

Sludge hydrothermal treatments. Oxidising atmosphere effects on biopolymers and physical properties

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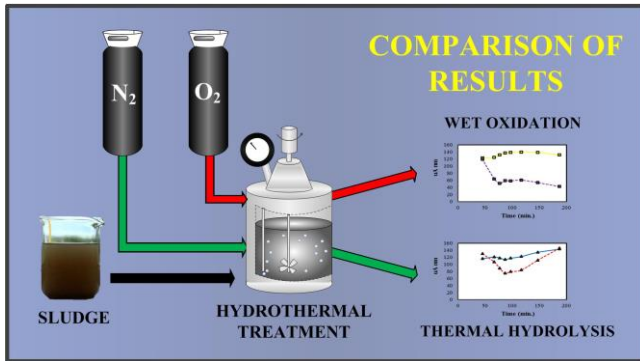
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ABSTRACT

In this work, the role of an oxidising atmosphere during the hydrothermal treatment of an activated sludge at 160 °C and 40 bar, was determined. The composition and molecular weight sizes of the soluble biopolymers generated during the sludge treatment in presence (wet oxidation “WO”) or absence (thermal hydrolysis “TH”) of oxygen were compared. Likewise, the characteristics of organic material, settleability, colour and pH of the treated sludge during both treatments were analysed. The thermal treatment in presence of oxygen provided better results in terms of solubilisation, settleability and mineralisation. WO initially favoured a more intense cellular lysis, causing a higher degree of solubilisation than that achieved by TH. Either in presence or absence of oxygen, thermal treatments caused a marked worsening of the settleability of the sludge. However, the degradation of biopolymers during WO led subsequently to an improvement of the settleability properties for longer reaction times. Both treatments caused a fast solubilisation of biopolymers at the beginning by effect of the release of extracellular and intracellular material from sludge. Subsequently, the presence of oxygen produced a significant decrease in the concentration of those biopolymers. In contrast, the proteins were the only one biopolymer that was degraded during TH.

KEYWORDS: Oxidation state; Proteins; Settleability; Size distribution; Thermal hydrolysis; Wet oxidation

TOC-abstract art



1. Introduction

Sewage sludge is an inevitable by-product in wastewater treatment plants (WWTP), which management is very complicated due to the high volumes generated and its high water content. Current sewage sludge treatment and disposal methods, such as landfilling, incineration and gasification require drying the sludge, a costly pre-treatment step, and/or risk contaminating the environment (Silva et al., 2016).

In this regard, hydrothermal processing has progressively been recognised as an attractive alternative for the sludge management during the last years. Hydrothermal treatments refer to technologies involving reactions carried out in an aqueous solvent at elevated temperatures and pressures, under inert (thermal hydrolysis) or oxidising (wet oxidation) atmospheres. Either wet oxidation (WO) or thermal hydrolysis (TH) allow the breakage of floc structure by means of solubilisation and degradation of EPS and cellular lysis (Hii et al., 2014).

In sludge treatment, hydrothermal processing has traditionally had three main goals: the enhancement of a subsequent anaerobic digestion process, the reduction of the solid COD and/or the reduction of waste mass and volume (Barber, 2016; Chung et al., 2009; Genç et al., 2002; Khan et al., 1999). These approaches explain why, although the literature about sludge thermal treatments is abundant, the vast majority of these studies are only focused on the measurement of degrees of solubilisation and mineralisation, biodegradability indexes and/or biochemical methane potentials before and after treatment (Abe et al., 2011; Strong et al., 2011; Urrea et al., 2015). Nevertheless, information about the effects of thermal treatments on the composition or on other properties of the hydrolysed sludge is very scarce or does not even exist. As example, thermal treatments involve the release of high amounts of polymeric substances into the bulk medium during the cellular lysis, whose composition, concentration and molecular

size will vary with the reaction time, especially under an oxidising atmosphere (Hii et al., 2014; Urrea et al., 2016). Evidently, information about the composition and properties of these biopolymers would be very interesting in order to design the following step of treatment of the hydrolysed sludge. For instance, fouling in membrane bioreactors is greatly affected by the protein and carbohydrates contents as well as their molecular sizes (Judd, 2011). In a similar way, the composition of soluble biopolymers in the medium also has effect on its viscosity, the settleability and wettability of the remaining solids or the biodegradability and chemical properties of the supernatant (Liu et al., 2013; Martins et al., 2011; Ruiz-Hernando et al., 2015; Wang et al., 2014; Zhang et al., 2015). Moreover, taking into account that sewage sludge consists of 61% proteins and 11% carbohydrates (Chen et al., 2007), this gives rise to the following question: is it possible to obtain valuable products from the sludge by means of thermal treatments? Obviously, the first step to answer this question is to know the products obtained and the mechanisms involved in their formation.

