Physico-chemical pre-treatments of anaerobic digestion liquor for aerobic treatment

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ABSTRACT

Centrifugation of anaerobically digested sewage sludge gives rise to a solid phase, which could be employed as a fertilizer, and a liquid fraction (ADL), which should be treated before being spilled out. This is not an easy task because this liquor is characterized for presenting high COD (~16000 mg O_2/L), high ammonium content (~4000 mg/L) and low biodegradability (BOD_5/COD ~0.2). With the objective to pre-treat this aqueous waste before its treatment by means of more traditional aerobic processes, different physico-chemical methods (ultrasound, ozonation, hydrolysis and wet air oxidation) were assessed in this work. Ultrasound and thermal hydrolysis gave solubilizations around 47% and 68% respectively. The best results in terms of total COD removal were obtained when wet air oxidation (8 h, 160 ºC-200 ºC and 6.0 MPa) and ozonation (8 h, 25 ºC, 12 g/h O_3) techniques were employed achieving COD degradations of 71% and 38%, respectively. The pre-treatment of ADL with the four assayed techniques improved considerably the biodegradability (BOD_5/COD) of the effluent, with values around 0.3-0.4, depending on the treatment. The experimental data were successfully fitted by kinetic models and the kinetic constants for the solubilization and degradation steps were obtained. Application of the proposed models can be of interest for the optimization and selection of the most suitable techniques and operational conditions, in each particular case.

Keywords: anaerobic digestion liquor; wastewater pre-treatment; biodegradability; advanced oxidation processes; hydrolysis; ultrasound

1. INTRODUCTION

Anaerobic digestion (AD) is a widely employed method that transforms organic wastes, such as sludge and organic fraction of municipal solid wastes, into biogas and digestate. The biogas is a product of high added value that can be used as biofuel in a sustainable and eco-friendly way (Xu et al., 2019). The anaerobic digestate, with a high nitrogen content, could be used as organic fertilizer to improve the quality of agricultural soil. However, some characteristics of the digestate, such as odour, viscosity and high content in volatile fatty acids can be harmful to the environment, and its application is not allowed without a previous pre-treatment (Zeng et al., 2016).

One common option is to separate the digestate into liquid and solid phases by filtration or centrifugation processes. After this solid–liquid separation, the solid phase, easy to transport and store, is suitable for composting processes due to the large amount of nutrients and organic components. By contrast, the liquid phase, known as anaerobic digestion liquor (ADL), is more difficult to be processed. This fraction contains 70% - 80% of the total ammonium and 35% - 40% of the total phosphorus from the initial digestate (Peng and Pivato, 2019). Its high organic load and heavy metal content may cause soil contamination and the eutrophication of nearby water. Therefore, it is necessary to treat this effluent before being spilled out in order to reduce the chemical oxygen demand (COD), nitrogen content and high colour, so that rules on wastewater discharged can be accomplished.

When the AD process takes place in a waste management centre, which includes waste disposal, a possible destination for the ADL is the leachate treatment plants, where a biological degradation is usually carried out through denitrification-nitrification processes (Díaz et al., 2019). However, it is not an easy task due to the high nitrogen content and low biodegradability of the organic matter contained in the liquor and, when

it is mixed with other leachates, it can result in an effluent with COD and nitrogen levels higher than the design parameters of the treatment plant. Therefore, the addition of an external carbon source, such as methanol, it is frequently necessary to achieve an effective denitrification when ADL and leachates are treated together. For this reason, it is necessary to investigate suitable pre-treatments that allows to obtain a final effluent with physical and chemical characteristics similar to those present in other leachates, so that ADL can be easily treated by biological treatments without modifying the usual operational parameters.

A novel technique used for the treatment of wastes which contain recalcitrant organic matter, is the irradiation with ultrasounds. This treatment generates pressure waves, gas and vapor bubbles. The implosion of this bubbles create regions with high temperatures and pressures (up to 5000 K and 100 MPa), which promote the physical disintegration of organic matter and/or the extraction of different compounds that could improve the oxidative degradation of organic pollutants (Li et al., 2018; Passos et al., 2014; Somers et al., 2018). In previous studies, the use of low frequencies (20 - 40 kHz) to pre-treat sludge gave the best results. The main advantages of this technique are the short time of treatment and the not necessity of chemical reagents (Tyagi et al., 2014).

Advanced oxidation processes, such as ozonation or wet air oxidation (WAO), are attractive technologies for the treatment of heavily polluted aqueous wastes. These techniques allow the oxidation of organic pollutants due to the generation of powerful chemical oxidants, majority hydroxyl radicals (Miklos et al., 2018). One of their main advantages, compared to conventional technologies, is their capacity to degrade a wide range of recalcitrant components without generating secondary residues (Dewil, 2017). Besides, this technology can also be used in presence of catalyst, such as activated carbon,

in order to use less severe operating conditions and/or improve its effectiveness (Abid et al., 2016).

