all the temperatures tested, from 42% for raw sludge it reduces up to 26% with pretreated sludge at 33ºC, at 50ºC from 48% it lowers to 26%, and for 55ºC from 41% to 24%. Similar tendency is seen in VS removal.

Regarding to soluble matter of the final digested sludge, it can be said that both thermal and sludge treated with H_2O_2 produce more stable effluent as soluble COD, soluble TOC and soluble BOD_5, are much lower for pre-treated sludge than for sludge without treatment at all temperatures tested. For instance, soluble COD at 33ºC is 3.5 g/L for sludge without treatment, and 2.8 g/L for thermal pretreatment, and 0.7 g/L for H_2O_2 pre-treatment. At 55ºC soluble COD for sludge without pretreatment is 16 g/L, whereas it is

only 4.2 g/L for thermally pretreated sludge and 3.8 g/L for peroxidated sludge.

The pre-treatments seem to enhance the biogas production, especially in mesophilic range, where 60% and 52% of increase is seen when thermally and peroxidated sludge is fed respectively. From a biogas production of 706 STP L/kg $VS_{destroyed}$ at 33ºC it raises to 1127 STP L/kg $VS_{destroyed}$ for thermal pretreatment and to 1073 STP L/kg $VS_{destroyed}$ for H_2O_2 pretreatment.. In the thermophilic range of 55ºC biogas increment is more moderate, around 22% and 8% for thermal and peroxidated sludge, respectively. Methane content of the biogas is always higher than 68% being a high quality biogas for possible use in co-generation units.

Despite the presence of *Salmonella* was not detected in the sludge thermally pretreated at 80ºC, it seems that a reactivation of *Salmonella* occurred in the subsequent anaerobic digestion at all temperatures tested; however the analysis of the pathogens in the stationary stage of the experiment was made only once. E-coli population is only below class A biosolids for the thermophilic temperature of 55ºC. When peroxidated sludge is fed it is observed that class A biosolids are not attained at any condition, no presence of *Salmonella* was detected at 55ºC, but E-coli population was higher than the limits, $2.4 \cdot 10^3$ NPM/g. More frequency of analysess would be needed for assuring these results.

The maximum VS removal is obtained with the mesophilic anaerobic treatment of 33ºC of thermally pre-treated sludge at 80ºC, with 60% of VS removal, also biogas production is enhanced more than the other conditions tested, around 1127 STP L/kg $VS_{destroyed}$ is produced with a 69% of methane.

Nevertheless if pathogen content is also evaluated, the optimal conditions correspond to the thermophilic anaerobic digestion at 55ºC of the thermally pre-treated sludge where a VS, TS, and COD removal of 55%, 45% and 67% is obtained with a biogas production of 1138 STP L/kg $VS_{destroyed}$ with 72% of CH_4. Pathogen content of *E-coli* is below class A biosolids requirements, however despite the no presence of *Salmonella* in the sludge thermally pre-treated, *Salmonella* was indeed found in the final effluent. This may suggest that *Salmonella* was present in the thermophilic inoculum. One can think that, if a thermophilic inoculum free of *Salmonella* is used, this issue will be solved.

Table 5.5. Data for the anaerobic digestion in semi-continuous reactors for the three types of feed studied: sludge without pre-treatment, and sludge thermally or chemically pre-treated; HRT=20 day

Parameter	SLUDGE WITHOUT PRE-TREATMENT				SLUDGE PRE-TREATED AT 80ºC					SLUDGE PRE-TREATED WITH 0.2 g H_2O_2/g COD at 30ºC				
	Feed.	33ºC	50ºC	55ºC	Feed	Pre	33ºC	50ºC	55ºC	Feed	Pre	33ºC	50ºC	55ºC
COD removal (%)	---	59	58	52	---	---	61	59	67	---	---	65	60	59
TS removal (%)	---	42	48	41	---	---	48	43	45	---	---	26	26	24
VS removal (%)	---	57	59	54	---	---	60	57	55	---	---	47	46	44
pH	6.2	7.3	7.8	7.7	6.2	6.1	7.3	7.6	7.8	6.0	6.2	7.5	7.7	7.7
COD soluble (g/L)	3.6	3.5	6.8	16	3.4	7.9	2.8	3.7	4.2	3.5	6.7	0.7	3.1	3.8
TOC soluble (g/L)	1.7	0.4	1.0	4.4	n.a.	2.4	0.8	0.7	1.1	n.a.	2.5	0.2	7.4	1.1
$BOD_{5\ soluble}$ (g/L)	1.3	0.4	1.4	4.6	1.4	n.a.	0.1	0.9	1.3	1.3	3.2	0.1	1.2	1.5
Total $Phosphorous_{soluble}$ (mg/L)	$1.0x10^2$	48	42	$1.8x10^2$	83	n.a.	33	23	26	76	70	31	24	27
Ammonical and organic $N_{2\ soluble}$ (g/L)	0.2	1.0	1.4	1.6	0.3	n.a	1.1	1.0	1.2	0.3	0.6	1.1	1.0	1.3
Conductivity (µS/cm 20ºC)	$2.7x10^3$	$6.8x10^3$	$8.2x10^3$	$8.8x10^3$	$2.9x10^3$	n.a.	$7.7x10^3$	$6.7x10^3$	$7.2x10^3$	$2.5x10^3$	$4.2x10^3$	$7.1x10^3$	$6.2x10^3$	$6.9x10^3$
Methane (%CH_4)#	---	68	73	74	---	---	69	72	72.	---	---	69	74	71
Biogas production (STP L/kg $VS_{removed}$)	---	706	n.a.	935	---	---	1127	1120	1138	---	---	1073	1061	1007
Salmonella (NMP/g)	P	P	P	S	P	NP	P	P	P	P	P	P	P	NP
E.Coli (NMP/g)	$60x10^4$	$3.6x10^2$	$2.2x10^2$	$2.5x10^2$	n.a.-	$5.0x10^4$	$2.5x10^4$	$2.3x10^3$	$1.9x10^2$	n.a.	$2.0x10^4$	$2.4x10^3$	$2.4x10^3$	$2.4x10^3$

P = Presence; S = Sometimes; NP= No presence
# normalized composition

From the results obtained, it was made an economic study, already published in Torrens et al. (2011), where it can be founf in more detail. A brief resume of it is presented above.

The study was conducted for the municipal WWTP from Reus, which has a depuration capacity for a population of 200000 equivalent inhabitants and assesses the transformation of the current mesophilic digestion units into thermophilic conditions and the implementation of pre-treatments. The main hypothesis of the approach is that the WWTP is equipped with a cogeneration system to recover energy from biogas. The estimation has been done taking into account only the changes in volatile matter and the derived biogas production, but no the probable higher yield of biogas, thus taking a conservative option. The costs related to construction of the facilities are not considered, because the impacts are negligible in front of those from the daily operation. The calculation basis for the feed sludge volume to the digester is taken to be 100 m^3/day.

After the estimation of the expected savings conducted for the two recommended pre-treatments followed by thermophilic anaerobic digestion, in the case of chemical pre-treatment with hydrogen peroxide, the benefits of the higher amount of stabilised sludge accomplishing sanitary conditions and the larger power production from additional biogas are mostly offset by the high cost of the reagents, for which hydrogen peroxide is the main contributor. Only in case that hydrogen peroxide could be obtained at a much lower cost, this option would be interesting.

On the contrary, thermal pre-treatment at temperature below 110ºC for 1 h gives unitary costs of the stabilised sludge three times lower that without using any pre-treatment, because most of the stabilised sludge is now estimated that can be dedicated to agricultural use. The savings are calculated in approximately 1 € per equivalent inhabitant and year in comparison to the present cost for landfilling. As the re-engineering needed for existing plants in this case is minimum, these savings assure a very short payback period (2-4 years), even in case of overestimation of the benefits.

Therefore, the transformation of mesophilic units into thermophilic units adding a thermal pre-treatment (figure 5.32) at non severe conditions (<110ºC, 1 h) is economically viable as the higher operating costs are widely compensated by the increase of biogas production and the extended use of the stabilised sludge for agricultural land use. This option requires minimum re-engineering of the plants and is especially interesting for plants with power cogeneration units implemented. As for those, the savings can be estimated in 1 € per equivalent inhabitant and year, which must cover any investment needed with a payback period of less than four years, even when a cogeneration plant must be build up.

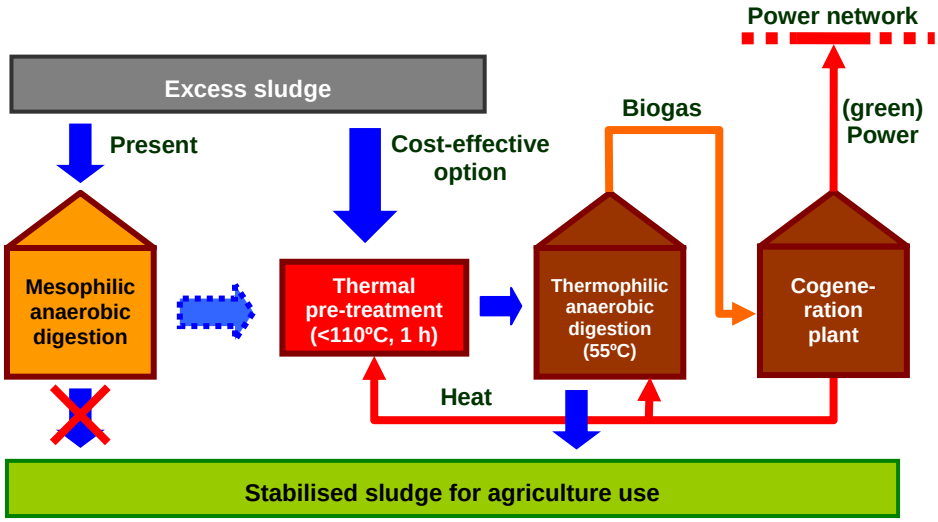

Figure 5.32. Re-engineering scheme proposed for the existing sludge mesophilic anaerobic digestion systems in WWTP.

5.2.5.3. Inoculum microbial activity tests

The objective of this section was to determine the quality of the thermophilic inoculum at 55ºC generated when feeding raw sludge, thermally pre-treated sludge at 80ºC and peroxidated sludge at 0.2 gH_2O_2/g COD.

The procedure followed is explained in Chapter 3, substrates tested were acetic acid for the determination of the acetoclastic methanogenic activity, propionic acid and butyric acid for the estimation of acetogenic activities, and finally glucose for hydrolytic activities and cellulose for cellulolytic activity (Angelidaki et al. 2009).

Figures 5.35-5.37 show the cumulative biogas production and individual VFA evolution for inoculum fed with raw sludge, which will be named IN-RW, figures 5.38-5.42 for inoculum fed with thermally pre-treated sludge IN-TH, and figures 5.43-48 for inoculum fed with sludge pre-treated with H_2O_2 IN-PX.

Methane potential of the different substrates is obtained by the hydrolysis rate constant determination, as it is the limiting step in the anaerobic conversion process. The hydrolysis constant (k_h) is determined assuming a first order hydrolysis model, following the equation 3.20 explained in Chapter 3.

The biomass was considered to be constant during the entire experiment since the theoretical increase in VS was too low compared to the initial VS concentrations. Therefore, the maximum specific substrate utilization rate (A_{max}) of the reactor was derived directly from k.

5.2.5.3.1. IN-RW, Thermophilic anaerobic inoculum feed with RAW SLUDGE

Endogenous biogas production of raw sludge inoculum (figure 5.35) is much higher than inoculum obtained with pre-treated sludge feeding (figures 5.38 and 5.43). This could indicate that the final effluent is much more stabilised when the sludge is pre-treated. As seen in figure 5.35, where biogas production of IN-RW (feed with raw sludge) is presented, biogas production is very high if compared with the endogenous production of the others inoculums acclimatized with the pre-treatment. In this case, endogenous production of the innoculum feed with raw sludge is more than 80 ml. whereas in the other inocolums feed with pretreated sludge is around 40 ml. A too high endogenous biogas production can blur the results of inoculum. Methanogenic activity results concerning raw sludge are presented in table 5.7.

During the degradation of the different substrates (cellulose, glucose, propionic acid, n-butyric acid, and acetic acid) tested in IN-RW, figures 5.34 to 5.37, acetic acid was found in all reactors. It can be observed the evolution of acetic acid in figure 5.33 at the different feed substances. Surprisingly, when glucose and n-butyric acid are the substrates, acetic acid concentration raises after incubation period of 24 h and 48 h, respectively.

Moreover, i-valeric acid also seems to be generated when acetic acid is anaerobically degraded, as figure 5.37 indicates. However, this observation must be taken with care, as i-valeric concentration value is near the low detection limit of the analysis, which is 20 mg/L.

Acetic, propionic and n-butyric acid where clearly degraded as figures 5.34, 5.35 and 5.36 evidence respectively. No n-valeric or i-butyric acid were detected in any of the reactors tested,

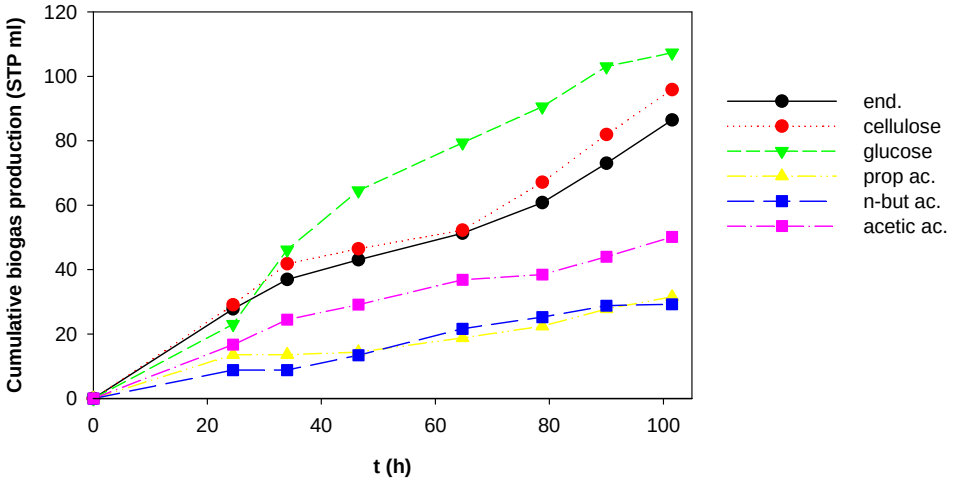

Figure 5.33. Cumulative biogas production in the activity tests of the semi-CSTR thermophilic anaerobic sludge reactor acclimatised with raw sludge (no pre-treatment) (HRT=20days) of the different substrates fed

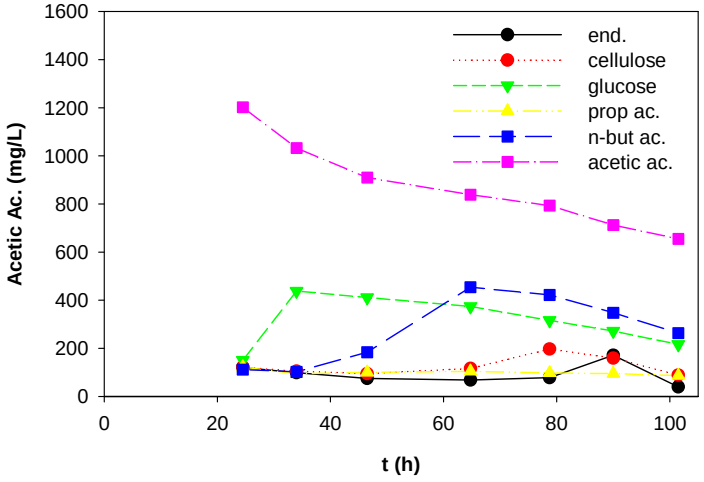

Figure 5.34. Evolution of acetic acid concentration in the activity test of the semi-CSTR thermophilic anaerobic sludge reactor acclimatised with raw sludge (no pre-treatment) (HRT=20days) of different substrates fed.