Nevertheless, as it was previously mentioned, information about composition and properties of the products formed during thermal treatments (soluble biopolymers, mainly) are very scarce and deals only with TH processes. Thus, Ramirez et al. (2009) pointed out that soluble proteins, carbohydrates and lipids concentrations increased with increasing temperature for a fixed time and that proteins were released easier than carbohydrates from the VSS. However, Bougrier et al. (2008) and Li and Noike (1992) indicated that carbohydrates were more hydrolysable than proteins, and proteins more hydrolysable than lipids in turn. For temperatures ranging from 130°C to 220°C, soluble carbohydrates concentration decreased due to reactions between them or with soluble proteins (Bougrier et al., 2008; Ramirez et al., 2009). In the case of proteins, Xue et al. (2015) observed that the rise in their concentration with temperature is accompanied by

an increase in the ammonia nitrogen concentration. Bougrier et al. (2008) and Donoso-Bravo et al. (2011) concluded that volatile fatty acids are produced by lipid degradation instead of by protein decomposition. Yin et al. (2015) studied the time and temperature dependence of soluble proteins and carbohydrates and ammoniacal nitrogen, and found that at 220 - 300°C, soluble proteins and carbohydrates went through a maximum with the reaction time, and that the higher the temperature, the lower the time at which the maximum appear. At this point, it is important to stress that, although information about the composition of soluble biopolymer during the sludge TH is available, there is no studies dealing with the properties of these biopolymers, such as their molecular weight size.

Regarding the WO of sludge, the majority of the works about this technique are exclusively focused on volatile fatty acids, which are the main chemicals generated by WO of biomass (He et al., 2008; Hii et al., 2014), and specially, on acetic acid, whose concentrations usually exceed those of the other acids. In fact, no studies on the effects of the WO on the composition of soluble biopolymers have been found. Regarding the properties of these polymers, to the best of our knowledge, there is only a work, corresponding to our research group, in which the molecular weight distribution of the solubilised matter during a WO treatment was determined by size exclusion chromatography (Urrea et al., 2016).

Therefore, based on the foregoing, the aim of this work is to study and compare, for the first time, the effects of hydrothermal treatments (TH and WO) on the composition and molecular weight sizes of the soluble biopolymers generated during the treatment as well as on the “classical” parameters of solubilisation, mineralisation and settleability.

2. Material and methods

2.1 Sludge samples

The activated sludge employed in the experiments was obtained from a municipal wastewater treatment plant of the region (Asturias-Spain). The sludge was extracted of a unit of thickening by flotation and stored at 4 °C until its subsequent use. The characteristics of the sludge were as follow: total suspended solids (TSS): 31.9 g/L, volatile suspended solids (VSS): 26.5 g/L, sludge volume index (SVI): 31 mL/g, total chemical oxygen demand (TCOD): 37.2 g O₂/L, soluble chemical oxygen demand (SCOD): 0.2 g O₂/L, soluble total organic carbon (soluble TOC) 0.4 g C/L, initial pH: 6.5, soluble protein: 181 mg/L, soluble humic acids: 281 mg/L and soluble carbohydrates: 82 mg/L.

2.2 Experimental setup

The experiments of TH or WO were carried out in a PARR series 4520 reactor with a propeller stirrer (500 rpm). Oxygen (WO) or nitrogen (TH) previously conditioned in a humidifier, were fed since the beginning of the experiment to a constant flow rate of 1.2 L/min. Pressure was adjusted through a backpressure controller located at the end of the gas line, whilst the reactor temperature and the oxygen flow were regulated by means of PID controllers. The operating conditions stablished to carry out the reaction were 160 °C and 40 bar. Eight samples were taken at different times of reaction. The first one was withdrawn when 100 °C were reached in the reactor (45 minutes). The following samples were extracted periodically from minute 67, when the operating conditions were reached, to the end of the treatment (187 minutes).