Ozonation is a method based on the high oxidant power of the ozone, which reacts with different organic pollutants such as humic substances (Carrère et al., 2010). Its use, as single technique or in combination with hydrogen peroxide, has been reported by other authors, who indicated its suitability to remove colour from industrial wastewaters, as well as to improve the solubilization and degradability of organic solid wastes (Bakhshi et al., 2018; Cesaro et al., 2019). The use of WAO has been widely studied at different conditions of temperature and pressure for the treatment of sewage sludge and other effluents that contain high concentrations of organic matter. This technique allows to improve the biodegradability and decolourization of the treated effluents (Sivagami et al., 2018; Urrea et al., 2017).

The employment of hydrolysis has been studied for anaerobic digestion processes in order to pre-treat the wastes to increase biogas production, or to post-treat the digestate solid fractions. Nevertheless, its use for the treatment of the ADL has not been almost studied till now. This technique results in decomposition of microbial cells, lipids, proteins and carbohydrates into lighter molecules, releasing it content into liquid fraction, and allowing better fermentation (Hii et al., 2014; Suárez-Iglesias et al., 2017; Svensson et al., 2018).

Most of the published works are focused on the use of these techniques as pre-treatment for sewage sludge or ADL, with the purpose of breaking down organic matter and increasing the biogas generation in anaerobic digestion processes (Gunes et al., 2019; Zhen et al., 2017; Zou et al., 2016). However, part of the generated ADL is not recirculated and needs to be stored for further treatment (Díaz et al., 2018).

In view of these considerations, the main aim of this work was to analyse the effect of different pre-treatment techniques (ultrasound, hydrolysis, ozonation and WAO) in the ADL degradation, in order to solubilize the particulate matter, decrease the chemical oxygen demand (COD) and/or improving the biodegradability. An additional objective of this work was to obtain a kinetic model that helps to select the optimal operating conditions for each particular treatment.

These pre-treatments would allow to adjust the characteristics of the liquor to the conditions of the treatment plant, so that ADL can be easily treated by conventional biological treatments. Additionally, an increase in the soluble COD could be beneficial for the recirculation of ADL to the anaerobic digester, favouring the microbiological hydrolysis step. Studies about the treatment of the liquid obtained after anaerobic digestate centrifugation (ADL) are scarce, and, as far as we know, there is not any published work that compares the four techniques here considered for the treatment of this effluent.

2. MATERIAL AND METHODS

2.1 Effluent description

The ADL used in this study corresponds with the liquid fraction obtained after centrifugation and decantation of the digestate coming from an anaerobic treatment plant. This digestate was obtained by anaerobic digestion of sewage sludge. The treatment plant is located in the waste treatment centre, COGERSA (Asturias, Spain). For more details of the process, see Diaz et al., (2018). A detailed description of the waste effluent is shown in Table 1. Slight differences were observed between the batch samples of ADL used for the different experiments, for this reason a range of values for each parameter is shown in Table 1.

TABLE 1

2.2 Apparatus and procedures

For ultrasound experiments, 100 mL of ADL was treated using a Sonopuls HD 2070 system (Bandelin, Germany), equipped with an VS 70 probe, at a frequency of 20 kHz. Suitable results to enhanced solubilization of COD, TOC and TN have been reported using a sonication frequency of 20 kHz (Garoma and Pappaterra, 2018). During the ultrasound process, temperature was maintained constant at 40 ºC using a water bath. Sonication amplitudes of 50% and 90% were tested. A sonication amplitude of 100% is equivalent to 80 μm. Samples were taken withdraw between 5 - 45 min, each 5 min of sonication.

The ozonation process was carried out introducing 300 mL of ADL in a cylindrical stirred reactor with a capacity of 1 L. For these experiments an ozone flow of 12 g O_3/h was bubbled through the reactor. Shabani et al. (2015) reported significant removals of COD, colour, and aromatic compounds after the use of this ozone flow during the treatment of landfill leachates. Ozone was generated from industrial grade oxygen using an ozone generator (ZonoSystem). The experiments were carried out at 25 ºC and samples were periodically taken for 8 h. Additionally, an assay with ADL after solid elimination was carried out at the same conditions. These solids were removed by centrifugation at 20 ºC and 13000 g for 15 min.