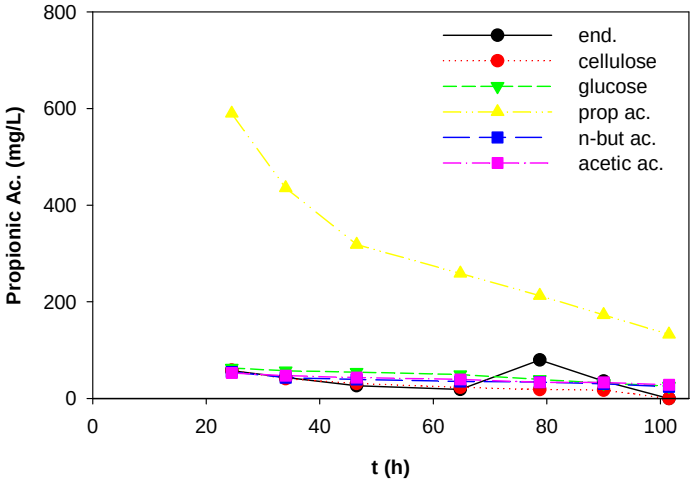

Figure 5.35. Evolution of propionic acid concentration in the activity test of the semi-CSTR thermophilic anaerobic sludge reactor acclimatised with raw sludge (no pre-treatment) (HRT=20days) of different substrates fed.

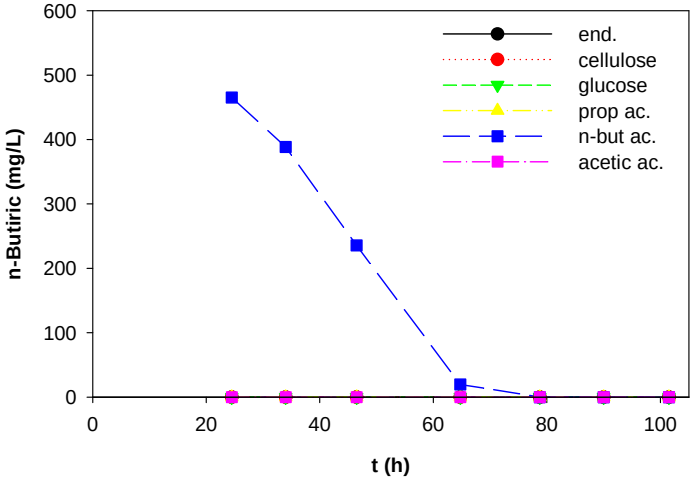

Figure 5.36 Evolution of n-butyric acid concentration in the activity test of the semi-CSTR thermophilic anaerobic sludge reactor acclimatised with raw sludge (no pre-treatment) (HRT=20days) of different substrates fed.

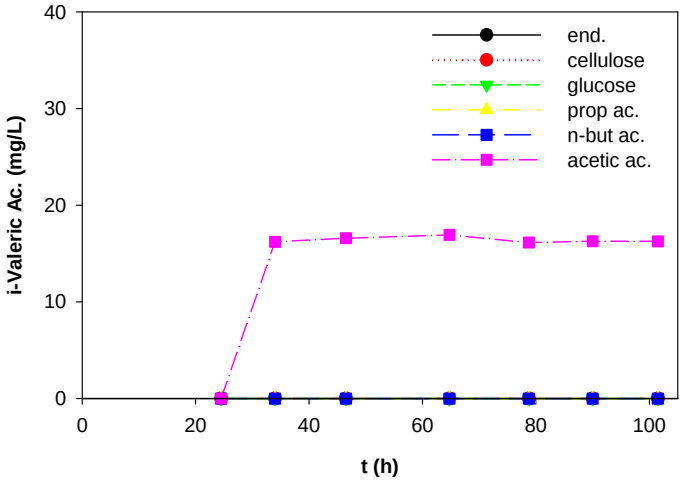

Figure 5.37. Evolution of i-valeric acid concentration in the activity test of the semi-CSTR thermophilic anaerobic sludge reactor acclimatised with raw sludge (no pre-treatment) (HRT=20days) of different substrates fed.

5.2.5.3.2. IN-TH, Thermophilic anaerobic inoculum feed with THERMAL PRETREATED sludge at 80ºC for 1h

In this case endogenous biogas generation is much lower than in previous section, figure 5.38. Thus influence of the different substrates added can be easily seen. Cellulose, glucose and acetate, in decreasing order, are the most anaerobically biodegradable substrates, with an increase of biogas production of 182, 121 and 85% respectively. Propionic acid and n-butyric acid led to similar results as endogenous.

When degradation of individual VFA is studied with this type of inoculum, results follow a similar tendency as in the previous inoculum. Therefore, acetic acid, propionic acid, and n-butyric acid are again degraded, figures 5.39-5.41.

Also, when glucose and n-butyric acid are the substrates, acetic acid concentration raises, but in this case after longer periods of incubation, at least with n-butyric acid, as figure 5.39 indicates.

Figure 5.40 present the evolution of propionic acid, where it can be seen that it is degraded if fed, and when other substrates are fed it gradually dimishes.

It was observed the presence of i-butyric in some reactors but below the detection limit 20 mg/L. Too, it was found production of n-butíric when glucose is degraded, as figure 5.41 indicates.

If i-valeric acid is evaluated, figure 5.42, it can be seen that is constantly present at the same concentration when glucose, i-butiric and acetic acid are fed, whereas with cellulose fed, n-valeric acid decreases to almost disappear at just 40 h, the same behaviour happens when propionic acid is fed, but after 110 h. No n-valeric acid was detected in any case.

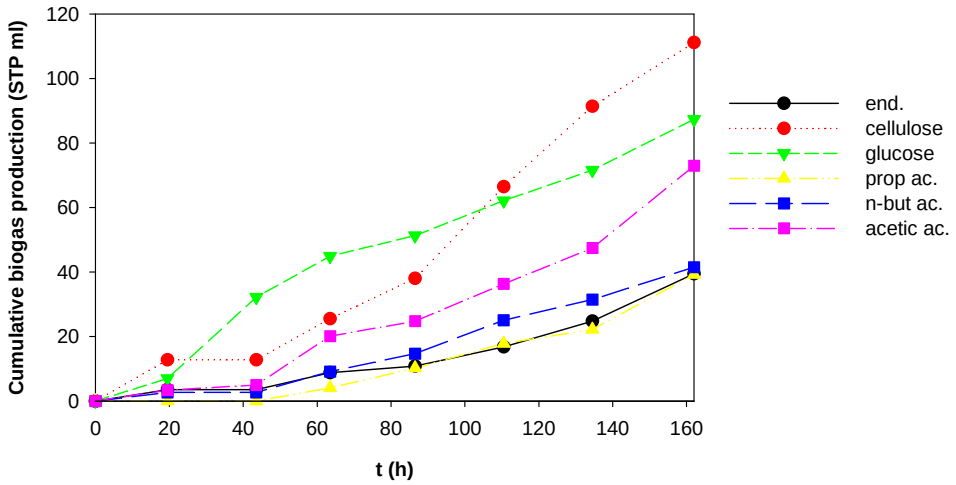

Figure 5.38. Cumulative biogas production in the activity tests of the semi-CSTR thermophilic anaerobic sludge reactor acclimatised with sludge pre-treated at 80ºC (HRT=20days) of the different substrates fed

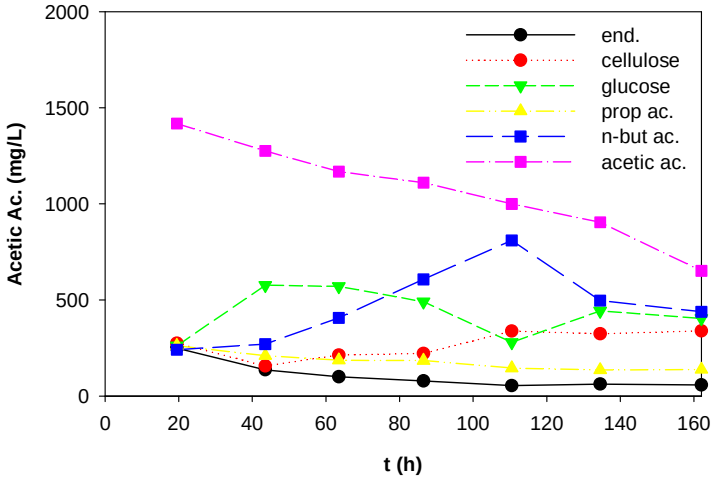

Figure 5.39. Evolution of acetic acid concentration in the activity test of the semi-CSTR thermophilic anaerobic sludge reactor acclimatised with sludge pre-treated at 80ºC (HRT=20days) of different substrates fed.

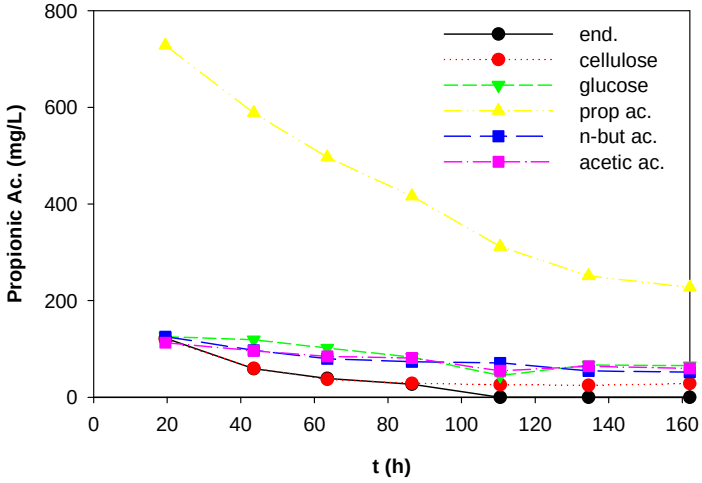

Figure 5.40. Evolution of propionic acid concentration in the activity test of the semi-CSTR thermophilic anaerobic sludge reactor acclimatised with sludge pre-treated at 80ºC (HRT=20days) of different substrates fed.

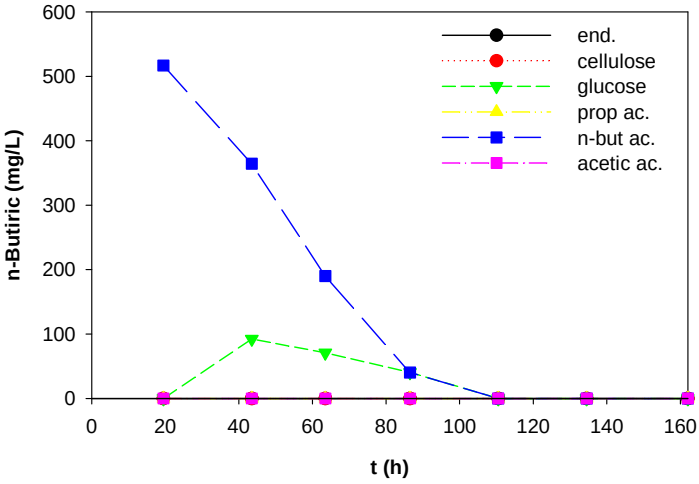

Figure 5.41. Evolution of n-butyric acid concentration in the activity test of the semi-CSTR thermophilic anaerobic sludge reactor acclimatised sludge pre-treated at 80ºC (HRT=20days) of different substrates fed.

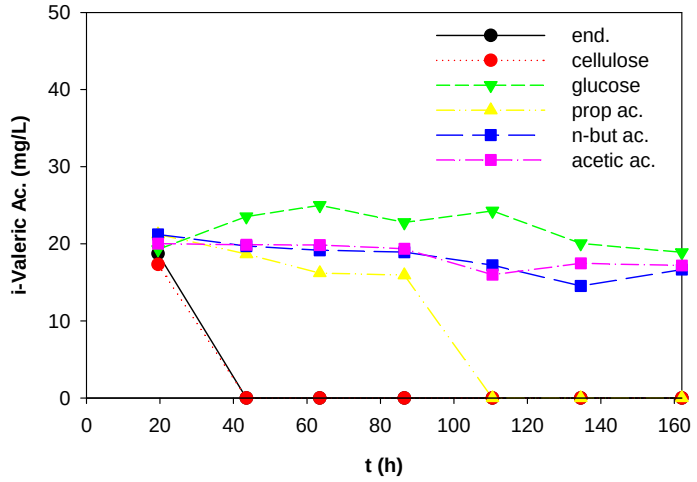

Figure 5.42. Evolution of i-valeric acid concentration in the activity test of the semi-CSTR thermophilic anaerobic sludge reactor acclimatised with sludge pre-treated at 80ºC (HRT=20days) of different substrates fed.

5.2.5.3.3. IN-PX, Thermophilic anaerobic inoculum feed with PEROXIDATED SLUDGE at 0.2 gH_2O_2/gCOD at 30ºC

Cumulative biogas production of IN-PX at the different substrates, figure 5.43, evidences that n-butyric acid is not very anaerobically biodegradable, however in this case cellulose, propionic acid and acetic acid, give moderate biodegradability, 29, 54, and 45% of biogas increase respectively. The best substrate degraded was the glucose, with an increase of 225%.