2.3 Analytical Methods

The analysis corresponding to total suspended solids (TSS), volatile suspended solids (VSS), fixed suspended solids (FSS), chemical oxygen demand (COD), sludge volume index (SVI) and pH were performed according to Standard Methods (APHA, 1998).

In order to quantify the biopolymers solubilisation, their concentrations were measured by the following colorimetric methods: proteins and humic acids by the modified Lowry method (Frolund et al., 1995), using BSA and humic acids as standards, respectively, and carbohydrates by the Dubois method (Dubois et al., 1956), employing glucose as standard. UV-VIS scans from 190 to 900 nm were performed for supernatants employing a T80 UV/VIS spectrophotometer (PG Instruments Ltd). The colour of the soluble samples was determined by means of the colour number (CN), which is defined according to equation 1 (Tizaoui et al., 2007).

$$CN = \frac{SAC_{436}^2 + SAC_{525}^2 + SAC_{620}^2}{SAC_{436} + SAC_{525} + SAC_{620}} \quad (1)$$

Where SAC_i corresponds to the spectral absorption coefficient at a wavelength of i nanometers.

Soluble total organic carbon (TOC) was measured using a TOC analyser (Shimadzu TOC-VCSH, Japan). The mean oxidation number of organic carbon (MOC) was calculated from the equation 2 (Vogel et al., 2000).

$$MOC = 4 - 1.5 \frac{COD}{TOC} \quad (2)$$

Where COD and TOC values are expressed in g O₂/L and g C/L, respectively, and MOC takes values from -4 (i.e. for methane) to +4 (i.e. for carbon dioxide).

2.4 Size exclusion chromatographic analysis (HP-SEC)

The size distribution of the solubilised biopolymers, commonly called “fingerprints”, was performed by High Performance Liquid Chromatography (Agilent 1200, Agilent Technologies Inc., California, USA), using a Yarra SEC-2000 (300 × 7.8 mm) column.

A NaNO₃ solution was employed in order to determinate the total column volume (11.8 mL). The mobile phase consisted of a buffer solution of 9 mM NaCl, 0.9 mM Na₂HPO₄ and 0.005% NaN₃, adjusted to pH 7.0 (\pm 0.1) with H₃PO₄, and with an ionic strength of 0.02. The flow rate employed was of 1 mL/min. All samples were filtered through 0.45 μ m PVDF filters (Millipore) prior to injection (20 μ l). The detection was carried out with a diode array UV detector at several wavelengths (210, 260 and 280 nm).

The calibration of the column was performed by means of a Protein Standard Mix (15-600 kDa) supplied by Sigma-Aldrich (69385), which was composed of four proteins: Ribonuclease A (13.7 kDa), Albumin (44.3 kDa), γ -Globulin (150 kDa) and Thyroglobulin (670 kDa), as well as a low molecular weight marker, *p*-aminobenzoic acid (0.14 kDa). The coefficient of determination (R^2) of the calibration curve was 0.93.