Hydrolysis experiments were carried out in a 1 L capacity semi-batch reactor (Parr T316SS) equipped with two six-bladed magnetically driven turbine agitators. The reactor was preceded by a 2-L stainless steel water reservoir. The loaded volume in each vessel was 700 mL in order to ensure safe operating conditions. The addition of 20 μL of antifoam 289 (Sigma-Aldrich) was required to avoid the formation of foam during the

experiment. The reactor was pressurized and heated up to the desired working conditions (160 ºC, 180 ºC and 200 ºC) and the stirrer speed was adjusted to 350 rpm for all the experiments. The operating pressure was provided by bottled compressed nitrogen that supplied a nitrogen flow of 1400 mL/min, controlled by an electronic mass flow controller (Brooks). The nitrogen was bubbled through the water reservoir in order to become saturated with water before being sparged into the reaction vessel. A valve and a coil fitted to the top of the vessel allowed the withdrawal of samples during the reaction. The pressure was kept constant at 6.0 MPa by means of a back-pressure controller placed at the end of the gas line. Samples were periodically taken for 8 h. Similar conditions of temperature and pressure were used by Urrea et al., (2015) to treat active sludge of a sewage treatment plant. Their results showed this technique as a positive alternative for improving the management of this waste, in the conditions tested.

Finally, for the (WAO) experiments, the equipment and experimental procedure were the same as that used in the hydrolysis experiments, with the only difference that an oxidizing gas (oxygen) was used instead of nitrogen. Similar conditions have been used successfully to treat effluents from the biological treatment of landfill leachates by Oulego et al. (2015). After treatment, the samples were stored at 4 ºC for 24 h prior to be analysed.

2.3 Analytical methods

The concentration of total chemical oxygen demand (tCOD) was spectrophotometrically measured (at 600 nm) by dichromate method according to Standard Methods (APHA, 1998) using a DR2500 spectrophotometer (Hach Company). This method was also employed for the analysis of soluble COD (sCOD) with the only difference that in this case, the sample was previously centrifuged at 20 ºC and 13000 g for 15 min (Kubota 6500 High Speed Refrigerated Centrifuge) to remove the solid particles.

Total organic carbon (TOC) analysis was performed using a TOC analyzer (Shimadzu TOC-VCSH, Japan) and biochemical oxygen demand (BOD_5) was determined using a manometric respirometry measurement system (Lovibond® Water Testing BD 600). The value of pH was measured by means of a pH- meter (Jenway 3510) and the absorbances (Abs) were measured at 436, 525 and 620 nm using a UV/vis spectrophotometer (Thermo Scientific, Hελios γ).

The change in the colour of the ADL by the treatments was determined by means of the colour number (CN), which is defined according to Equation (1) (Tizaoui et al., 2007).

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

Spectral absorbance coefficients (SAC) are defined as the ratio of the values of the respective absorbance (Abs) over the cell thickness (x).

All analytical measurements were done at least in triplicate.

2.4 Parameter calculations

Non-soluble COD (nsCOD) was calculated as the difference between total COD (tCOD) and soluble COD (sCOD) for each reaction time (see Equation 2).

$$\mathrm{nsCOD} = \mathrm{tCOD} - \mathrm{sCOD} \qquad \text{Eq (2)}$$

The percentage of solubilization achieved with each treatment was determined according to Equation (3), where $nsCOD_0$ is the initial value of non-soluble COD, and nsCOD is the value of non-soluble COD at the considered time.

$$\text{Solubilization (\%)} = \frac{\mathrm{nsCOD_0} - \mathrm{nsCOD}}{\mathrm{nsCOD_0}} \qquad \text{Eq (3)}$$

The average oxidation stage of carbon atoms (AOSC) was also studied. This parameter allowed to evaluate the oxidation degree for the reacting mixture after different treatments. This parameter was obtained as follows (Vogel et al., 2000):

$$\mathrm{AOSC} = 4 - 1{,}5 * \left(\frac{\mathrm{COD}}{\mathrm{TOC}}\right) \qquad \text{Eq (4)}$$

The AOSC values must always lie between the range 4 and –4. Low AOSC values indicate that the oxidation is not complete, whereas high AOSC values indicate a high oxidation state of the organic compounds (Garg and Mishra, 2010).

Finally, biodegradability was calculated as the ratio of BOD_5 over tCOD (or sCOD if solids were removed).

2.5 Kinetic models

Models proposed in this study are based on the kinetics models described by Oulego et al., (2016) for advanced oxidation treatments. In all cases, the kinetic constants were determined by fitting the model to experimental data using Micromath Scientist 3.0.

2.5.1 Ultrasound

The kinetic model proposed to fit the experimental data of ultrasound treatment is shown in Equations (5) and (6), as next indicated:

$$\frac{\mathrm{dnsCOD}}{\mathrm{dt}} = -\mathrm{k_{U1}}(\,\mathrm{nsCOD} - \mathrm{R_1}) \qquad \text{Eq (5)}$$

$$\frac{\mathrm{dsCOD}}{\mathrm{dt}} = \mathrm{k_{U1}}(\mathrm{nsCOD} - \mathrm{R_1}) - \mathrm{k_{U2}}\mathrm{CODs} \qquad \text{Eq (6)}$$

It is considered that nsCOD was turned into sCOD and this sCOD was subsequently degraded to CO_2. In this model, k_{U1} is the kinetic constant for the solubilization of nsCOD

into sCOD and k_{U2} is the kinetic constant for the degradation of sCOD. R_1 is the value of nsCOD at final times.