Showing a similar tendency as IN-RW and IN-TH when glucose, n-butyric acid and cellulose are the substrates, acetic acid is produced in the digestion, as figure 5.44 indicates.

Propionic acid evolution is presented in figure 5.45, where it can be seen that is anaerobically well degraded when is used as substrate, in all other substrate feeds it slowly lowers.

N-butyric acid was almost not detected in any of the substances feed, as figure 5.46 indicates. When n-butyric acid is feed as substrate it nearly complete degrade in quite short time, only 90 h. In turn, i-butyric acid is present in this type of inoculum, as figure 5.47 shows, and slightly lowers during the test in all reactors.

When i-valeric acid is evaluated, figure 5.48, it presents a similar behaviour than the innoculum acclimatized with thermal pre-treatment. It is constantly present at the same concentration when glucose, i-butiric and acetic acid are fed, whereas with cellulose fed, n-valeric acid decreases to almost disappear at just 40 h; the same evolution is seen when propionic acid is fed, but after 110 h. Once more, n-valeric acid was not detected in any reactor.

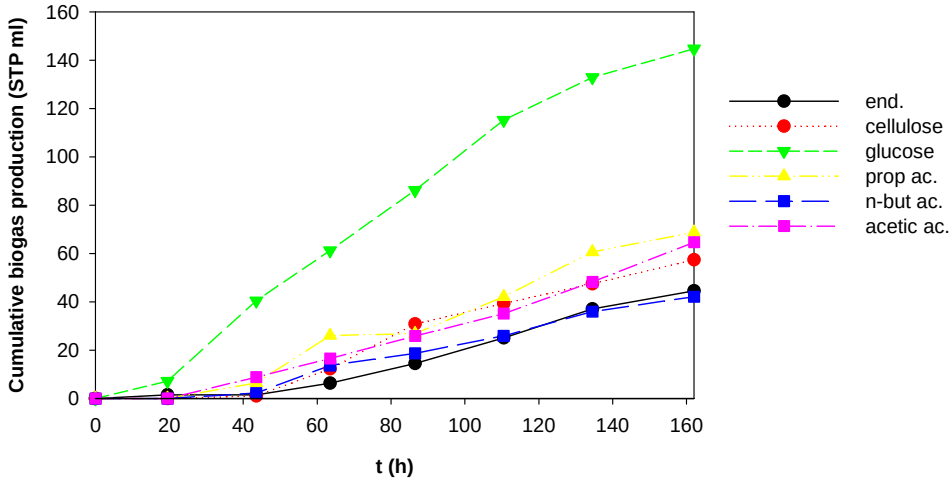

Figure 5.43. Cumulative biogas production in the activity tests of the semi-CSTR thermophilic anaerobic sludge reactor acclimatised with sludge pre-treated with 0.02 g H_2O_2/g COD (HRT=20days) of the different substrates fed

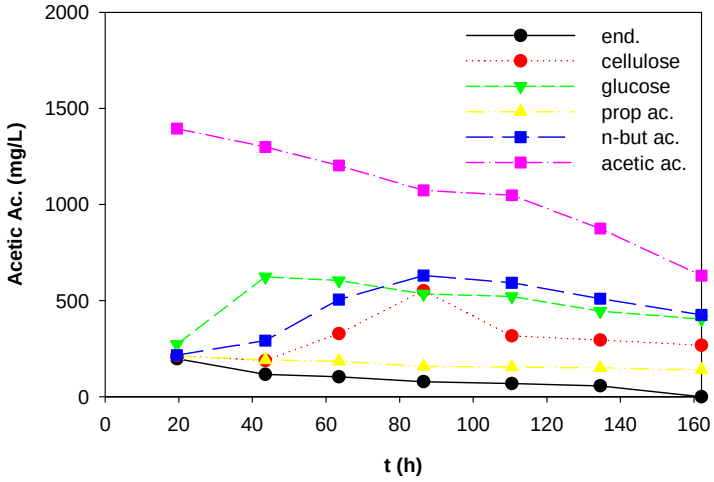

Figure 5.44. Evolution of acetic acid concentration in the activity test of the semi-CSTR thermophilic anaerobic sludge reactor acclimatised with sludge pre-treated with 0.02 g H_2O_2/g COD (HRT=20days) of different substrates fed.

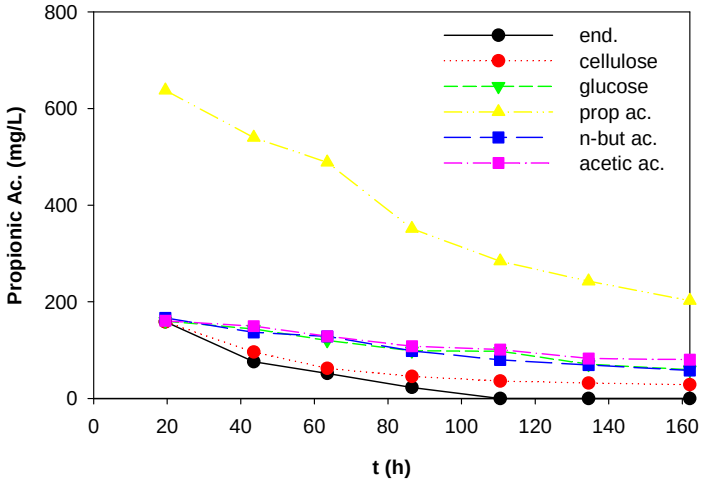

Figure 5.45. Evolution of propionic acid concentration in the activity test of the semi-CSTR thermophilic anaerobic sludge reactor acclimatised with sludge pre-treated with 0.02 g H_2O_2/g COD (HRT=20days) of different substrates fed.

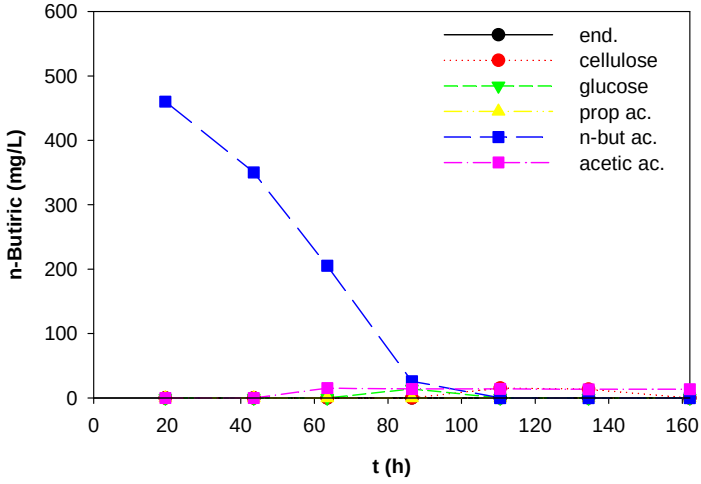

Figure 5.46. Evolution of n-butyric acid concentration in the activity test of the semi-CSTR thermophilic anaerobic sludge reactor acclimatised with sludge pre-treated with 0.02 g H_2O_2/g COD (HRT=20days) of different substrates fed.

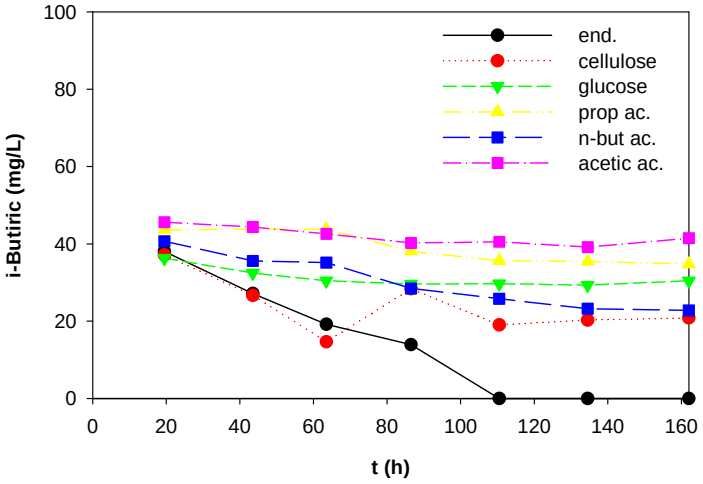

Figure 5.47. Evolution of i-butyric acid concentration in the activity test of the semi-CSTR thermophilic anaerobic sludge reactor acclimatised with sludge pre-treated with 0.02 g H_2O_2/g COD (HRT=20days) of different substrates fed.

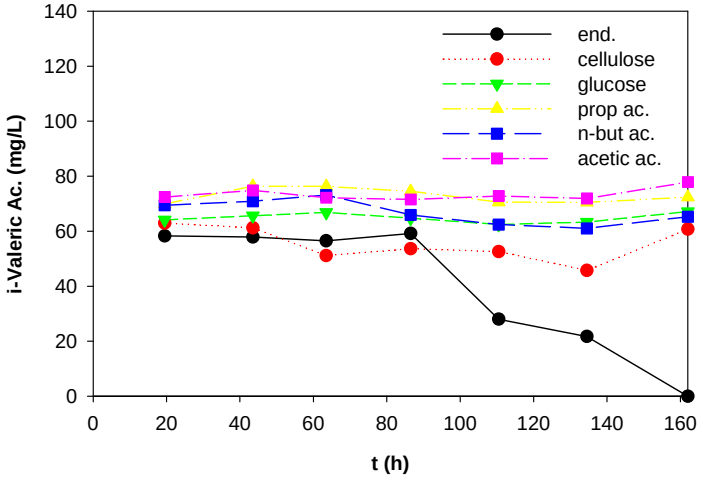

Figure 5.48. Evolution of i-valeric acid concentration in the activity test of the semi-CSTR thermophilic anaerobic sludge reactor acclimatised with sludge pre-treated with 0.02 g H_2O_2/g COD (HRT=20days) of different substrates fed.

Inoculum activity measurements in table 5.7 indicate the degradation activity of each substrate, so it gives information about how active are the different trophic groups present in the inoculum. The kinetic behaviour is represented

by a zero order model, as the inoculum concentration (X_o) is considered to be much higher than the amount of biomass produced ($Y_{SX}\cdot(S_o-S)$).

The most active bacteria in the inoculum feed with raw sludge are acidogenic > hydrolytic > acetogenic > acetoclastic. If thermally pre-treated sludge is fed, then the hierarchy of the bacteria turns to be hydrolytic > acetogenic > acidogenic > acetoclastic. Finally, when the inoculum feed consists of peroxidated sludge, it was found to follow acidogenic > acetogenic > hydrolytic > acetoclastic.

Table 5.6. Methanogenic specific activity constants

INOCULUM (Feed sludge)	**Substrate**	**$A_{max}\cdot10^2$** $\left(g\,COD_{CH_4}/g\,VSS\cdot day\right)$
IN-RW (RAW)	Cellulose	4.33
	Glucose	4.70
	Propionic acid	0.901
	n-butyric acid	0.897
	Acetic acid	1.30
IN-TH (P-TH80)	Cellulose	3.17
	Glucose	2.07
	Propionic acid	1.34
	n-butyric acid	1.21
	Acetic acid	17.6
IN-PX (P-H_2O_2)	Cellulose	2.24
	Glucose	5.08
	Propionic acid	2.33
	n-butyric acid	1.39
	Acetic acid	2.06

The first order hydrolysis constants can be found in table 5.8.

Table 5.7. Hydrolysis rate constants

INOCULUM (Feed sludge)	**Substrate**	**$K_h \cdot 10^2$ $\left(day^{-1}\right)$**
IN-RW (RAW)	Cellulose	20.4
	Glucose	42.9
	Propionic acid	49.4
	n-butyric acid	116
	Acetic acid	34.6
IN-TH (P-TH80)	Cellulose	6.88
	Glucose	32.1
	Propionic acid	25.2
	n-butyric acid	35.6
	Acetic acid	22.8
IN-PX (P-H_2O_2)	Cellulose	6.88
	Glucose	12.7
	Propionic acid	4.81
	n-butyric acid	5.36
	Acetic acid	22.8

5.3. Conclusions

A pilot plant with 5 litres effective semi-continuous reactors was constructed in order to study anaerobic digestion at three different operation conditions at the same time. It has been studied digestion at 33ºc, 50ºC, 55ºC and 60ºC at 10, 15 and 20 HRT. Also sludge pre-treatments were evaluated in semi-continuous operation.

It was found that the thermophilic temperatures studied, 33ºC, 50ºC, 55ºC and 60ºC, are not yet enough for obtaining class A biosolids at the HRT fixed. There is not a significant improvement in thermophilic temperatures over mesophilic concerning organic matter removal, moreover thermophilic temperature of 60ºC leads to poorer results. The maximum biogas production is observed at 55ºC, 935 STP L/kg $VS_{destroyed}$, 30% of improvement if compared with mesophilic. Again at 60ºC, a very low biogas production, 36 STP L/kg $VS_{destroyed}$, is observed, suggesting that methanogens are not very effective.

When single stage mesophilic, and thermophilic digestion process is compared with dual-phased reactors TPAD, the best results were obtained at TPAD systems. They showed better performance in terms of COD (66%), VS (48%) and TS (63%) destruction, and process stability as the final effluent content had low soluble organic matter and VFA content. It seems that the TPAD is efficient enough to obtain Class A biosolids, however only one analysis of pathogens was only done. The principal drawback of the dual system is that requires the construction of new anaerobic reactor when adapting existing facilities.

It was studied the effect of the thermal pre-treatment at 80ºC for 1 h and also the effect of the chemical pre-treatment with hydrogen peroxide at a dose of 0.2 gH_2O_2/gCOD at 30ºC in combination with the anaerobic digestion at three different temperatures, 33ºC (mesophilic range), and two different thermophilic temperatures 50ºC and 55ºC with an hydraulic retention time of 20 days in a semi-continuous reactor.

The maximum VS removal is obtained with the mesophilic anaerobic treatment at 33ºC of thermal pre-treated sludge at 80ºC, with 60% of VS removal. The pre-treatments seem to increase the biogas production, especially in mesophilic range, where 60% and 52% enhancement was found when thermally pre-treated and peroxidated sludge is fed. In the thermophilic range of 55ºC, biogas increment is around 22% and 8% for thermal and peroxidated sludge respectively. Methane content of the biogas is always higher than 68% being a high quality biogas for possible use in co-generation units.