3. Results and discussion

3.1 Behaviour and characteristics of organic material during hydrothermal treatments

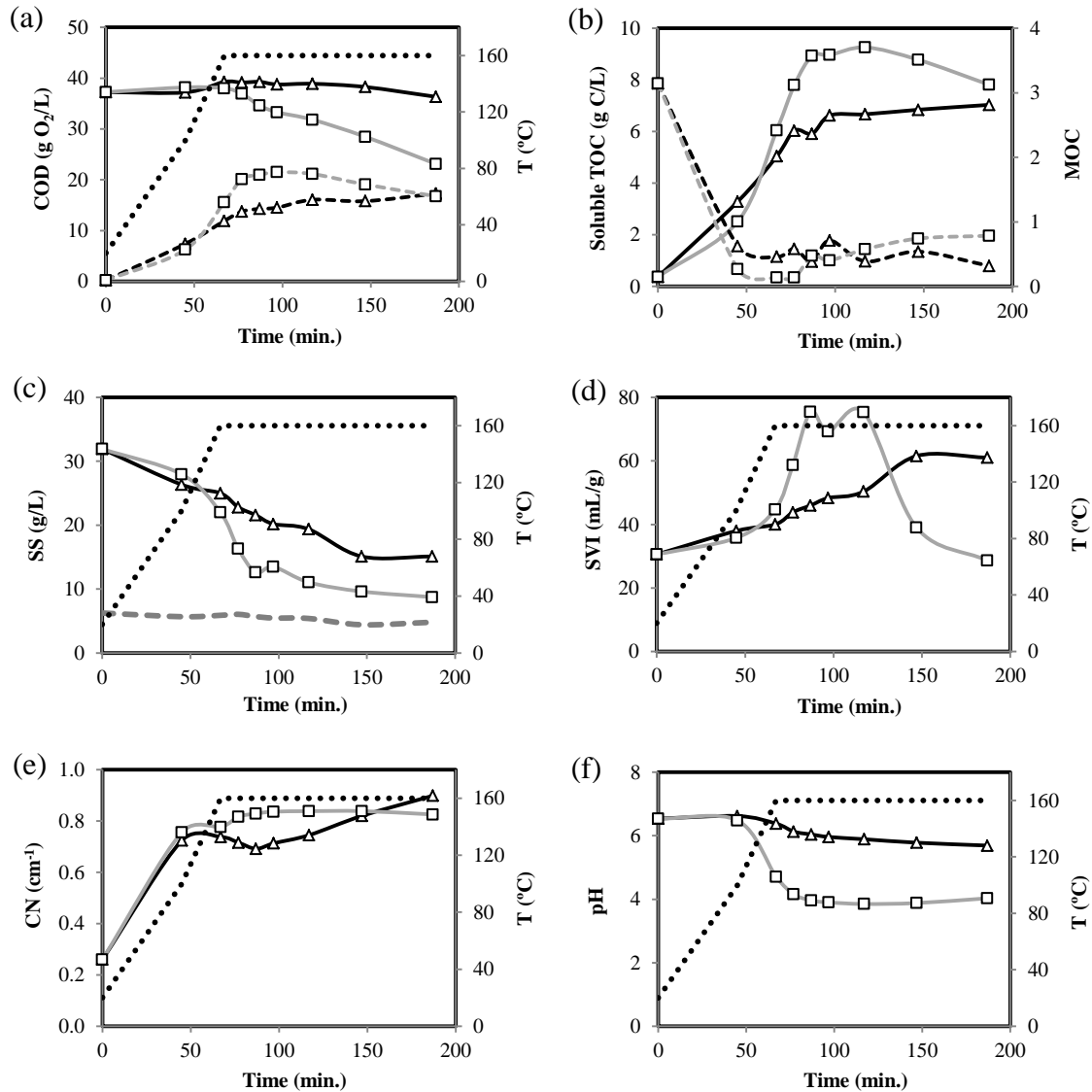


Figure 1. Effect of the presence (■) or absence (▲) of an oxidising atmosphere on sludge properties during the hydrothermal treatment at 160 °C and 40 bar. (a) COD evolution (solid and dashed lines represent TCOD and SCOD, respectively), (b) Soluble TOC (solid lines) and MOC (dashed lines) evolution, (c) TSS evolution (dashed line corresponds to FSS), (d) SVI evolution, (e) CN evolution and (f) pH evolution. Dotted lines represent the reactor temperature.

Figure 1a shows the evolution of total and soluble COD fractions during the TH or WO of an activated sludge. As has widely been commented in the literature, both treatments caused an increase in the soluble COD (SCOD), but WO also provoked a partial mineralization of the organic load of the sludge, thus observing a steady reduction of total COD (TCOD). In this case, TCOD decreased a 38% after 187 minutes of reaction in the case of WO, whereas it remained constant for TH.

It is interesting to point out that initially, when the temperature is not high enough (first 45 minutes, temperature lower than 160°C) the degree of mineralization achieved with both techniques was null. Nevertheless, the presence of an oxidising atmosphere does have effect on the solubilisation of the sludge, even at these low temperatures. The solubilisation of organic compounds from sludge was faster when reactions of oxidation were involved. So, when the operating conditions were achieved (67 minutes), the SCOD for WO was a 30% higher than for TH, while TCOD remained constant in both experiments. After 187 minutes of treatment, the solubilisation degrees of solid COD (COD_S) were 83% and 49% for WO and TH, respectively, as Figure 1a shows. Thus, it seems reasonable to propose that free radicals initially formed tend to attack the solid COD instead of mineralising the soluble COD, thus favouring a higher solubilisation. Therefore, it can be concluded that an oxidising atmosphere offers a higher effectiveness in terms of sludge solubilisation than an inert one.