2.5.2 Ozonation

For the experiments carried out with solids, the kinetic model for solubilization and degradation followed Equations (7) and (8). In this model, k_{O1} is the kinetic constant for the solubilization of nsCOD into sCOD, k_{O2} is the kinetic constant for the degradation of sCOD and R_1 and R_2 are the values of nsCOD and sCOD, respectively, at final time. In the case of sample without solids, Equation (9) was used

$$\frac{\mathrm{dnsCOD}}{\mathrm{dt}} = -\mathrm{k_{O1}} * (\mathrm{nsCOD} - \mathrm{R_1}) \qquad \text{Eq (7)}$$

$$\frac{\mathrm{dsCOD}}{\mathrm{dt}} = \mathrm{k_{O1}} * (\mathrm{nsCOD} - \mathrm{R_1}) - \mathrm{k_{O2}} * (\mathrm{sCOD} - \mathrm{R_2}) \qquad \text{Eq (8)}$$

$$\frac{\mathrm{dsCOD}}{\mathrm{dt}} = -\mathrm{k_{O2}} * (\mathrm{sCOD} - \mathrm{R_2}) \qquad \text{Eq (9)}$$

2.5.3 Hydrolysis

A kinetic model according to Equations (10) and (11) was used to fit the experimental data as shown in Fig. 3a.

$$\frac{\mathrm{dnsCOD}}{\mathrm{dt}} = -\mathrm{k_{H1}} * (\mathrm{nsCOD} - \mathrm{R_1}) \qquad \text{Eq (10)}$$

$$\frac{\mathrm{dsCOD}}{\mathrm{dt}} = \mathrm{k_{H1}} * (\mathrm{nsCOD} - \mathrm{R_1}) \qquad \text{Eq (11)}$$

In this model, k_{H1} is the apparent constant for the solubilization of nsCOD into sCOD. The k_{H1} is an apparent constant because the operating conditions were not reached before 60-90 min of treatment, depending on each experiment. So, the first experimental data correspond with lower temperature and pressure values.

2.5.4 Wet Air Oxidation (WAO)

Equations (12) and (13) show the kinetics of the process, considering that nsCOD was transformed into sCOD and this sCOD was subsequently degraded into CO_2.

$$\frac{\mathrm{dnsCOD}}{\mathrm{dt}} = -\mathrm{k_{W1}} * (\mathrm{nsCOD} - \mathrm{R_1}) \qquad \text{Eq (12)}$$

$$\frac{\mathrm{dsCOD}}{\mathrm{dt}} = \mathrm{k_{W1}} * (\mathrm{nsCOD} - \mathrm{R_1}) - \mathrm{k_{W2}} * (\mathrm{CODs} - \mathrm{R_2}) \qquad \text{Eq (13)}$$

In this model, k_{W1} is the apparent constant for the solubilization of nsCOD and k_{W2} is the apparent constant for the degradation of sCOD. Again, k_{W1} and k_{W2} are apparent constants because the operating conditions were not reached before 60-90 min of treatment.

3. RESULTS AND DISCUSSION

3.1 Ultrasound treatment

The changes of tCOD, sCOD and nsCOD concentrations with time for ultrasound treatment are shown in Fig. 1a. Important changes in sCOD and nsCOD were observed, even though tCOD degradation was very low. The most significant increase in sCOD was obtained after 45 min of sonication in both cases, reaching almost an increase of 40% for 90% amplitude. Li et al. (2018), reported an increase of 4.6–23.06 times of sCOD in waste activate sludge after 20–100 min of ultrasound at 20 kHz, concluding that times greater than 80 min was not effective. However, the trend in this study might infer that sonication times higher that 45 min would allow higher increases in sCOD concentrations.

FIGURE 1

The sCOD/tCOD ratio showed an increase from 0.48 to 0.62 and 0.71 for 50% and 90% amplitudes, respectively. Oz and Uzun, (2015), who carried out an anaerobic digestion of olive mill wastewater pre-treated with ultrasound (20 kHz, 10 min), reported an increase

in sCOD/tCOD ratio from 0.59 to 0.79, and consequently, an increase of 20% in biogas production.

With the aim of obtaining a liquor that could be treated by an activated sludge system, it is important to emphasize that a significant increase in the biodegradability of the final effluent was obtained for 90% amplitude (see Fig. 1b). The BOD_5/tCOD ratio increased progressively throughout the sonication time resulting in a moderately biodegradable leachate after 45 min of sonication (BOD_5/tCOD ~ 0.28).

The AOSC value was calculated for each time and amplitude of treatment giving the values shown in Fig. 1c. The use of 90% of amplitude decreased the AOSC value significantly from 15 min of treatment, while for 50% of amplitude AOSC remained almost constant. This technique promotes the physical organic matter disintegration encouraging the solubilization of different compounds, so, the important decrease of AOSC with 90% of amplitude could be a consequence of the solubilizations achieved at the same time.