However, if pathogen content is taken into account, the optimal conditions correspond to the thermophilic anaerobic treatment at 55ºC using thermally pre-treated sludge, for which a VS, TS, and COD removal of 55%, 45% and 67% is observed. Pathogen content of *E-coli* is below the class A biosolids requirements. The only drawback is that *Salmonella* was found in the final effluent despite it was not detected at sludge previously pre-treated at 80ºC. But if thermophilic inoculum free of Salmonella is used, this digested sludge could be used for fertilize uses.

The transformation of mesophilic units into thermophilic units adding a thermal pre-treatment at non severe conditions (T<110ºC, 1 h) is economically viable as the higher operating costs are widely compensated by the increase of biogas production and the extended use of the stabilised sludge for agricultural land use. This option requires minimum re-engineering of the plants and is especially interesting for plants with power cogeneration units already implemented. As for those, the savings can be estimated in 1 € per equivalent inhabitant and year, which must cover any investment needed with a payback period of less than four years, even when a cogeneration plant must be build up.

CHAPTER 6

Thermophilic aerobic digestion of sludge

6.1. Introductory remarks

A pilot plant consisting of a 7 L cylindrical reactor of stainless steel was constructed with an active effective reaction volume of 5 L. A thermocouple monitories reactor temperature, two proves are introduced in the cap in order to measure the pH and the dissolved oxygen. Mixing is provided with an electrical stick stirrer at 400 rpm equipped with a paddle stirrer located at its end. The reactor was maintained at the thermophilic temperature of 55ºC by circulating water from a thermostatic bath. Air input value was around 16-20 L/h. In order to minimise water loss by evaporation, air input was saturated with water at 55ºC before entering the reactor.

The achieving of thermophilic temperature depends on taking advantage of the heat released during the oxidising process while organic matter is degraded. The design key points that most affect the operating temperature achieved include the efficiency of the aeration system, the proper reactor insulation, the foam management, and the sludge pre-thickening.

The objective of this chapter was to establish the viability of thermophilic aerobic sludge stabilisation and obtain an auto-self maintained thermophilic aerobic reactor (autothermal aerobic reactor, ATAD). Firstly, it was also planned to study the application of pre-treatments to the feed sludge.

Again the raw sludge examined was a mixture of thickened primary sludge (PS) and thickened (WAS) and among others the main objective was the evaluation of the pathogen sludge content.

The specific objectives were:

- Build-up an aerobic digestion pilot plant.
- Study if class A biosolid are obtained after the thermophilic aerobic process.
- Analyse the biological performance at different HRT at aerobic digestion conditions.

6.2. Results and discussion

Sludge provided by the Reus Wastewater Treatment Plant was used as a substrate for autothermal digestion. The feed consists of a mixture of primary and secondary waste sludge in order to keep the same conditions described in Chapter 5, where anaerobic digestion was studied. The mixture composition corresponds to the sludge rate produced in the physical-chemical and secondary aerobic treatment of this municipal wastewater plant, 65% PS-35% WAS, which is typically encountered in small-medium size WWTP. After collection, raw sludge was stored at 4ºC until use, being the maximum storage time one week in order to maintain fresh sludge for the experiments.

An accurate picture of the autothermal digestion efficiency is provided through the analytical parameters listed in table 6.1, which illustrate the process evolution and quality of the end product. Treated sludge samples were analysed as soon as possible, meanwhile stored at 4ºC to prevent the sludge from varying its properties.

Table 6.1. Frequency and responsible of analyses in ATAD study.

Variable	Frequency	Responsible
ST	2 days/week	URV
SV	2 days/week	URV
DQO	daily	URV
Salmonella	2 day/month	External analysis
E. coli	2 day/month	External analysis
Dissolved oxygen	Daily	URV

The main goal of autothermic process is to decompose, in aerobic conditions, a portion of waste organic solids generated from wastewater treatment. As a result of this oxidative process, heat is released, which allows increasing the temperature.

For succeeding in autothermal digestion some requirements were reported in a few previous wastewater and sludge treatment studies.

- High strength waste is needed; approximately organic feed should ensure a minimum concentration of COD 40000-50000 mg/L and a minimum feed volatile solid content of 2.51% w/w.
- Total solids should be below a maximum concentration 4-6% w/w, to allow adequate mixing.
- Air-input value is recommended at 4 $m^3/h/m^3$ of active reactor volume, in order to achieve the high oxygen demand for treating organic matter producing the sufficient energy for self-heating.

The sludge feed provided by Reus WWTP accomplishes all the requirements for autothermal digestion as COD = 51000 mg/L, TS = 4.17% w/w and VS = 3.19% w/w.

The aerobic inoculum for the ATAD plant was also provided by the Reus WWTP, although the inoculum was taken at mesophilic temperature of 30ºC. Therefore, it was necessary to slowly acclimate the microorganisms into thermophilic conditions. The strategy followed was to increase the temperature at intervals of 5ºC, starting from 30ºC, every two weeks, up to thermophilic conditions (at 55ºC). Feed was made intermittently.

In figure 6.1, it can be seen the evolution of final COD against time at the two HRT studied (10 and 8 days) after thermophilic aerobic digestion. Reduction of COD is presented in figure 6.2 with a mean value of 62% of COD, see Figure 6.2.

Large oscillations are observed in the removal efficiency, with a minimum of COD elimination of 40% and a maximum of almost 88% being found. Oscillations in COD feed measurements may be the principal reason. Feed sludge was weekly obtained from the real wastewater plant and the sludge conditions differed depending on the population and mainly weather conditions. In addition, non homogeneity of the sludge sample can cause differences in COD analysis. Final soluble COD after aerobic thermophilic treatment was around 20 g/L.

Similar behaviour can be observed in solid fractions, presented in figure 6.3 depicting TS and VS content, in which solid removal decreases up to 34% and 40%, respectively. It must be pointed out that non significant differences are observed between 10 and 8 days of HRT in terms of COD or solids.

Thermophilic aerobic treatment reached almost complete hygienisation of the sludge. Pathogen content decreased from the original 2800000 NMP/g to just 23 NMP/g of E. coli, and from 5 NMP/g to 0 NMP/g of *Salmonella*. E. coli population was always measured below the limit for class A biosolids classification, and only one of the five *Salmonella* analyses overtakes the threshold limit.

Also dissolved oxygen in the reactor was measured. It was observed that as the reactor operated in a daily fill mode, when the sludge was fed, the dissolved oxygen in the reactor decrease up to nearly zero values, after 8-9 hours the concentration started to increase again up to the saturation value, which at 55ºC is around 4 mg/L. This indicates that when the sludge is fed, a strong restriction of oxygen availability occurs in the reactor, however in continuous operation system this could be avoided as the feed is slowly and continuously added.

It must be outlined that this performance was obtained with a non-optimised design of the ATAD bench-scale plant. Only open technology was used without the use of any patented equipment. In such an environment, the results compare very well with the performance reported for many of the ATAD plants operating (usually based on Fuchs and NILSA technology).

Therefore, ATAD provides comparable elimination of organic material at more than the half of the HRT for anaerobic digestion. For instance, anaerobic digestion at the same thermophilic temperature of 55ºC leads to a 52% in COD removal, 41% and 54% in TS and VS removal, respectively, but at an HRT of 20 days. Also the hygienisation of the sludge seems to be improved with aerobic treatment if compared with anaerobic at the same temperature, E. coli population in anaerobic digestion was 320 NPM/g, and Salmonella was detected more than one time in the 5 analyses conducted, whereas in aerobic treatment E. coli almost disappeared, only 23 NMP/g was measured, and *Salmonella* was only detected once out of 5 analyses.

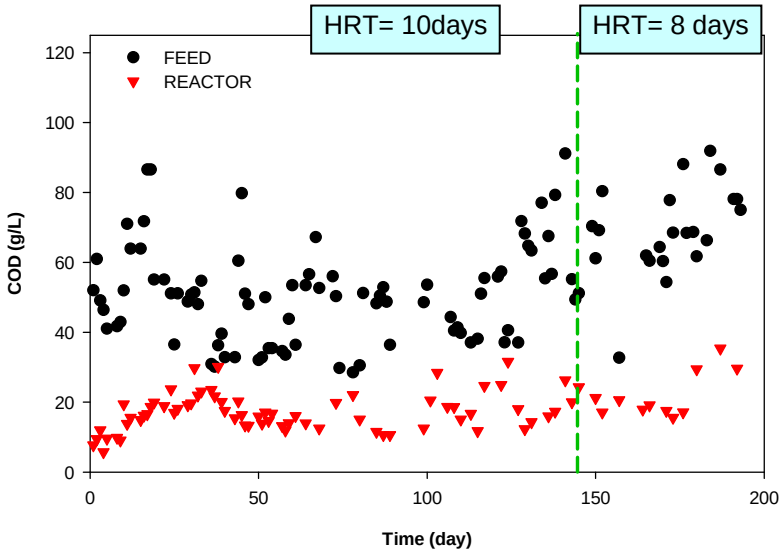

Figure 6.1. Evolution of the initial and final COD in the ATAD plant at 55ºC.

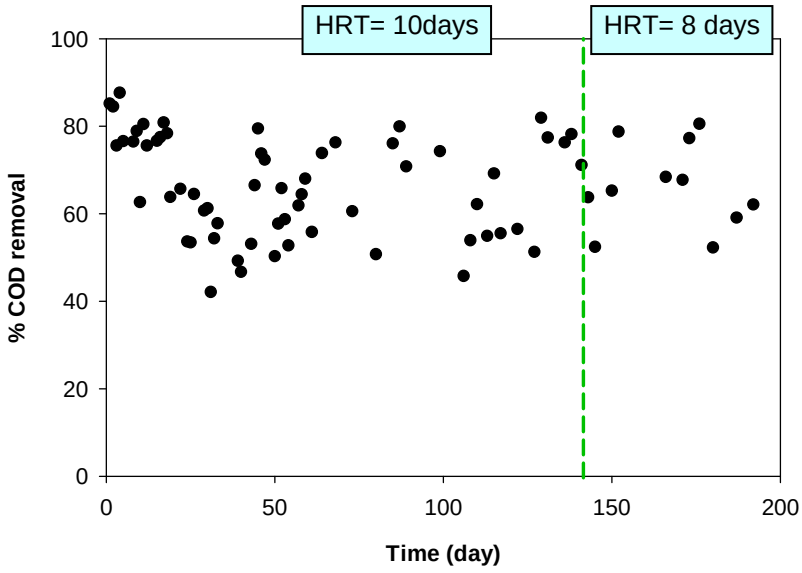

Figure 6.2. Evolution of the COD removal in the ATAD plant at 55ºC.

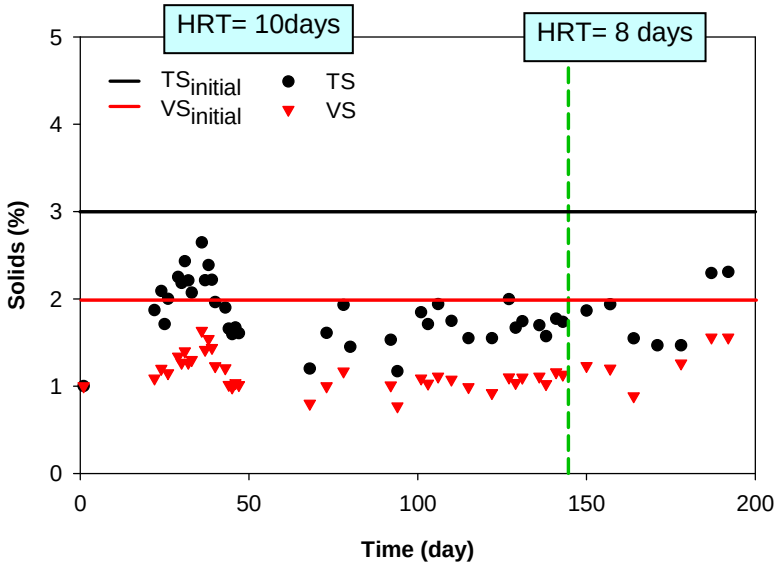

Figure 6.3. Evolution of the total and volatile solids in the ATAD plant at 55ºC.

Although this large COD removal measured should actually allow achieving autothermal conditions (Gomez et al., 2007), auto-sustained temperature was not achieved and extra-heating was needed to maintain the thermophilic temperature. Typical biological heat production is reported to be from 14190-14650 kJ/kgO_2, so theoretically 2243 kJ of heat is released due to 62% of COD removal in the lab-scale reactor. This heat is more than three times the energy needed to increase the sludge temperature from 25ºC to 55ºC, which is around 630 kJ.

Results presented here were the basis to assess the economic impact of the ATAD application (Torrens et al. 2011, Ch. 2). Again the estimation was conducted for the application of ATAD in the WWTP of Reus, which has a depuration capacity for a population of 200000 equivalent inhabitants. The investment costs for new equipment were not taken into account and the calculation basis for the feed sludge volume to the digester was taken to be 100 m^3/day.

The overall operational costs were estimated to be 120.8€/t of ST which is 446.9 €/day, taking into account the oxygen needs and the power for the aeration requirements. If compared with anaerobic digestion at 55ºC (Torrens et al. 2011, Ch. 1) a ratio of 84.9€/t ST is obtained, which is a daily cost of 314€/day. Clearly anaerobic digestion is economically more viable than aerobic.

6.3. Conclusions and recommendations

A literature revision evidences that, even being considered an established process, not too much information is yet accessible for potential users on performance and design of ATAD systems. Most designs are proprietary technologies with limited open knowledge and, in many cases, still reporting operation problems such as insufficient aeration. Although lab-scale studies demonstrate the feasibility of this alternative for sludge sanitation and stabilisation, to date very few full-scale plants are in operation, mainly when compared to the huge amount of operational municipal WWTP. The lack of a wider implementation must probably be assigned to the fact that patented technology is needed, which increases the investment cost, and insufficient open literature makes difficult a supported decision for engineers.

Digestion/stabilisation of sludge can be carried out both aerobically and anaerobically. The anaerobic digestion is the most widespread and probably represents an environmentally friendly use of this waste because of its potential to yield biogas, which can be applied to cut carbon dioxide emissions and contribute to reach the Kyoto's objectives (Rulkens, 2008), although direct combustion has been also suggested (Werther and Ogada, 1999). However, biogas use requires adapted installations and cogeneration system to generate electricity and the investment needed for this option could not be justified in small-medium scaled WWTP. In such cases, Autothermal Thermophilic Aerobic Digestion (ATAD) appears to be an attractive alternative to reduce sludge amount and produce Class A biosolids that can be applied to agricultural land without restrictions.