Obviously, as the CODs decreases, oxidation reactions of the soluble COD prevail, which explain the continuous TCOD and SCOD reductions observed after an hour and a half of treatment by WO, whereas SCOD increased over time for TH experiments. In fact, although the degree of solubilisation was higher for WO (83%) than for TH (49%), similar SCOD were achieved at the end of the both treatments (a 46% of the initial TCOD of the sludge).

Soluble TOC results also corroborate the dual effect of the oxidising atmosphere on the thermal treatment of the sludge, improving the solubilisation of solid matter and, in turn, oxidising the dissolved one (Figure 1b). The final soluble TOC reduction observed for WO also reveals that part of the COD removal was due to total oxidation of the soluble organic matter towards carbon dioxide and water.

Regarding the mean oxidation number of organic carbon (MOC), results showed that the oxidation state of soluble compounds decreased sharply with both treatments, from an initial value of 3.2 ± 0.1 to 0.45 ± 0.15 after only 45 minutes of reaction. This reduction of the MOC was attributed to the release of extracellular polymeric substances (EPS) and intracellular material, whose oxidation state is lower than that of soluble biopolymers of raw sludge (higher COD per unit of organic carbon) (Urrea et al., 2016). Likewise, it was also noted that the initial decrease in the MOC was more marked for WO than for TH, probably due to the higher solubilisation of the sludge in presence of an oxidising atmosphere. In a previous work (Urrea et al., 2016), the relationship between more hydrophobic characteristics of organic compounds and lower MOC was theoretically proved. Therefore, the lower MOC obtained in WO experiments is explained by the higher degree of cell destruction attained, as the biopolymers that integrate the cell membrane, such as phospholipids and proteins, have a hydrophobic character. Nevertheless, as the reaction progresses, WO caused a moderated increase in the MOC since minute 97, due to the oxidation of those biopolymers towards more hydrophilic products, such as volatile fatty acids. In contrast, the MOC in TH decreased slightly as a result of the solubilisation but no oxidation mechanism.

3.2 Solubilisation of SS and effect on settleability

The TSS disintegration and its effect on the settleability properties of the sludge for each treatment are showed in Figures 1c and 1d. As previously explained, WO caused a

stronger impact on the solubilisation of the sludge than TH. In fact, the solubilisation degree of TSS achieved with WO after 77 minutes of treatment (49%) was almost the same obtained after 187 minutes of TH (53%). To the end of the reaction, TSS concentrations were 27% and 47% of the initial value for WO and TH, respectively. As expected, FSS concentrations do not change throughout both treatments.

It should be also pointed out that CODs/VSS ratio remained almost constant during the treatments, obtaining values of $1.5 \pm 0.2 \text{ g O}_2 \text{ g VSS}^{-1}$ and $1.6 \pm 0.2 \text{ g O}_2 \text{ g VSS}^{-1}$ for WO and TH, respectively. Burger and Parker (2013) reported a value of 1.44 for this ratio in an aerobic sludge without treatment, whereas 1.42 is commonly mentioned in the literature, which is obtained theoretically from the oxidation of the biomass ($\text{C}_5\text{H}_7\text{NO}_2$). No changes in the CODs/VSS ratio discard either the selective solubilisation of some compounds instead of others or the oxidation of the organic matter in the solid phase.

Regarding the effect of the thermal treatments on the settleability, both techniques initially lead to an increase in SVI, which means a worsening of its management during that stage (Figure 1d), as a result of an increase in the repulsion between particles by electrostatic forces. When 100 °C were reached, the flocculate structure of the sludge was destroyed by both thermal treatments, causing the release of extracellular polymeric substances and the formation of smaller particles. At this time, an initial slight increase of SVI was detected. Afterwards, while the concentration of TSS continued to decrease, the amount of solubilised biopolymers increased in the medium, which goes hand in hand with an increase in the SVI. These changes suggest that a higher concentration of solubilised biopolymers led probably to an increase in the negative surface charge of remaining solid particles, which caused a worse compaction of the latter such, as clearly reflected in the SVI evolution. In fact, the SVI remained constant between minutes 147

and 187 during the TH, coinciding with the period in which the solubilisation reactions had concluded. Zhen et al. (2012) reported that the zeta potential of an activated sludge decreased from -12.6 to -18.0 mV after its treatment by TH at 80 °C, being that result an evidence of the abovementioned.