The changes in colour and pH are shown in Fig. 1d. The colour number (CN) was increased around 30% in all samples for both amplitudes studied. The value of pH remained almost constant between 8.0 and 8.4.

3.2 Ozonation treatment

When the ADL with solids was treated, a fast solubilization occurred during the first hour of treatment, dropping the nsCOD more than 50%. At the same time, an initial increase occurred in sCOD values and after 45 min decrease again, reaching final values very similar to initial one. While nsCOD was solubilized, sCOD was degraded, so that the tCOD decreased by 35% in just 300 min. For the experiment with centrifuged ADL, a 31% of sCOD removal was achieved at final time (see Fig. 2a).

FIGURE 2

The results of the biodegradability index are shown in Fig. 2b. An improvement of the biodegradability of treated samples from ADL with and without solids was obtained. In both cases, a moderately biodegradable effluent after 8 h of ozonation (BOD_5/COD~0.3 and BOD_5/COD~0.37, respectively).

The changes of AOSC values showed, in the case of ADL with solids, a fast drop in during the first minutes. This fact indicated that the dissolving of compounds from the solid particles that were rapidly degraded, giving place to the subsequent increase in AOSC values. For the final samples, both in presence and absence of solids, an increase in the AOSC values were observed, reaching values over 1.0 (Fig. 2c).

As observed in Fig. 2d, the ozonation treatment allowed an important removal of colour, decreasing by 73% and 82% during the first 60 min of reaction in presence and absence of solids, respectively. For centrifuge ADL, colour number continues decreasing achieving a removal of 96% after 8 h.

Finally, pH values slightly increased during the first hour of reaction in both cases. Afterwards, when solids were present, the pH values began to decrease with a final pH of 7.5. However, in the absence of solids, pH variations were much lower. Several authors reported that higher values of pH increase the degradation efficiency of ozonation treatments, due to the faster formation of hydroxyl radicals at higher pH (Sivagami et al., 2018).

3.3 Hydrolysis treatment

As can be shown in Fig. 3a, hydrolysis treatment did not degrade the tCOD of the ADL, which remained practically constant for the three tested temperatures. However, as occurred during ultrasound treatment, sCOD increased as a consequence of the

solubilization of nsCOD, which decreased. The use 200 ºC and 6.0 MPa gave an increase of 54% in the sCOD after 90 min of treatment, which corresponds with a solubilisation of nsCOD around 70%.

FIGURE 3

A moderately biodegradable effluent was reached after 4 h of reaction (BOD_5/COD ~ 0.30), independently of the operating temperature (see Fig. 3b). This improvement in the biodegradability of pre-treated effluent make easier its treatment in a biological process. In addition, part of the pre-treated effluent could be recirculated to the anaerobic reactor in order to improve biogas production as a consequence of a better use of the organic matter. Previous studies have reported that sewage sludge treated by hydrolysis is more assimilable by anaerobic microorganisms, allowing a faster and higher methane production (Donoso-Bravo et al., 2011). Yang et al. (2019) analysed the effect of thermal hydrolysis in a digested sludge coming from a domestic WWTP. The digested sludge was hydrolysed, dewatered and recirculated to the digester for re-digestion with raw sludge. They concluded that the hydrolysis treatment increased the concentration of sCOD in the sludge by disintegrating the recalcitrant organic matter and resulting in further improvement of methane production.

As can be seen in Fig. 3c, there is a relationship between the treatment temperature and the final AOSC value. When the higher temperature is used (200 ºC) a drop in AOSC values was observed during the first minutes with negative values after 100 min. These low values indicate a higher breakage of the organic matter as a consequence of the higher temperature employed.

The Fig. 3d shows the changes in colour number (CN) and pH. The value of pH progressively increased up to values around 10. Concerning to colour number, it increased

gradually, obtaining a treated effluent with greater coloration compared with initial sample.

3.4 WAO treatment

When the ADL was treated by WAO, both solubility and degradation of pollutants were obtained. Fig. 4a shows the changes of tCOD, sCOD and nsCOD during the experiments at different temperatures.

FIGURE 4

A fast drop in nsCOD occurred and after 200 min of treatment almost all the nsCOD was solubilised in all cases. As expected, the treatment at highest temperature (200 ºC) achieve the highest removals of tCOD, i.e, 65% and 71%, after 4 h and 8 h of treatment, respectively. For the treatments carried out at 180 ºC and 160 ºC removals achieved were 57% and 34%, respectively. The tCOD degradation degree showed an increase directly proportional to the temperature used.