Bench scale tests of ATAD performance demonstrate that this option is an effective, robust technique for sludge stabilisation. Even treating raw sludge with high oscillations of solids content, the mean output was maintained at 60% COD removal with a HRT of just eight days. TS and VS removal content were up to 34% and 40%, respectively. It must be noted that HRT seems not to be a key parameter as setting the HRT at ten days did not provide better performance. Thermophilic aerobic treatment reached almost complete hygienisation with respect to pathogen content; E coli population is below the limit for class A biosolids classification, the threshold limit for Salmonella indicator is overtaken in only one out of five analyses. Pathogen content decreased from the original 2800000 NMP/g to just 23 NMP/g of E-coli, and from 5 NMP/g to 0 NMP/g of Salmonella as mean values.

The level of COD destruction attached should be enough to maintain autothermal conditions. However, heat loss was too high in the reactor constructed, where the ratio S/V is almost 30 (V = 7 L), while it is considered that only S/V ratios lower than 5 can minimize the heat loss through the area of reactor, i.e. for reactor volumes greater than 1 m^3.

Therefore, although disappearance of organic matter does exist, true autothermal conditions were not achieved as extra-heating was added to sustain the thermophilic temperature. This was caused by the small size of the bench-scale reactor, with too high area to volume ratio, which leads to excessive heat loss. However, the COD removal achieved assures (by energy balance) that higher scale plants would work under auto-sustained operation.

Moreover, in order to assure enough COD removal to attain autothermic conditions at thermophilic temperatures, oxygen mass transfer limitations must be avoided and the level of aeration required must be guaranteed by mechanical agitation using proper design of impellers. This is a field that requires dedicated studies.

Despite non self-maintenance of the reactor temperature, the feasibility of thermophilic aerobic digestion was demonstrated using non-dedicated equipment, no requiring owned or patented technologies. Freely available agitation systems were able to give enough mixing to reach acceptable level of COD conversion. However, the operation was still limited by the oxygen mass transfer rate as the oxygen concentration was very low in the reactor.

CHAPTER 7

Conclusions

- Thermal pre-treatment and peroxidation were applied over a mixture of primary and secondary sludge from a municipal WWTP with the aim of improving the subsequent digestion at mesophilic and thermophilic temperatures and the derived hygienisation and biogas production.
- In the range of 30-80ºC of thermal pre-treatment, the highest temperature leads to an increase over 100% in soluble COD content in just 1 h of treatment. TDS shows the same behaviour. This suggests that part of the homogeneous COD (or TS content) solubilises, but no organic matter is destroyed, i.e. is completely mineralised. A rapid increase of soluble COD was observed during the first hour of pre-treatment, especially at 60ºC and 80ºC, which also correlates with the rising in TDS content; beyond this time non noticeable improvement of the solubilisation is found. Therefore, 1 h thermal treatment is recommended.
- In the thermal treatment conducted in the range 110-200ºC, the tendency is similar. Therefore, the solubilisation increases as temperature does; from an starting soluble TOC of 3.2 g/L, it reached

up to almost 14 g/L at 200ºC for 0.5 h of treatment. Only beyond 170ºC and 8 h of treatment, elimination of TS is observed at significant extent. In turn, VS only is removed at 200ºC and 16 h. Therefore, no evident advantages can be drawn for treatment at high temperature as there is a higher investment associated and even full mineralisation can be eventually achieved, which reduces the potential for biogas production. Only sludge pre-treated above 110ºC can be directly classified as Class A biosolid.

- Although no significant organic removal is observed after addition of hydrogen peroxide at 30ºC at dose below 0.9 g H_2O_2/g COD for 1 h, it seems to occur solubilisation of the solids, which results in an increase of soluble COD and TDS if compared with the initial values. A dose of 0.03 g H_2O_2/g COD is enough increase soluble COD more than 70% of the initial soluble COD. At higher doses, 1.16 and 1.45 g H_2O_2/g COD, complete mineralisation occurs at some extent. There is an elimination of organic matter, expressed as VSS, 41 and 34.5%, respectively, and also a decrease in the solids, expressed as TS, 22.5 and 14%, respectively. However, the addition of hydrogen peroxide at these two higher doses also leads to an increase of the reaction volume, raising the residual volume in a 31.5 and 39.5% respectively, which is in turn an unfavourable consequence. Hydrogen peroxide promotes *Salmonella* destruction, but does not practically have any effect on faecal coliform densities, even at the highest dosage tested, 0.6 g H_2O_2/g COD.
- The addition of hydrogen peroxide at 60ºC is found to be more efficient than at 30ºC as it is partially combined with thermal pre-treatment. Up to doses of hydrogen peroxide below 0.55 g H_2O_2/g COD, removal of organic matter is found up to a maximum for the ratio 0.88 g H_2O_2/g COD, where the elimination of TS and VS content is around 46.1 and 28.3%, respectively. The maximum removal of VSS, 37.7%, is obtained using 1.11 g H_2O_2/g COD. The effect of the reaction time at the sludge pre treated with hydrogen peroxide at 60ºC proves a higher solubilisation of the mineral matter; however no improvement is seen in the elimination of organic matter.
- According to the above results, the more feasible pre-treatment is the thermal pre-treatment at temperatures near 100ºC for 1 h to achieve a better pathogen removal. At this temperature, VDS increases approximately six folds, which results into 50% more biogas production measured in controlled batch experiments.
- Although hydrogen peroxide pre-treatment also gives significant improvement in the conditioning of the raw sludge, only low doses of peroxide are suggested. The recommended dose is 0.2 g H_2O_2/g COD as higher doses do not provide significant additional improvement.

- After pre-treatment evaluations, it was decided to select for studies of thermophilic anaerobic digestion in the lab-plant scale semi-CSTR, thermal pre-treatment at 80ºC and peroxidation with a dose of 0.2 g H_2O_2/g COD. Despite higher temperatures lead to larger biogas production, the temperature of 80ºC is preferred as is below the boiling point of water. Equipment that would be required beyond this point is much more expensive and critical. Moreover, at 80ºC class A biosolids are obtained so sanitary conditions for fertilize use is presumably acceptable. Concerning dosages of hydrogen peroxide, the most decisive parameter has been the pathogen content, specifically the *Salmonella*, dosage of 0.2 g H_2O_2/g COD clearly promotes the reduction of *Salmonella*, within an acceptable addition of chemicals.
- Thermophilic temperatures studied, 50ºC, 55ºC and 60ºC at an HRT of 15, 20 and 25 days, are not enough for complete pathogenic destruction at the residence time fixed. However, a high reduction of solid content is found, yet biogas production is lower than expected at thermophilic temperatures.
- When single stage mesophilic and thermophilic digestion process is compared with dual-phased reactors, TPAD, the best results were obtained at TPAD systems. They showed better performance in terms of COD (66%), VS (48%) and TS (63%) destruction, and process stability as the final effluent content has low soluble organic matter and VFA content. It seems that the TPAD is efficient enough to obtain class A biosolids, however it was only made one pathogen analysis. The principal drawback of the dual system is that the construction of a new anaerobic reactor is needed in existing facilities.
- Bench scale tests of ATAD performance demonstrate that this option is an effective, robust technique for sludge stabilisation. The mean output was maintained at 60% COD removal with a HRT of just 8 days. TS and VS removal content were up to 34% and 40%, respectively. Thermophilic aerobic treatment reached almost complete hygienisation regarding to pathogen content; thus, E coli population is below the limit for class A biosolids classification, and the threshold limit for *Salmonella* indicator is overtaken in only one out of five analyses.
- The level of COD destruction attached would be enough to maintain autothermal conditions. However, heat loss was too high in the experimental reactor used, since the ratio S/V is almost 30 (V = 7 L), while it is considered that only S/V ratios lower than 5 can minimize the heat loss through the reactor area, i.e. for reactor volumes greater than 1 m^3. Therefore, it was not possible to prove the auto-sustainability of the operation.

- When thermal pre-treatment at 80ºC for 1 h and peroxide pre-treatment at a dose of 0.2 gH_2O_2/gCOD at 30ºC are studied in combination with mesophilic and thermophilic anaerobic digestion in a semi-continuous reactor, the maximum VS removal is obtained with the mesophilic anaerobic treatment at 33ºC of thermal pre-treated sludge at 80ºC, yielding 60% of VS removal. The pre-treatments seem to increase the biogas production, especially in mesophilic range, where 60% and 52% enhancement was found when thermally or peroxidated sludge is fed. In the thermophilic temperature of 55ºC, biogas increment is around 22% and 8% for thermal and peroxidated sludge, respectively. Methane content of the biogas is always higher than 68% being a high quality biogas for possible use in co-generation units
- If pathogen content is taken into account, the optimal conditions correspond to the thermophilic anaerobic treatment at 55ºC using thermally pre-treated sludge, for which a VS, TS, and COD removal of 55%, 45% and 67% is observed. Pathogen content of *E-coli* is below the class A biosolids requirements. The only drawback is that *Salmonella* was found in the final effluent despite it was not detected at sludge previously pre-treated at 80ºC. But, if *Salmonella*-free thermophilic inoculum is used, this digested sludge could be used for fertilize applications.
- In the case of chemical pre-treatment with hydrogen peroxide, the benefits of the higher amount of stabilised sludge accomplishing sanitary conditions and the larger power production from biogas is mostly offset by the additional cost of the reagents, for which hydrogen peroxide is the main contributor. On the contrary, thermal pre-treatment at 80ºC for 1 h gives unitary costs of the stabilised sludge three times lower that without using any pre-treatment. The savings are estimated in approximately 1€ per equivalent inhabitant and year. As the re-engineering needed for existing plants in this case is minimal; these savings assure a very short payback period (2-4 years), even in case of overestimation of the benefits.

References

ACA, Programa d'actuacions per a la gestió dels fangs residuals generats en els processos de depuració d'aigües residuals urbanes de Catalunya per el període 2009-2014. In http://aca-web.gencat.cat/aca/appmanager/aca/aca?_nfpb=true&_pageLabel=P32200317612864385783332. [Last accessed the 4th of March 2013].

APHA, Standard Methods for the Examination of Water and Wastewater. 1998 20th edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

Ahring, B.K.; Westermann, P., Kinetics of butyrate, acetate and hydroge metabolism in a thermophilic, anaerobic butyrate-degrading

triculture, *Applied and Environmental Microbiology* 53 (1987) 434-439.

Alsop, M.G.; Cpmwau, R.A. Improved thermal sludge conditioning by thermal treatment with acids and bases, *Journal of the Water Pollution Control Federation* 54 (1952) 146-152.

Angelidaki, I.; Alves, M.; Bolzonella, D.; Borzacconi, L.; Campos, J.L.; Guwy, A.J.; Kalyuzhnyi, S.; Jenicek, P.; van Lier, J.B., Defining the biomethane potential (BMP) of solid organic wastes and energy crops: a proposed protocol for barch assays, *Water Science and Technology* 59 (2009) 927-934.

Angelidaki, I.; Sanders, W., Assessment of the anaerobic biodegradability of macropollutants, *Reviews in Environmental Science and Biotechnology* 3 (2004)117-129.

Bougrier, C.; Albasi, C.; Delgenès, J.P.; Carrère, H. Effect of ultrasonic, thermal and ozone pre-treatment on waste activated sludge solubilisation and anaerobic biodegradability, *Chemical Engineering and Processing* 45 (2006a) 711-718.

Bougrier, C.; Delgenès, J.P.; Carrère, H. Combination of thermal treatments and anaerobic digestion to reduce sewage sludge quantity and improve biogas yield, *Process Safety and Environmental Protection* 84 (2006b) 280-284.

Bougrier, C.; Delgenès, J.P.; Carrère, H. Impacts of thermal pre-treatments on the semi-continuous anaerobic digestion of waste activated sludge, *Biochemical Engineering Journal* 34 (2007) 20-27.

Bougrier, C; Delgenès, J.P.; Carrère, H. Effects of thermal treatments on five different waste activated sludge samples solubilisation, physical properties and anaerobic digestion, *Chemical Engineering Journal* 139 (2008) 236-244.

Boušková, A.; Dohányos, M.; Schmidt, J.E.; Angelidaki, I.; Strategies for changing temperature from mesophilic to thermophilic conditions in

anaerobic CSTR reactors treating sewage sludge, *Water Research* 39 (2005) 1481-1488.

Barlindhaug, J.; Ødegaard, H. Themal hydrolysate as carbon source for denitrification, *Water Science and Technology* 33 (1996) 99-108.

Böhler, M., Siegrist, H. Partial ozonation of activated sludge to reduce excess sludge, improve denitrification and control scumming and bulking. *Water Science and Technology* 49 (2004), 41–49.

Burghardt, R.; Krull, R.; Hempel, D.C.; Braunschweig, R.H.; Pelousek, H.; Bahnmüller, H. Alkalische hydrolyse von Klärschlamm am Beispiel del Kläranlage dormagen der Bayer AG, *Korrespondenz Abwasser* 44 (1997) 1806-1811.

Carrère, H.; Dumas, C.; Battimelli, A.; Btstone, D.J.; Delgenès, J.P.; Steyer, J.P.; Ferrer, I., Pretreatment methods to improve sludge anaerobic degradability: A reveiw, *Journal of Hazardous Materials* 183 (2010) 1-15.

Cacho Rivero, J.A.; Suidan, M.T. Anaerobic Digestion of Thermo-Oxidized Excess Municipal Sludge, *Water Environment Research* 78 (2006a) 510-521.

Cacho Rivero, J.A.; Suidan, M.T. Effect of H_2O_2 dose on the thermo-oxidative co-treatment with anaerobic digestion of excess municipal sludge, *Water Science and Technology* 54 (2006b) 253-259.

Camacho, P.; Deleris, S.; Geaugey, V.; Ginestet, P.; Paul, E. A comparative study between mechanical, thermal and oxidative disintegration techniques of waste activated sludge, *Water Science and Technology* 46 (2002) 79-87.

CAMBI-biosolids treatment. In www.cambi.com. [Last accesed the 27th of November 2012].

Chen, Y.; Jiang, S.; Yuan, H.; Zhou, Q.; Gu, G. Hydrolysis and acidification of waste activated sludge at different pHs, *Water Research* 41 (2007) 683-689.

Cheunbarn, T.; Pagilla, K., Anaerobic thermophilic/mesophilic dual-stage sludge treatment, *Journal of Environmental Engineering*. 126 (9) (2000) 796-801.

Chua, L.; Yanb, S.; Xingb, X-H.; Sunc, X.; Jurcikc, B. Progress and perspectives of sludge ozonation as a powerful pretreatment method for minimization of excess sludge production, *Water Research* 43 (2009)1811–1822.