In accordance with the previous explanation, the higher solids disintegration caused by the oxidant also involved a higher deterioration of the settleability, expressed as SVI. Nevertheless, as WO reactions progress, the SVI, after achieving a maximum in minute 117, began to drop. This is caused by the oxidation of the soluble biopolymers, thus reducing the negative surface charge of the solid matter and, therefore, the repulsion by electrostatic forces. Therefore, in the case of WO, it is noteworthy to stress that the evolution of SVI is strongly linked to the balance of reactions developed during the process. That is to say, SVI increased when the reactions of thermal hydrolysis were predominant. Subsequently, SVI remained stable when the magnitude of the reactions between thermal hydrolysis and oxidation were similar. At the end, SVI began to decrease from the time in which the oxidation reactions prevailed over the hydrolysis ones (see SCOD evolution in Figure 1a).

3.3 Effects on colour and pH

The effects of WO or TH on the colour number (CN) and on pH of the solubilised samples from sludge are showed in Figures 1e and 1f. For both treatments, the CN experienced a sharp increase in its value at the beginning of the reaction, then remaining approximately constant around 0.85 since minute 45. Comparing CN and SCOD, it can be concluded that their trends are analogous, particularly for HT. In this case, the higher SCOD concentration, the higher CN was achieved, as expected. This trend is also observed for the first part of WO, where solubilisation reactions prevail. In fact, CNs between 45-147 minutes of treatment were higher for WO than for TH, since during this

period the former caused a greater level of lysis cellular, achieving in turn higher SCOD concentration than the latter. Nevertheless, when oxidation reactions became dominant, reducing the SCOD, no significant decrease in the CN was observed. At the end of treatments (187 minutes), the CN obtained with TH was a bit higher (8% more) than that with WO, despite the SCOD concentrations were very similar between the final effluents of both treatments. The ability of WO to reduce the colour on different wastewater or sewage sludge has been widely proved (Fu and Kyzas, 2014; Oulego et al., 2016; Urrea et al., 2014) as well as the generation of high coloured intermediates during the oxidation of phenol-like compounds, such as quinhydrones (Collado et al., 2010). So, the no CN change observed for WO was probably due to a balance between the formation of highly coloured intermediates from the initially solubilised compounds and the oxidation of them to non-coloured products, such as low molecular weight acids (LMWA). The pH evolution also supports the higher formation of LMWA in presence of an oxidising atmosphere. While TH caused a minimum effect on the pH of sludge, WO produced a remarkable acidification of the medium (Figure 1f). During TH, the pH decreased slightly from 6.5 to 5.7, being this the result of a small formation of volatile fatty acids (VFA). Eskicioglu et al. (2006) reported the increase in the concentration of VFA from 281 to 936 mg/L for an activated sludge subjected to TH at 96°C, which was withdrawn from the reactor exactly when this temperature was reached. Similarly, they observed that the pH slightly decreased with the treatment from 7.5 to 7.0.

In the case of WO, an abrupt drop in the pH values (4.7) was obtained when reaching the operating conditions (67 minutes). In that point of the reaction, no decrease in TCOD was noticed. Therefore, this indicates that the attack of the hydroxyl radicals during the initial solubilisation step of WO caused the formation of biopolymers with a stronger acid character than those formed only for TH. Afterwards, the oxidation

reactions take place, causing a further decline in the pH value (4.0), which remained stable during the rest of the experiment. The acidification of the medium during WO is a common result of this process due to the production organic acids, which are considered as the main final product of reaction (Genç et al., 2002).