Baroutian et al. (2015), studied the treatment of an anaerobically digested municipal sludge and reported similar results during a treatment at 240 ºC and 2.0 MPa. They observed an initial drop of tCOD, that decrease at a slower rate afterwards, reaching removal efficacies above 60%. Chung et al. (2009), who investigated the treatment of sludge by wet oxidation, reported reductions of tCOD around 40% after 90 min of treatment at 200 ºC and pressures of 4.0-5.0 MPa. Oulego et al. (2016), studied the effect of wet oxidation on a mixture of old and young leachate after nitrification-denitrification process. They reported a tCOD reduction around 51% after 100 min of treatment at 180 ºC and 6.0 MPa. With respect to sCOD, an increase during the initial hours of the treatment was observed for all temperatures studied, due to the solubilization of the solids present in the initial sample.

Results of biodegradability are shown in Fig. 4b. The use of 160 ºC allowed an improvement in the biodegradability of the sample obtaining a moderately biodegradable liquor after 8 h of reaction (BOD_5 /COD ~ 0.38). It is important to highlight that the use of the highest temperature (200 ºC) resulted in a liquor with the high biodegradability index, only after 4 h of oxidation (BOD_5 / COD ~ 0.43).

The AOSC values showed an important variability over time (see Fig. 4c). In all cases an initial decrease directly proportional to the temperature was obtained during the first 30 min of treatment due to the solubilization of nsCOD. After this time, the value was significantly increased. The values obtained for the final samples indicated that the treatment at 160 ºC and 180 ºC gave final samples with AOSC similar to the initial sample. The treatment at 200 ºC caused a decrease of around 30% in the AOSC value, like in the previous techniques. It was maybe consequence for the partially oxidation of the easily oxidizable organics compounds which were degraded into gaseous products. This transformation results in the enrichment of the ADL with other short chain carboxylic acid products, which is consequently reflected in lower AOSC values.

The colour number was increased during the first 30 min, coinciding with the increase in sCOD and COT at this time. After 1 hour of reaction, the colour number, shown in Fig. 4d, began to decrease until achieving a practically complete colour removal (91%) after 8 h of reaction. Finally, the data obtained after WAO treatment shown the increase in pH from values of 8 to almost 10. The increase in pH can be due to the degradation of the acids present in the sample. This fact could be considered as disadvantage for the subsequent treatment, however, the increase in the sample could be damped due to the mix of the ADL treated with young and mature leachates, which are added in greater proportion and present lower values of pH.

3.5 Comparison of the techniques in terms of the solubilization and degradation efficacies

The percentages of solubilization and degradation were calculated for each treatment at final time (Fig. 5a and Fig. 5b, respectively) and important differences were observed between them.

FIGURE 5

The percentages of nsCOD solubilization obtained with WAO were significantly higher than those obtained for the rest of the assayed treatments, reaching values around 90% for the three temperatures tested. When hydrolysis was used for the treatment, the solubilization degree showed an increase with temperature, reaching values of 39%, 52% and 68% for 160°C, 180°C and 200°C, respectively. It has been reported that the use of temperatures higher than 170°C in hydrolysis treatments gives high solubilizations of nsCOD, mainly due to the solubilization of the proteins present in samples (Donoso-Bravo et al., 2011). When strong operating conditions were used (200 ºC and 6.0 MPa), solubilizations around 65% were achieved after 4 h of reaction. This value was similar to that achieved with ozonation after 8 h.

The use of ultrasounds with the highest amplitude (90%) gave a solubilization of 47% just after 45 min, whereas the values obtained for amplitudes of 50% at the same time was 33%. Oz and Yarimtepe, (2014), who studied the effect of sonication on leachates, reported solubilizations of 63% after 45 min at 20 kHz.

In relation to tCOD degradation, the highest percentage was achieved with WAO at 200 ºC, obtaining a final tCOD degradation of 71%, as shown in Fig. 5b. The use of a lower temperature (160 ºC) gave a tCOD degradation around 35%, similar to that obtained after the ozonation treatment (37%).

The use of any of the assayed treatments increased the biodegradability index and enabled to obtain an effluent moderately biodegradable, which is beneficial for a subsequent biological treatment such as nitrification-denitrification and activated sludge. In this sense, ozonation (8 h, 25 ºC, 12 g/h O_3) and WAO (8 h, 160-200 ºC and 6.0 MPa) were are the most appropriate techniques, achieving a BOD_5/COD ratio around 0.4. In particular, after only 4 h of reaction, WAO gave a treated effluent with similar biodegradability and tCOD values to the mixture of young and mature leachates that are treated in a biological plant sited in the waste treatment centre that supply the ADL samples.

The tCOD degradations obtained using hydrolysis and ultrasound methods was low, i.e. lower than 8% in both cases. However, significant solubilizations were obtained, increasing the biodegradability index without decreasing the content in organic matter. The effluents so obtained could be interesting for their recirculation to the anaerobic digester. Microbiological hydrolysis of sewage sludge is the rate limiting step of anaerobic digestion, that could be enhance with the additional input of easily-biodegradable organic matter from solid solubilization. Hence, these techniques could also be useful to improve the biogas production and decrease the time to reach the maximum biogas volume (Rasapoor et al., 2019).