Christchurch city council . In http://www.ccc.govt.nz/homeliving/wastewater/treatmentplant/chchwastewatertreatmentplant/flowdiagram.aspx. [Last accesed 7th May 2013].

Climent, M.; Ferrer, I.; Baeza, M.M.; Artola, A.; Vázquez, F.; Font, X. Effects of thermal and mechanical pretreatments of secondary sludge on biogas production under thermophilic conditions, *Chemical Engineering Journal* 133 (2007) 335-342.

De la Rubia, M.A.; Romero, L.I.; Sales, D.; Pérez, M., Temperature conversion (mesophilic to thermophilic) of municipal sludge digestion, *AICHE Journal* 51 (2005) 2581-2586.

De la Rubia, M.A.; Perez, M.; Romero, L.I.; Sales, D., Effect of solids retention time (SRT) on pilot scale anaerobic thermophilic sludge digestion, *Process Biochemistry* 41 (2006) 79-86.

Dreywood, R., Qualitative Test for Carbohydrate Material. *Industrial and Engineering Chemistry-Analytical Edition* 18 (1946): p. 499-499.

Dubois, M., et al., Colorimetric Method for Determination of Sugars and Related Substances. *Analytical Chemistry*, 1956. 28(3): 350-356.

Dwyer, J.; Stanrrenburg, D.; Tait, S.; Barr, K.; Batstone, D.J.; Lant, P. Decreasing activated sludge thermal hydrolysis temperature reduces product colour, without decreasing degradability, *Water Research* 42 (2008) 4699-4709.

Elliott, A.; Mahmood, T. Review: Pretreatment technologies for advancing anaerobic digestion of pulp and paper biotreatment residues, *Water Research* 41 (2007) 4273-4286.

EPA/625/10-90/007, Autothermal Thermophilic Aerobic Digestion of Municipal Wastewater Sludge; Environmental Regulations and Technology; U.S. Environmental Protection Agency, Washington, United States (1990).

EPA 832-R-06-005. Emerging technologies for biosolids management. Office of waste water management. U. S. Environmental Protection Agency, Washington, United States (2006)

Eskicioglu, C.; Kennedy, K.J.; Droste, R.L. Characterisation of soluble organic matter of waste activated sludge before and after thermal pre-treatment, *Water Research* 40 (2006) 3725-3736.

Everett, J.G. The effect of heat treatment on the solubilization of heavy metals, *Journal of the Water Pollution Control* 73 (1974) 207-209.

Ewing, W.H. and Ball, M.M. The biochemical test of the genus Salmonella. National Centre for Disease Control and Prevention, Atlanta, Georgia, United States (1996).

Fang, H.H. P.; Lau, I.W.C. Startup of thermophlic (55ºCI UASB reactors using different mesophlic seed sludges, *Water Science and Technology* 34 (1996) 445-452.

Ferrer, I.; Ponsa, S.; Vazquez, F.; Font, X. Increasing biogas production by termal (70ºC) sludge pre-treatment prior to thermophilic anaerobic digestion, *Biochemical Engineering Journal* 42 (2008) 186-192.

Ferrer, I.; Serrano, E.; Ponsa, S.; Vazquez, F.; Font, X. Enhancement of thermophilic anaerobic sludge digestión by 70ºC pre-treatment: energy considerations. *Journal of Residuals Science & Technology* 6 (2009) 11-18.

Gavala, H.G.; Yenal, U.; Skiadas, I.V.; Wastermann, P.; Ahring, B. Mesophilic and thermophilic anaerobic digestion of primary and secondary sludge. Effect of pre-treatment at elevated temperature, *Water Research* 37 (2003) 4561-4572.

Ge, H.; Jensen, P.D., Batstone, D.J Temperature phased anaerobic digestion increases apparent hydrolysis rate for waste activated sludge, *Water Research* 45 (2011) 1597-1606.

Ge, H.; Jensen, P.D., Batstone, D.J. Pre-treatment mechanisms during thermophilic-mesophilic temperature phased anaerobic digestion of primary sludge, *Water Research* 44 (2010) 123-130.

GEC, Global Environment Centre Foundation. In http://www.gec.jp/JSIM_DATA/WATER/WATER_4/html/Doc_283.html. [Last accesed the 27th of November 2012].

Gonzalez-Gil, G.; Kleerebezem, R.; Lettinga, G., Assessment of metabolic properties and kinetic parameters of methanogenic sludge by on-line methane production rate measurements, *Applied Microbiology and Biotechnology* 58 (2002) 248-254.

Goossens, H.; Wauters, G.; De Boeck, M.; Janssens, M.; Butzler, J.P., Semisolid selective motility medium for isolation of Salmonella from faecal specimens. *Journal of Clinical Microbiology*, 19 (1984) 940-941.

Guellil, A.; Boualam, M.; Quiquampoix, H.; Ginestet, P.; Audic, P.; Block, J.C. Hydrolysis of wastewater colloidal enzymes extracted from activated sludge flocs, *Water Science and Technology* 36 (1997) 189-192.

Guwy, A.J., Equipment used for testing anaerobic biodegradability and activity, *Reviews in Environmental Science and Biotechnology* 3 (2004) 131-139.

Han, Y.; Sung, S.; Dague, R.R., Temperature-phased anaerobic digestion of wastewater sludges, *Water Science and Technology* 36 (1997) 367–374.

Haug, R.; Stuckey, D.C.; Gossett, J.M.; McCarty, P.L. Effect of thermal pre-treatment on digestibility and dewateratiblity of organic sludge. *Journal of the Water Pollution Control* (1978) 73-85.

Harper, S.R., Pohland, F.G., 1986. Recent developments in hydrogen management during anaerobic biological waste water treatment. *Biotechnology Bioengineering* 28, 585–602.

Hansen T. L., Svard A., Angelidaki I., Schmidt J. E., Jansen J., Christensen T. H., Chemical characteristics and methane potentials of source-separated and pre-treated organic municipal solid waste. *Water Science and Technology* 48 (2003) 205-208.

Huyard, A.; Ferran, B.; Audic J-M., The two phase anaerobic digestion process: Sludge stabilization and pathogens reduction, *Water Science and Technology* 42 (2000) 41-47.

Ichiro, Y. The volume reduction technology of sludge: The capacity increase of waste water treatment facilities and introduction of the sludge volume reduction equipment (Biodiet), Sangyo to Kankyo 32 (2003)101-103.

INE; Instituto nacional de estadistica. INEbase. Entorno físico y medio ambiente. Estadísticas sobre medio ambiente http://www.ine.es/inebmenu/mnu_medioambiente.htm, [Last accesed the 27th of November 2012].

Iranpour, R.S.Oh.; Cox, H.H.J.; Shao, Y.J.; Moghaddam, O.; Kearney, R.J.; Deshusses, M.A.; Stenstrom, M.K. Ahring, B.K. Changing mesophilic wastewater sludge digestion into thermophilic operation

at terminal island treatment plant, *Water Environmental Research* 47 (2002) 494-507.

ISO/DIS 14853 Evaluation of ultimate anaerobic biodegradation of plastic materials in an aqueous system –method by analysis of carbon conversion to carbon dioxide and methane. International Organization for Standardization, Geneva (1997).

ISO/DIS 19250-2003 Water quality - Determination of Salmonella species. International Organization for Standardization, Geneva (2003).

ISO/FDIS 9308-3- COR.1-2000 Water Quality – Detection and enumeration of Escherichia coli and Coliform bacteria in surface and waste water – Part 3: Miniaturized Method (Most Probable Number) by Inoculation in Liquid Medium. International Organization for Standardization, Geneva (1998).

Juuti, P.S.; Katko, T.S.; Vuorinen, H.S. A Brief History of Water and Health from Ancient Civilizations to Modern Times *IWA water iki* (http://www.iwawaterwiki.org/xwiki/bin/view/Articles/-ABRIEFHISTORYOFWATERANDHEALTHFROMANCIENTCIVILIZATIONSTOMODERNTIMES (2007) [Last accessed the 27th of November 2012].

Khanal, S.K.; Grewell, D.; Sung, S.; Van Leeuwen J.H. Ultrasound application in wastewater sludge pretreatment: A Review, *Critical Reviews in Environmental Sciende and Technology* 37 (2011) 277-313.

Kim, J.; Park, C.; Kim, T.-H.; Lee, M.; Kim, S.; Kim, S.-W.; Lee, J. Effect of various pretreatments for enhanced anaerobic digestion with waste activated sludge, *Journal of Bioscience and Bioengineering* 95 (2003) 271-275.

Kovacs G.L. US Patent 5,087,373 (1992).

Li, Y.-Y.; Noike, T. Upgrading of anaerobic digestion of waste activated sludge by thermal pre-treatment, *Water Science and Technology* 26 (1992) 857-866.

Li, H.; Jin, Y.; Mahar, R.; Wang, Z.; Nie, Y. Effects and model of alkaline waste activated sludge treatment, *Bioresource Technology* 99 (2008) 5140-5144.

Liu, Y.; Tay, J-H. Strategy for minimization of excess sludge production from the activated sludge process, *Biotechnology Advances* 19 (2001) 97-107.

Lu, J.; Gavala, H.N.; Skiadas, I.V.; Mladenovska, Z.; Ahring, B.K. Improving anaerobic sewage sludge digestion by implementation of a hyper-thermophilic prehydrolysis step, *Journal of Environmental Management* 88 (2007) 881-889.

Metcalf, E. 2003. Wastewater Engineering: Treatment, disposal, and reuse. Boston, McGraw-Hill.

MICROSLUDGE. Paradigm Environmental Technologies INC. In www.microsludge.com [Last accesed the 27th of November 2012].

Müller, J.A., Prospects and problems of sludge pre-treatment process, *Water Science and Technology* 44 (2001) 121-128.

Nadal, M.; Schuhmacher, M.; Domingo, J.L., Cost–benefit analysis of using sewage sludge as alternative fuel in a cement plant: a case study. *Environmental Science and Pollution Research* 16 (2009) 322 – 328.

Neyens, E.; Baeyens, J. A review of thermal sludge pre-treatment process to improve dewaterability, *Journal of Hazardous Materials* B98 (2003) 51-67.

Neyens, E.; Baeyens, J.; Creemers, C. Alkaline thermal sludge hydrolysis. *Journal of hazardous Materials* B97 (2003) 295-314.

Neyens, E.; Baeyens, J.; Dewil, R.; De heyder, B. Advanced sludge treatment affects extracellular polymeric substances to improve activated sludge dewatering. *Journal of hazardous Materials* 106B (2004) 83-92.

Pavlostathis, S.G.; Giraldo-Gomez, E. Kinetics of Anaerobic Treatment A Critical Review, *Critical Reviews in Environmental Control* 21 (1991) 411-489.

Perry, R.H. Green, D.W., Perry's Chemical Engineers' Handbook 7th Edition, Mc Graw Hill, USA1997.

Pinnekamp, J.; Effects of thermal pretreatment of sewage sludge on anaerobic digestion, *Water Science and Technology* 21 (1988) 97-108.

Pokorná, D.; Vodicka, O; Rosenberg, T., Volattile fatty Acid anlyse on Gas Chromatography (Cromatografické stanovení koncentrace nišžćel mastnŷch kyselin), *Proceedings of the V conference Anaerobie* 2001, 117-121.

Puchajda, B.; Oleszkiewicz, J., Thermophilic anaerobic acid digestion of biosolids: hydrolysis, acidification, and optimization of retention time of acid digestion, *Journal of Environmental Engineering Science* 2006. 5: p. 187-195.

Rajan, R.V.; Lin, J.; Ray, B.T. Low-level chemical pre-treatment for enhanced sludge solubilization, *Journal of the Water Pollution Control Federation* 31 (1989) 1678-1683.

Ray, B.T.; Lin, J.; Rajan, R.V. Low-level chemical pre-treatment for enhanced sludge solubilization, *Journal of the Water Pollution Control Federation* 62 (1990) 81-87.

Riau, V.; de la Rubia, M.A.; Péreza, M., Temperature-phased anaerobic digestion (TPAD) to obtain classes A biosolids: A semi-continuous study, *Bioresource Technology* 101 (2010) 2706-2712.

Rittmann, B.E.; McCarty, P.L. 2001 Environmental biotechnology: principles and applications, McGraw Hill, New York, USA.

Roberts, R.; Davies, W.J.; Forster, C.F., Two-Stage, Thermophilic-Mesophilic Anaerobic Digestion of Sewage Sludge, *Process Safety and Environmental Protection*, 77 (1999) 93-97.

Roš, M.; Zupančič, G. D. Thermophilic anaerobic digestion of waste activated sludge, *Acta Chimica. Slovenica* 50 (2003) 359-374.

Rozzi, A.; Remigi, E., Methods of assessing microbial activity and inhibition under anaerobic conditions: a literature review, *Reviews in Environmental Science and Biotechnology* 3 (2004) 93-115.

Rubio-Loza, L.A.; Loyola, A., Two-phase (acidogenic–methanogenic) anaerobic thermophilic/mesophilic digestion system for producing Class A biosolids from municipal sludge, *Bioresource Technology* 101 (2010) 576–585.

Schmitz, U.; Berger, C.R.; Orth, H., Protein analysis as a simple method for the quantitative assessment of sewage sludge disintegration, *Water Research* 34 (2000) 3682-3685.

Schonberg, J.C.; Bhattacharya, S.K., Madura, R.L.; Mason, S.H.; Conway, R.A., Evaluation of anaerobic treatment of selected petrochemical wastes, *Journal Hazardous Materials* 54 (1997) 47-63.

Siegert, I., Banks, C., 2005. The effect of volatile fatty acid additions on the anaerobic digestion of cellulose and glucose in batch reactors. *Process Biochemistry* 40 (11), 3412–3418.

SIEMENS- Siemens water and Wastewater, Zimpro Systems. In http://www.water.siemens.com/en/about_us/legacy_brands/Pages/zi

mpro.aspx and http://www.water.siemens.com/en/products/physical_chemical_treatment/hydrothermal_oxidation_wao/Pages/Zimpro_Wet_Air_Oxidation.aspx. [Last accessed November 2012].

Singh, T.; Patterson, J.W. Improvement of the aerobic sludge digestion process efficiency, *Journal of the Water Pollution Control Federation* 46 (1974) 102-112.

Smith, G.; Göransson, J. Generation of an effective internal carbon source for denitrification through thermal hydrolysis of pre-precipitated sludge, *Water Science and Technology* 25 (1992) 211-218.