In addition to this, the changes in UV-VIS spectra obtained with each of the treatments (see Figure S1 in the supplementary material) allowed to establish more detailed differences between the characteristics of the coloured compounds solubilised either by WO or TH. According to the evolution of the spectra and considering only the VIS zone (380-780 nm), it can be noted that the absorbance values for 530-780 nm decreased with both treatments after reaching the operating conditions, being this decrease more marked in presence of oxygen. Subsequently, the VIS spectrum for TH conserved its shape, being observed a continuous increase in the absorbance in the entire region with the advance of the reaction, that is to say, with the increase in the SCOD. On the other hand, the solubilised biopolymers by WO showed higher levels of absorbance to lower wavelengths (380-528 nm) than those by TH, specifically, during the first 147 minutes of reaction. Besides, the absorbance values increased up to be completed 117 minutes of WO, decreasing after this time. At the end of the treatments, the spectra area between 380-528 nm and 530-780 nm was of 143 and 146 uA nm for TH, and of 132 and 43 uA nm for WO, respectively.

3.4 Solubilised biopolymers. Yield and size distribution

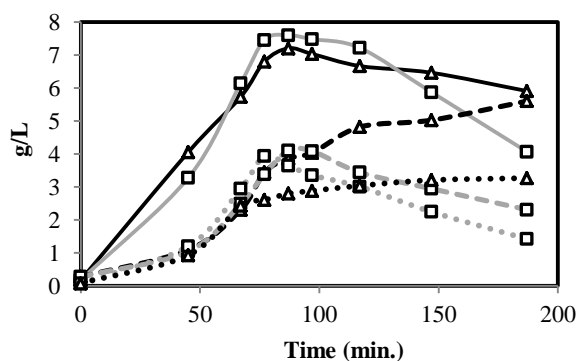


Figure 2. Solubilised biopolymers by effect of the presence (■) or absence (▲) of an oxidising atmosphere during the hydrothermal treatment of the sludge at 160 °C and 40 bar. Solid, dashed and dotted lines represent proteins, humic acids and carbohydrates, respectively.

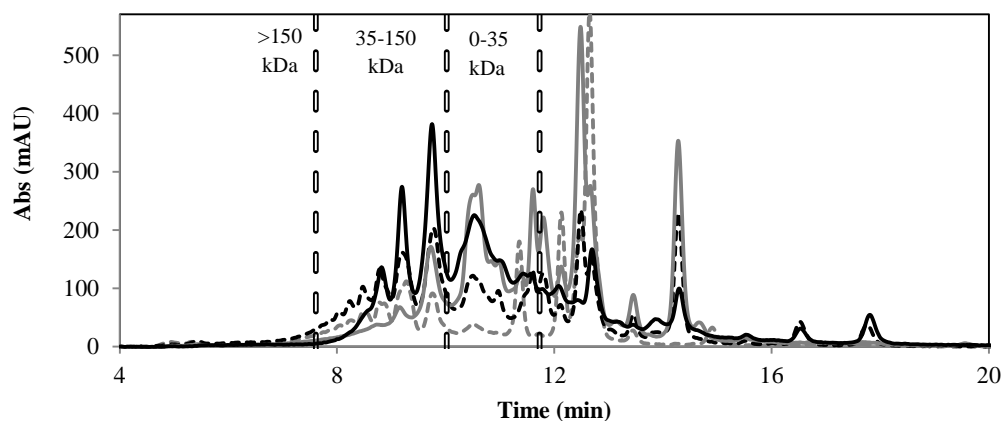


Figure 3. Changes on the fingerprints of supernatants by effect of the presence (black lines) or absence (grey lines) of an oxidising atmosphere during the hydrothermal treatment of the sludge at 160 °C and 40 bar. Dashed and continue lines correspond to time sampling of 67 and 187 minutes, respectively.

The solubilisation of biopolymers from sludge and their size distribution during WO or TH treatments are collected in Figures 2 and 3, respectively. Both treatments caused a considerable increase in the concentration of soluble biopolymers, with the proteins being identified as the main components. Initially, a fast increase in the soluble