3.6 Kinetic model

The values of the kinetic constants and the apparent kinetic constants obtained by fitting the models (previously described in Material and Methods section) to the experimental data are shown in Table 2. The comparison between model and experimental data for each technique can be seen in Supplementary Material (Figures S1-S4).

TABLE 2

For ultrasound technique, the solubilization constants were higher than the degradation constants for both amplitudes. This fact corresponds with the low tCOD degradation observed in relation with the increase in sCOD. The use of the highest amplitude showed an increase in the value of the solubilization constant, although a decrease in the value of the degradation constant was observed.

Considering hydrolysis, it was observed an increase in the values of the solubilization constants with temperature. Xue et al., (2015), studied the effect of the thermal hydrolysis on organic matter solubilization in sludge. They reported that the use of this technique increased the sCOD concentration in the sludge. A direct increase of the solubilization with temperature was also reported.

For ozonation the degradation constant for centrifuged ADL was lower than that obtained for ADL with solids, indicating that the organic compounds that came from solids solubilization were more easily oxidizable than the compounds that were initially dissolved in the ADL. In relation with this, Bakhshi et al. (2018), who carried out a research on the use of ozonation as pre-treatment for sludge, reported that anaerobic digestion of ozonated municipal sludge showed better performance than conventional anaerobic digestion in terms of biosolids reduction and increasing biogas yield.

Regarding WAO method, the solubilization constants increased with temperature, whereas degradation constants remained almost constant. This is translated in the higher degradation of tCOD previously commented.

4. CONCLUSIONS

This work focuses on the pre-treatment of the liquid obtained after anaerobic digestion of sludge (ADL). This is an issue scarcely studied before, despite of the fact of being a real

environmental problem due to the high content in non-biodegradable organic matter of ADL and the increasing number of anaerobic digestion plants worldwide.

The four pre-treatment methods here evaluated (ultrasounds, ozonisation, hydrolysis and WAO) were effective for the solubilization of nsCOD, reaching values above 90% for the best cases. Additionally, the application of these techniques allowed to improve considerably the biodegradability of ADL samples.

Besides, when ozonation (8 h, 25 ºC, 12 g/h O3) and WAO (8 h, 200 ºC and 6.0 MPa) were used, significant decolourization and tCOD removal were achieved (37% and 71% respectively) obtaining physico-chemical characteristics in ADL similar to those found in other municipal landfill leachates. These results could be interesting to subsequently processed ADL in an aerobic system, together with other leachates. In this sense, the treated ADL could be added to the process, without significant changes in the usual operating conditions. Other potential advantage would be the recirculation of part of the pre-treated ADL to the anaerobic reactor in order to improve the biogas production. These both possibilities have not been yet tested, so further investigation would be of interest.

The kinetic models proposed for each of the four techniques have successfully fitted the experimental data in the conditions tested. These models may be useful in order to estimate the best operating conditions for the treatment of ADL, depending on each particular composition and on the objectives of the treatment, i.e. improving its biodegradability or removing its COD content.

5. ACKNOWLEDGMENTS

This work was co-financed by COGERSA, S.A.U. (Project FUO-EM-138-15), IDEPA (Project IDE/2015/000245), Spanish MINECO, (Projects CTM2015-63864-R and MINECO-17-BES-2016-077963), Foundation for the Promotion of Applied Scientific

Research and Technology in Asturias (Project FC-GRUPIN-IDI/2018/000127) and FEDER funds from European Union.

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Table 1. Characteristics of the anaerobic digestion liquor (ADL)

Parameter	Value
pH	7.96 – 8.26
tCOD (mg O_2/L)	15179 - 16802
sCOD (mg O_2/L)	7205 - 8098
sTOC (mg/L)	3218 - 3788
BOD_5 (mg O_2/L)	2135 - 2960
Colour Number (CN)	0.899 – 1.275
AOSC	0.580 – 0.904
NH_4^+ (mg/L)	3812 - 4166

Table 2. Kinetic constants calculated from experimental data

Treatment	Conditions		k (min^{-1})		r^2
US	50% of amplitude	Eq (5)	k_{1U}	0.010	0.998
		Eq (6)	k_{2U}	0.004	0.997
	90% of amplitude	Eq (5)	k_{1U}	0.014	0.998
		Eq (6)	k_{2U}	0.002	0.997
O_3	With solids	Eq (7)	k_{1O}	0.016	0.998
		Eq (8)	k_{2O}	0.027	0.987
	Without solids	Eq (9)	K_{2O}	0.006	0.998
H	160 ºC. 6.0 MPa	Eq (10,11)	k_{1H}	0.014	0.997
	180 ºC. 6.0 MPa	Eq (10,11)	k_{1H}	0.018	0.998
	200 ºC. 6.0 MPa	Eq (10,11)	k_{1H}	0.045	0.995
WAO	160 ºC. 6.0 MPa	Eq (12)	k_{1W}	0.015	0.998
		Eq (13)	k_{2W}	0.013	0.991
	180 ºC. 6.0 MPa	Eq (12)	k_{1W}	0.019	0.995
		Eq (13)	k_{2W}	0.014	0.982
	200 ºC. 6.0 MPa	Eq (12)	k_{1W}	0.036	0.994
		Eq (13)	k_{2W}	0.014	0.995