Solera, R.; Romero, L.I.; Sales, D., The evolution of biomass in a two-phase anaerobic treatment process during start-up, *Chemical and Biochemical Engineering Quarterly*. 16 (2002), pp. 25–29.

Song, Y-Ch.; Kwon, S-J.; Woo, J-H., Mesophilic and thermophilic temperature co-phase anaerobic digestion compared with single-stage mesophilic- and thermophilic digestion of sewage sludge, *Water Research* 38 (2004) 1653–1662.

Sonotrogic ultrasonics technology, In www.sonotronic.com. [Last accessed the 27th of November 2012].

Speece R.E. Anaerobic biotechnology for industrial Wastewaters 1996, Vanderbilt University.

Sponza, D.T., Toxicity and treatability of carbontetrachloride and tetrachloroethylene in anaerobic batch cultures, *International biodeterioration & biodegradation* 51 (2003) 119-127.

STOWA-Stichting Toegepast Onderzoek Waterbeheer. In http://www.stowa-selectedtechnologies.nl/ [Last accessed the 27th of November 2012].

Stuckey, D.C.; McCarty, P.L. The effect of thermal pre-treatment on the anaerobic biodegradability and toxicity of waste activated sludge, *Water Research* 18 (1984) 1343-1353.

Stuckey, D.C.; McCarty, P.L. Thermochemical pre-treatment of nitrogenous materials to increase methane yield, *Biotechnology and Bioengineering Symposium* 8 (1979) 219-233.

Stumm, W.; Morgan, J., Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. Wiley Interscience, New York, USA.

Suh Y.-J., Rousseaux, P. An LCA of alternative wastewater sludge treatment scenarios. *Resources, Conservation and Recycling*, 2002. 35(3): p. 191-200.

Talinli I., A.G.K., Interference of hydrogen peroxide on the standard COD test. *Water Research*, 1992. 26(1): p. 107-110.

Tanaka, S.; Kamlyama, K. Thermochemical pre-treatment in the anaerobic digestion of waste activated sludge, *Water Science and Technology* 46 (2002) 173-179.

Tanaka, S.; Kobayashi, T.; Kamiyama, K.I.; Bildan, L.N. Effects of thermochemical pre-treatment on the anaerobic digestion of waste activated sludge, *Water Science and Technology* 35 (1997) 209-215.

Thomas, L.; Jungschaffer, G.; Sprössler, B. Improved sludge dewatering by enzymatic treatment, *Water Science and Technology* 28 (1993) 189-192.

Tiehm, A.; Mickel, K.; Zellhorn, M.; Neis, U. Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization, *Water Research* 35 (2001) 2003-2009).

Torrens, E.; Stüber, F.; Fabregat, A.; Fortuny, A.; Bengoa, C.; Font, J.; Cabré, J., Oriol, I.; García, R., Bresó, J.; Rovira, E. (2011).

Chapter 1: Reduction and stabilisation of the excess and toxicity of sludge in anaerobic conditions. A Reduction, Modification and Valorisation of Sludge. REMOVALS (pp. 1 - 36). IWA Publishing - N. ISBN: 978-1843393450.

Torrens, E.; Stüber, F.; Fabregat, A.; Fortuny, A.; Bengoa, C.; Font, J.; Legrand, J.; Loubière, K.; Cabré, J., Oriol, I.; García, R., Bresó, J.; Rovira, E. (2011). Chapter 2: Sludge stabilisation in autothermal conditions. A Reduction, Modification and Valorisation of Sludge. REMOVALS (pp. 37 - 51). IWA Publishing - N. ISBN: 978-1843393450.

UNE-EN 1189:1997, Water quality. Determination of phosphorous, ammonium molybdate spectrometric method. Asociación Española de Normalización y Certificación (1997), Madrid, Spain.

UNE-EN 25663:1994, Water Quality. Determination of Kjeldahl nitrogen. Method after mineralization with selenium (ISO 5663:1984) Asociación Española de Normalización y Certificación (1994). Madrid, Spain.

UNE 77003:1989, Water Quality. Determination of biochemical oxygen demand after *n* days (BOD_n). Dilution and seeding method. Asociación Española de Normalización y Certificación (1989), Madrid, Spain.

Valcke, D.; Verstraete, W., A practical method to estimate the acetoclastic methanogenic biomass in anaerobic sludges, *Journal Water Pollution Control Federation* 55 (1983) 1191-1195.

Valo, A.; Carrère, H.; Delgenès, J.P. Thermal, chemical and thermo-chemical pre-treatment of waste activated sludge for anaerobic digestion, *Journal of Chemical Technology and Biotechnology* 79 (2004) 1197-1203.

Vlyssides, A.G.; Karlis, P.K.; Thermal-alkaline solubilization of waste activated sludge as a pre-treatment stage for anaerobic digestion, *Bioresource Technology* 91 (2004) 201-206.

Wantanabe H., Kitamura T., Ochi S., Ozaki M., Inactivation of pathogenic bacteria under mesophilic and thermophilic conditions, *Water Science and Technology 36 (1997) 25-32.*

Wang, Q.; Noguchi, C.; Hara, Y.; Sharon, C.; Kakimoto, K.; Kato, Y. Studies on anaerobic digestion mechanism: influence of pretreatment temperature on biodegradation of waste activated sludge, *Environmental Technology* 18 (1997) 999-1008.

Wang, W.; Hiraoka, M.; Takeda, N.; Sakai, S.; Goto, N.; Okajima, S. Solubilization of sludge solids in thermal pre-treatment for anaerobic digestion. *Proceedings of Environmental Sanitary Engineering Research* 24 (1988) 41-54.

Wang, Z.; Wang, W.; Zhang, X.; Zhang, G. Digestion of thermally hydrolyzed sewage sludge by anaerobic sequencing batch reactor, *Jorunal of Hazardous Materials* 162 (2009) 799-803

Wantanabe H., Kitamura T., Ochi S., Ozaki M., Inactivation of pathogenic bacteria under mesophilic and thermophilic conditions, *Water Science and Technology* 36 (1997) 25-32

Wayne T.W., W.I.C., Ping H.L., Kwang V.L., A Hydrogen Peroxide/Microwave Advanced Oxidation Process for Sewage Sludge Treatment. *Journal of Environmental Science and Health Part A,* 2006. 41: p. 2623-2633.

Weemaes, M.; Verstraete, W. Evaluation of current wet sludge disintegration techniques, *Journal of Chemical Technology and Biotechnology* 73 (1998) 83-92.

Wei, Y.; Van Houten, R.T.; Borger, A.R.; Eikelboom, D.H.; Fan, Y. Minimization of excess sludge production for biological wastewater treatment, *Water Research* 37 (2003) 4453–4467.

Wolin, E.A.; Wolin, M.J.; Wolfe, R.S., Formation of methane by bacterial extracts, *The Journal of Biological Chemistry*, 288 (1963) 2882-2886.

Wong, W.T.; Chan, W.I.; Liao, P.H.; Lo, K.V. A Hydrogen Peroxide/Microwave Advanced Oxidation Process for Sewage Sludge Treatment, *Journal of Environmental Science and Health Part A* 41 (2006) 2623-2633.

Woodard, S.E.; Wukasch, R.F. A hydrolysis/thickening/filtration process for the treatment of waste activated sludge, , *Water Science and Technology* 30 (1994) 29-38.

WHO, World health organisation, http://www.who.int/topics/cholera/about/en/index.html [Last accesed the 27th of November 2012]

Yang, P.I.; Gaudy, Jr. A.F. Control of biological solids concentration in extended aeration, *Journal of the Water Pollution Control Federation* 46 (1974) 543-553.

Yang, P.I.; Gaudy, Jr. A.F. Nitrogen metabolism in extended aeration processes operated with and without hydrolytic pre-treatment of portions of the sludge, *Biotechnology and Bioengineering* 16 (1974) 1-20.

Kang Y.W., C.J.-J., Hwang K.-Y., Correction of hydrogen peroxide interference on standard chemical oxygen demand test. *Water Research*, 1999. 33(5): p. 1247-1251.

Yeom, I.T.; Lee, K.R.; Lee, Y.H.; Ahn, K.H.; Lee, S.H. Effects of ozone treatment on the biodegradability of sludge from municipal wastewater treatment plants, *Water Science and Technology* 46 (2002) 421-425.

Zábranská J., Štěpová J., Wachtl R., Jeníček P., Dohányos M., The activity of anaerobic biomass in thermophilic and mesophilic digesters at

different loading rates, *Water Science and Technology* 42 (9) 49-55, 2000.

U.S. Peroxide, Product information: interferences with analytical methods.

ANNEX I

Applicable legislation

AI.1. Catalan legislation

This section presents the applicable legislation concerning bio solids waste management in Catalonia (ACA, Programa d'actuacions per a la gestió dels fangs de deupuradora d'aigües residuals urbanes per al 2009-20014)

- Legislative Decree 3/2003, of 4 November, which approves the revised text of the legislation on water in Catalonia.
- Decree 380/2006, of 10 October, which approves the Regulation of water planning.
- Decree 130/2003, of 13 May, which approves the Regulation of public sewage services.
- Legislative Decree 1/2009, of 21 July, approving the revised text of the waste regulation law.
- Decree 93/1999 of 6 April on waste management procedures.
- Decree 1/1997 of 7 January on the disposition of the rejection of waste in controlled landfills.
- Decree 283/1998, of 21 October, Designation of vulnerable areas related to nitrate contaminants generated from agricultural sources.
- Order 22 October 1998, the Code of agricultural practices in relation to nitrogen.
- Decree 93/1999 of 6 April on management procedures waste.
- Governmental agreement of 3 April 2000 on the prevention and correction plans of nitrate pollution.
- Decree 119/2001, of May 2, approving environmental measures for the prevention and correction of water pollution by nitrates.
- Decree 476/2004 of 28 December, which is declares new vulnerable areas related with nitrate contaminants generated by agriculture sources.
- Decree 221/2005 of 11 October, on the application of conditionality in relation to the direct support of the common agricultural policy.
- Decree 136/2009 of 1 September, approving the action plan applicable to vulnerable areas in relation to nitrate pollution originating from agricultural sources and management of livestock manure.
- Governmental agreement 128/2009 of 28 July, review and designation of new vulnerable areas in relation to nitrate pollution from agricultural sources.

AI.2. Spanish legislation

This section presents the applicable legislation concerning bio solids waste management in Spain (ACA, Programa d'actuacions per a la gestió dels fangs de deupuradora d'aigües residuals urbanes per al 2009-20014)

- Royal Decree 1310/1990, of 29 October, which regulates the utilisation of sewage sludge in the agricultural sector.
- Order of 26 October 1993 on the use of sewage sludge in agriculture.
- Royal Decree-Law 11/1995, of 28 December, which establishes the rules for the treatment of urban waste water.
- Royal Decree 261/1996 of 16 February on the protection of waters against pollution caused by nitrates from agricultural sources.
- Order MAM/304/2002 of February 8, where are published the valorization and disposal wastes and the European waste list.
- Resolution of 20 January, 2009, approving the National Integrated Waste Plan for the period 2008 -2015.
- Royal Decree 653/2003, of May 30, about waste Incineration.
- Royal Decree 2352/2004, of 23 December, about on the application of conditionality in relation to direct payments under common agricultural policy.
- Royal Decree 824/2005 of 8 July on fertilizer products.

AI.3. European legislation

This section presents the applicable legislation concerning bio solids waste management in Europe (ACA, Programa d'actuacions per a la gestió dels fangs de deupuradora d'aigües residuals urbanes per al 2009-20014)

- Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture.
- Directive 2006/12/EC of the European Parliament and of the Council of 5 April 2006 on waste (Text with EEA relevance).

- Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives (Text with EEA relevance).
- Council Regulation (EEC) No 259/93 of 1 February 1993 on the supervision and control of shipments of waste within, into and out of the European Community.
- Council Directive 80/68/EEC of 17 December 1979 on the protection of groundwater against pollution caused by certain dangerous substances.
- Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment.
- Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources.
- Council Resolution of 24 February 1997 on a Community strategy for waste management.
- Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste.
- Working Document on Sludge 3rd Draft, ENV.E.3/LM, Brussels. 27th April 2000.
- 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.
- Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste.
- 2000/532/EC: Commission Decision of 3 May 2000 replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste (notified under document number C(2000) 1147) (Text with EEA relevance).
- Council Regulation (EC) No 1782/2003 of 29 September 2003 establishing common rules for direct support schemes under the common agricultural policy and establishing certain support schemes for farmers and amending Regulations (EEC) No 2019/93, (EC) No 1452/2001, (EC) No 1453/2001, (EC) No 1454/2001, (EC) 1868/94, (EC) No 1251/1999, (EC) No 1254/1999, (EC) No 1673/2000, (EEC) No 2358/71 and (EC) No 2529/2001.
- Commission Regulation (EC) No 796/2004 of 21 April 2004 laying down detailed rules for the implementation of cross-compliance,

modulation and the integrated administration and control system provided for in of Council Regulation (EC) No 1782/2003 establishing common rules for direct support schemes under the common agricultural policy and establishing certain support schemes for farmers.

- 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.

ANNEX II

Use of pre-treatments. Industrial applications

AII.1. CAMBI and BioThelys PROCESS

The Cambi and BioThelys (CAMBI-biosolids tratement, 2012) are the commercial name of what is known as the thermal hydrolysis process (THP), where sludge is pre-treated with a high pressure steam before anaerobic digestion.

Its main purpose is to increase the biological degradation of the organic part of the sludge and also the biogas production by the principle of enhancing hydrolysis which generates readily available organic matter for the subsequent anaerobic digestion. It also facilitates the separation of solid and liquid phase after digestion.

The process diagram can be seen in figure AII.1. and it can be summarized as follows. First the sludge is dewatered to 16-17% dry solids (DS). Then the sludge is pre-heated in the pulper tank by recycled steam. The process gases generated are compressed and reinjected in the digesters to broken down biologically in the digesters (no odour). The thermal hydrolysis takes place in a reactor operated in a batch mode, at 165ºC for 20-30 minutes where steam is added at P~12bar. After that the pressure is released at approximately 2 bar and the sludge temperature is decreased to approximately 102º C in the flash tank. Before anaerobic digestion the sludge is cooled at the required digestion temperature partly by adding dilution water and partly with heat exchangers.