biopolymers concentrations was observed for both TH and WO during the first 67 minutes of reaction. This preliminary solubilisation was the result of the destruction of the flocculate structure of the sludge, which caused the release of extracellular polymeric substances towards the supernatant, as well as of intracellular material from the cell lysis. In the following minutes, the rate of solubilisation of biopolymers decreased for both treatments, being this due to the lower VSS concentration, as well as to oxidation reactions in the case of WO. Nevertheless, the biopolymers evolution was different for both treatments since minute 87. On one hand, when 87 minutes of WO was reached, the concentration of biopolymers achieved a maximum with values of 291, 164, 141 mg/g VSS for proteins, humic acids and carbohydrates respectively, but afterwards, their concentrations began to continuously decrease. On the other hand, although proteins concentration also achieved a maximum during TH in minute 87 (272 mg/g VSS), their removal after this minute was significantly slower than in the case of WO. As expected, protein decomposition is faster in presence of an oxidising atmosphere (oxidative plus thermal decomposition) than in its absence (only thermal decomposition). Another difference between both treatments is that humic acids and carbohydrates concentrations increased throughout the reaction of TH, meaning that these biopolymers were less sensitive to thermal degradation than proteins. At the end of TH (187 minutes), the concentrations of proteins, humic acids and carbohydrates was of 223, 212 and 123 mg/g VSS, respectively. The values obtained by WO for the same time were 158, 97 and 57 mg/g VSS for proteins, humic acids and carbohydrates, respectively. These values correspond to 54, 59 and 40% of the maximum soluble proteins, humic acids and carbohydrates concentrations, that is to say, those achieved in the minute 87 of WO.

In order to compare the changes in the size distribution of the solubilised biopolymers caused by each of the treatments, the evolution of their fingerprints was analysed (Figure 3). To carry out a more exhaustive analysis, the fingerprints area was divided into four categories as follows: three of them were established in the size exclusion zone for low (0–35 kDa), medium (35–150 kDa) and high (>150 kDa) molecular weights, whilst the fourth one corresponded to the area out of the column total volume. The presence of peaks out of the column total volume has been related to molecules with hydrophobic characteristics that interact with the filling material of the column (Görner et al., 2003). After an hour of treatment, the areas for low (0–35 kDa), medium (35–150 kDa) and high (>150 kDa) molecular weight biopolymers were 4, 8 and 1.2 AU s for TH and of 9, 14 and 1.5 AU s for WO, respectively. These results indicate that WO produced a higher solubilisation of low and medium size polymers than TH. Regarding to hydrophobic biopolymers, areas corresponding to times higher than that for total elution were 13.4 and 14 AU s for TH and WO, respectively. Taking into account that the polymers eluted in the zone of size exclusion should be those with hydrophilic characteristics, and that this kind of polymers is mainly located in the cell cytoplasm, it seems reasonable to suggest that the presence of an oxidising atmosphere favours a higher degree of cellular lysis in the initial stage of thermal treatment of sludge, rather than the complete hydrolysis of the cellular components, that is to say, the solubilisation of the cellular wall and membrane.

Finally, when both treatments were concluded, the peaks located at lower elution times in the fingerprints disappeared, whilst peaks corresponding to medium and low size biopolymers increase their height. These changes demonstrated that both reactions, thermal hydrolysis and oxidation, caused the hydrolysis of the larger polymers, which were initially solubilised from sludge, to form other of lower molecular weight.

According to the established categorisation, the areas of the fingerprints for final effluents were of 15, 7, 0.7 and 24 AU s for TH and 15, 15, 0.4 and 15 AU s for WO. As it can be observed, a higher proportion of hydrophobic polymers was obtained by TH than by WO. This is because oxidation reactions make the oxidised compounds more hydrophilic.

4. Conclusions

TH and WO showed a high efficiency to reduce the volume of activated sludge, causing a high solubilisation degree of the extracellular and cellular components of the sludge. However, the use of an oxidising atmosphere offered a more complete solution of treatment, providing better results of solubilisation, settleability and mineralisation of the sludge than an inert one.

The free radicals initially formed by WO favoured a higher solubilisation of the sludge instead of its mineralising. Likewise, these radicals showed particularly high affinity to cause the cellular lysis at the beginning of the reaction, rather than the complete hydrolysis of the cellular components such as cellular wall and membrane.

Despite of that WO caused a higher degree of solids solubilisation than TH, the yield of solubilisation of the main component of the sludge, the protein, was similar between both techniques. This result was a factor of the degradation of proteins caused by free radicals formed under an oxidising atmosphere.

The presence of oxygen during the hydrothermal treatment of sludge favoured a higher solubilisation of low and medium size polymers, as well as a higher hydrophilic character in the composition of the effluent. In addition, an oxidising atmosphere caused the degradation of each solubilised biopolymers from sludge, whilst an inert one only

caused the degradation of proteins, demonstrating thus that proteins were more sensitive a thermal decomposition.

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