Performance:

- The thermal hydrolysis process can dissolved about 27% of the COD in the sludge. (STOWA, 2012)
- Followed by anaerobic digestion can convert 50-65% of the organic matter (VS content) into biogas
- Complete pathogen destruction
- It shortens the retention time in the anaerobic digestion to 10-12 days.
- The dewaterability of the digested sludge is highly improved; DS contents of 30-40% can be achieved.

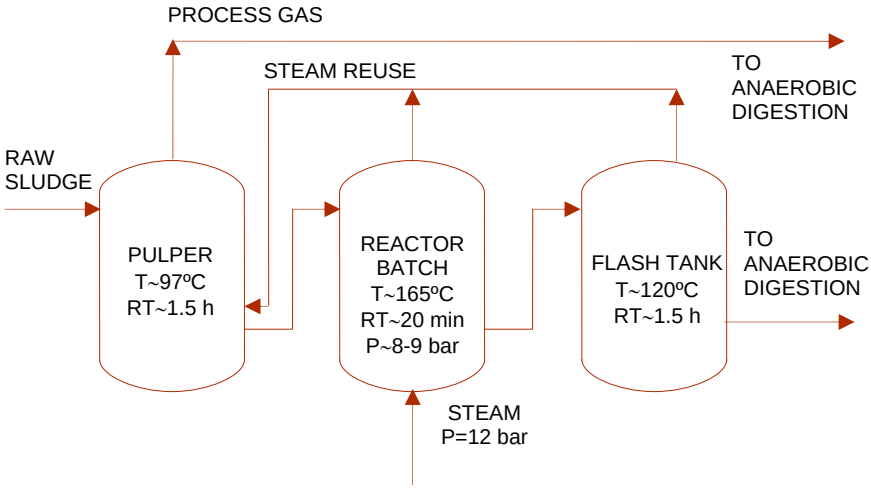

Figure AII.1. Cambi process design

This technology has been successfully applied to treat sludge from wastewater treatment plants for populations upwards from 150000, with a sludge production from approximately 4000 dry tonnes/year of sludge and up. In table AII.1 are listed several industrial applications and the type of substrate treated.

The CAMBI technology that has been used since 1995 by, it has been commercialised by Cambi AS, a company based in Norway, in table AII.1 are listed several industrial applications of this process. BioThelys^{TM} is commercialized by Veolia Water Solutions & Technologies and has also been implemented successfully in Samur (France) with an operation capacity of 1400 tonnes DS/year, and in Château-Gontier (France) design for 1000 tonnes DS/year, both operating since 2

004.

Table AII.1. Industrial applications of Cambi process over sludge

WWTP	Capacity (tonnes DS/year)	Sludge type
HIAS, Hamar,Norway (1995)	3600	Municipal, mixed primary, secondary and chemical
Thames Water, Chertsey, England (1999)	8000	Municipal, mixed primary and secondary
The Næstved Plant, Denmark (2000)	1600	Municipal, waste activated sludge
Nigg Bay WWTP Aberdeen, Scotland	16500	Municipal, mixed primary and secondary

(2001)		
Ringsend Sewage Treatment Works, Dublin, Ireland (2002)	36000	Municipal, mixed primary and secondary
Fredericia, Denmark (2002)	8000	Municipal and industrial waste activated sludge
Borregaard Industries Ltd., Sarpsborg, Norway (2000)	4000	Waste activated sludge from pulp factory
"Mjøsanlegget" plant for bio-waste Lillehammer, Norway (2001)	14000	Bio-degradable MSW
Niigata, Japan (pilot/test plant) (2002)	1200	Municipal, mixed primary, secondary
WWTP Kapusciska, Bydgoszcz, Poland (2005)	7650	Municipal, mixed primary, secondary
Bruxelles Nord, Belgium (2006)	18800	Municipal, mixed primary, secondary
Oxley Creek, Brisbane, Australia (2006)	10800	Municipal waste activated sludge
Ecopro Multiwaste Plant, Verdal, Norway (2006)	40000-45000	Biodegradable fraction of Municipal Solid Waste

Capital costs for installing Cambi process in the Hammar WWTP (Norway) for treating 3600tn DS/year have been reported to be $6 million dollar with an approximate operational and maintenance cost of $360 per dry tone of sludge treated (EPA 832-R-06-005 2006).

AII.2. MICROSLUDGE®

MicroSludge® (MICROSLUDGE, 2012) is a chemical and pressure pre-treatment process that increases both the rate and extent that WAS is degraded in an anaerobic digester. It is commercialised by Paradigm Environmental Technologies Inc.

Again, this technology pursues the hydrolysis enhancement of the organic material in order to improve anaerobic sludge digestion. The process diagram is depicted in figure AII.2. The process is designed to operate for continuous flow. Thickened sludge (5 to 10% TS) first flows through a coarse filter, before caustic (NaOH) is added in order to weaken cell membranes and reduce viscosity. Sludge and caustic are mixed and moved to the conditioning tank. Then the chemical treated sludge is transferred through a gas/liquid separator and fine self-cleaning filter, before being fed to the Cell Disrupters, where pressure is drop from approximately 830 bar to 3.5 bar in one millisecond, with a temperature increase of around 25ºC causing bacterial cell lyses before the aerobic digester.

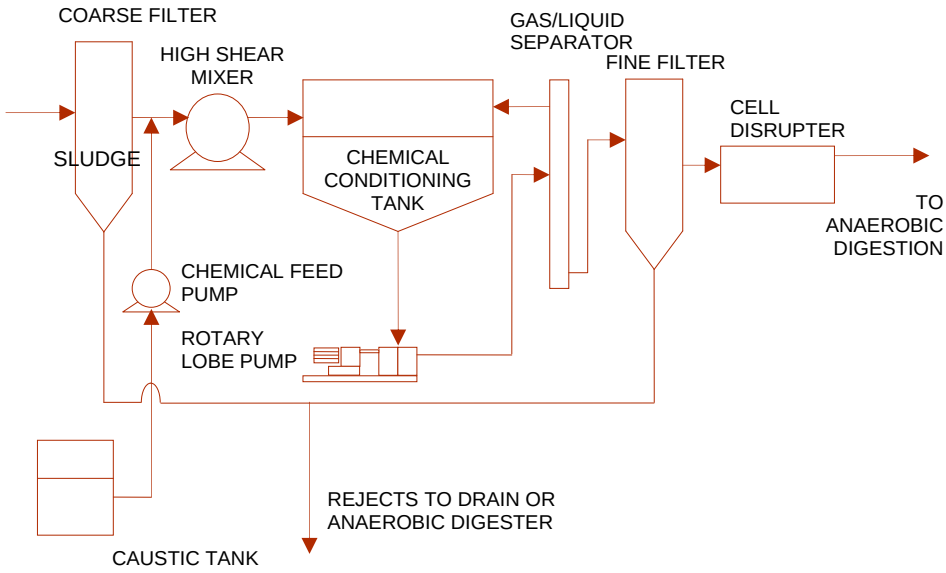

Figure AII.2. Microsludge® process diagram

This technology has been tested in full-scale at the Chilliwack Wastewater Treatment Plant near Vancouver, Canada in 2004 and in Los Angeles County Sanitation Districts Joint Water Pollution Control Plant in October 2005. Neither is currently operating (EPA 832-R-06-005 2006).

Performance:

- Average of 85% of VS reduction as compared to 30% VS reduction without MicroSludge.
- Reduces the total quantity of biosolids for disposal by an additional 60%.
- MicroSludge destroys pathogens (MICROSLUDGE, 2012)
- Biogas is increased, but not reported.

For processing approximately 70000m^3 of thickened WAS/year the capital costs would be between 1.7-2 million USD, (without installation costs). The operational and maintenance are estimated to be $68-$119 per dry ton of WAS. Electricity is the largest operating cost contributor requiring 500-1000kWh/ton of dry solids (EPA 832-R-06-005 2006).

AII.3. ULTRASOUND

Ultrasound is applied at high intensity and between low and medium frequencies to sludge in order to break down the cell walls by cavitation.

Cavitation causes a rapid creation, growth and collapse and implosion of microscopic bubbles as is represented in Figure AII.2, the collapsing bubbles disrupt adjacent bacterial cells by extreme shear forces, rupturing the cell wall and membranes (Khanal et al. 2011).

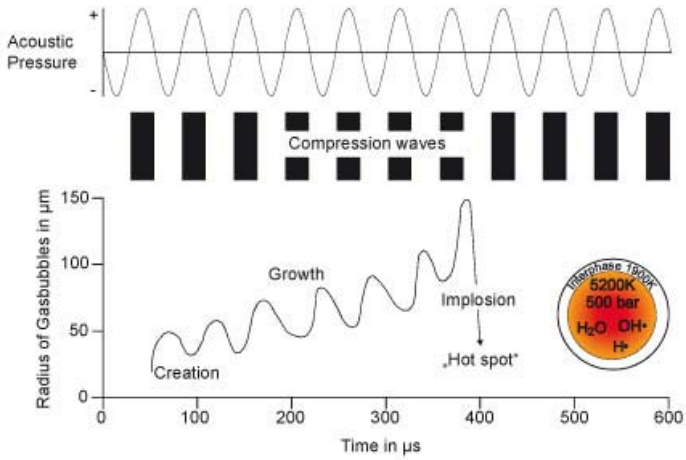

Figure AII.3. Representation of the cavitation phenomena (www.http://www.sonotronic.com)

The Sonix™ and the Sonolyzer™ are technologies that can be found in the market commercialised by Ovivo and Sonotronic Ultrasound Technology respectively. They have been mainly applied into thickened WAS making

the sludge easier to digest, industrial applications can be found in table AII.2.

The Sonotronic system works with the frequency of 20 kHz which gives the best reactions and effects in the biomass. Again the power consumption significantly impact operational and maintenance costs. (EPA 832-R-06-005 2006).

Performance (Sonotronic ultrasonics technology, 2012)

- Increased profitability of biogas installations, methane content of the biogas increases (up to 70% of CH_4)
- Increased biogas production (up to 50%)
- Shortening of digestion time (up to 60%)
- Reduction in residual sludge (up to 30 %)
- Reduction in the costs of a waste water treatment plant in sludge treatment by roughly 50 %

Table AII.2. Industrial aplications of ultrasound pretreatment over sludge

WWTP	Capacity (tonnes DS/year)	Sludge type	Ultrasound load (kW)
Darmstadt MWTP Germany (2000)	180000	Municipal, mixed primary, secondary	16
Süd Treatment W. Germany (2000)	40000	Municipal waste activated sludge	6
Detmold Germany (2000)	95000	Municipal, mixed primary, secondary	14
Mannheim Germany (2001)	725000	Municipal, mixed primary, secondary	24
Rüsselsheim MWTP Germany (2001)	800000	Municipal, mixed primary, secondary	10
Wiesbaden MWTP Germany (2002)	360000	Municipal, mixed primary, secondary	48
Kävlingue MWTP Sweden (2002)	N.A.	Municipal, mixed primary, secondary	N.A.
Bad Bramstedt SW Germany (N.A.)	N.A.	N.A.	N.A.
Mangere MWTP New Zeland (N.A.)	80000	N.A.	432

N.A.: Information not available

The capital costs based on a 19000-30000m ^{3} facility are reported to be approximately $265000. The operational and maintenance are estimated to be $10000-$20000. Electricity again significantly impact this latter costs (EPA 832-R-06-005 2006).

AII.4. OTHERS

Biodiet technology has been developed by Kankyo Engineering Company in Japan. It is applied into WAS. BioDiet method promotes biological disintegration of the organic matters into water and carbon dioxide gas reducing sludge volume. The technology is applied in a single module where a reducing agent is added, with a reaction period of about 1.5 hr (GEC, 2012). It is claimed to be applied in a food plant leading to a 80% of reduction of secondary sludge generation, in this case, the Biodiet process is applied to the WAS and then re-introduced in the aerobic tank (Ichiro 2003). No more information about this process has been found available.

Porteous process This process is based in thermal hydrolysis, where sludge is heated to 130–200ºC for about 30 minutes at the corresponding vapour pressure (Neyens and Baeyens 2003). This process has been one of the first hydrolysis processes implemented in the industry, but mainly applied in the conditioning step to improve dewaterability. The first Porteous process installation were in UK, Halifax and Horsham in 1939, and up to 30 installations were installed in the late 1960s, in table AII.3. are reported some installations. Operating problems and energy costs increase make the operation of these plants unaffordable and where closed in the 1980s.

Table AII.3. Industrial applications of porteous process

WWTP	Sludge type	Effect
Halifax and Horsham , UK	Not specified	52% of TS
Colorado Springs	Not specified	from 20 – 25 % DS to 40 – 50 % DS
Pudsey	Not specified	50% DS

Zimpro process (SIEMENS, 2012). This is a wet air oxidation process, which was extended to the municipal sewage market in the late ‘50s and early ‘60s. This process originally worked at 250ºC at pressures less than 35 bar, and it is reported to destroy up to 65% of COD. In 1961 Zimpro installed a wet oxidation plant able to treat 3 ton DS /day in Wausau. Also in Wheeling was installed and operated a wet oxidation unit of 5.6 tons DS/day and one oxidation system of 200 ton DS/day was installed at the West-

Southwest Treatment Plant of the Metropolitan Sanitary District of Greater Chicago. The main objective of these plants was sludge destruction, however all were closed due problems of odous, corrosion and high strength COD liquor (Neyens and Baeyens 2003). Latter modifications of this Zimpro process in 1967, lead to the creation of the Zimpro Low Pressure Oxidation (LPO or Thermal Sludge Conditioning) system (SIEMENS, 2012), which works at reduced temperatures (<200ºC) and very little oxidation is occurring. This process is still industrially used but as a conditioning step for dewatering improvement.

Synox, Protox and Krepro. This commercial process are based on acid or alkaline or combined with thermal process in order to improve sludge hydrolysis, however it has not been successfully commercialized due to high costs and poor-quality product. Neyens and Baeyens 2003)

Kady Biolysis. Mechanical treatment

Kurita Bioleader. Ozone treatment, (Camacho et al. 2002). The process works by withdrawing sludge from the aeration tank or secondary clarifier and passing it through an ozone contactor before recirculating it to the aeration tank. The ozonation results in an increased biodegradability thus decreasing the overall amount of sludge generated in the treatment. About 0,05 to 0,15 kg O_3/kg DS are required

The operating costs are mainly linked to the electricity consumption of the process. Electricity is necessary for the ozone production and additional aeration in the aeration tanks. The energy consumption is in the range of 0,6 to 1,8 kWh/ kg dry solids (DS). With a current price of 0,08 euro/kWh (12/2001) the overall operating costs are given as 52 to 160 euro/t DS (STOWA)