FIGURE CAPTIONS

Figure 1. a) Changes of tCOD (dashed lines), sCOD (solid lines) and nsCOD (dotted lines) during ultrasound treatment at 50% of amplitude (dark colour and triangle markers) and 90% of amplitude (light colour and circle markers). **b)** Changes of BOD_5 (lines and markers) and biodegradability (columns). **c)** Change of AOSC and **d)** Changes of pH (lines and markers) and colour number (columns). The standard deviations (SD) of the experimental data were in all cases lower than 3% of the mean value

Figure 2. **a)** Changes of tCOD (dashed lines), sCOD (solid lines) and nsCOD (dotted lines) during ozonation treatment. The experiment A corresponds to the sample with solids (dark colour and triangle markers) and the experiment B corresponds to the sample without solids (light colour and circle markers). **b)** Changes of BOD_5 (lines and markers) and biodegradability (columns). **c)** Changes of AOSC. **d**) Changes of pH (markers) and CN (columns). The standard deviation (SD) of the experimental data were in all cases less than 4% of mean value.

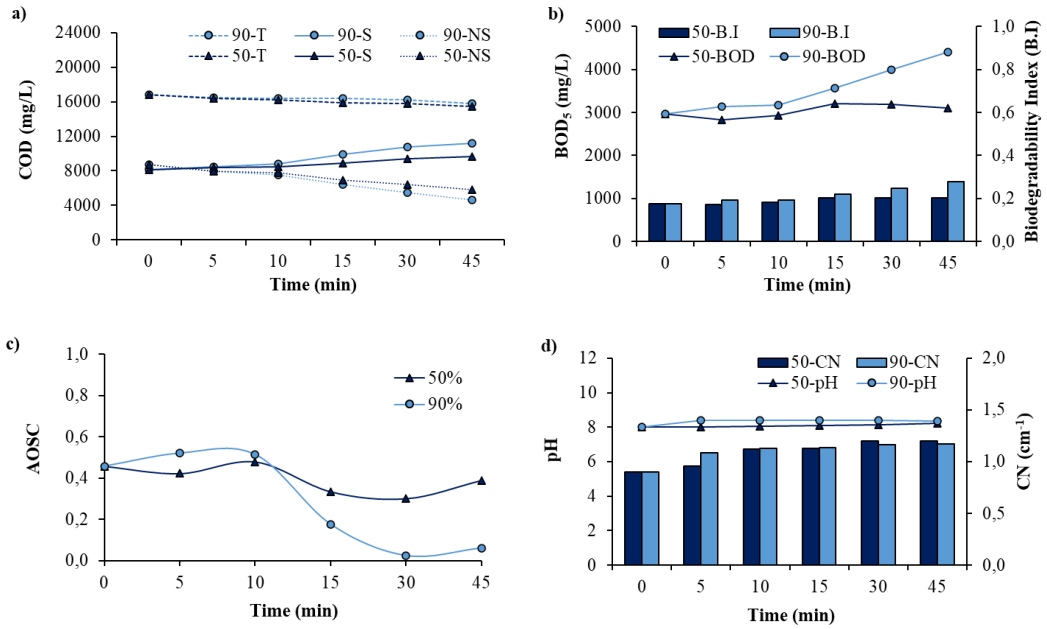
Figure 3. a) Changes of tCOD (dashed lines), sCOD (solid lines) and nsCOD (dotted lines) during hydrolysis treatment at 160 ºC (light colour and triangle markers), at 180 ºC (intermediate colour and square markers) and at 200 ºC (dark colour and circle markers).. **b)** Changes of BOD_5 (markers) and biodegradability (columns). **c)** Changes of AOSC **d)** Changes of pH (markers) and CN (columns). The standard deviation (SD) of the experimental data were in all cases lower than 4% of the mean value.

Figure 4. **a)** Changes of tCOD (dashed lines), sCOD (solid lines) and nsCOD (dotted lines) during wet air oxidation treatment at 160 ºC amplitude (light colour and triangle markers), at 180 ºC (intermediate colour and square markers) and at 200 ºC (dark colour and circle markers). **b)** Changes of BOD_5 (markers) and biodegradability (columns). **c)**

Changes of AOSC. **d)** Changes of pH (markers) and CN (columns). The standard deviation (SD) of the experimental data were in all cases lower than 10% of mean value.

Figure 5. Results of solubilization degree **(a)** and tCOD degradation **(b)** for the different treatments. The segments in the upper part of the bars indicate the standard deviations.

Figure 1.



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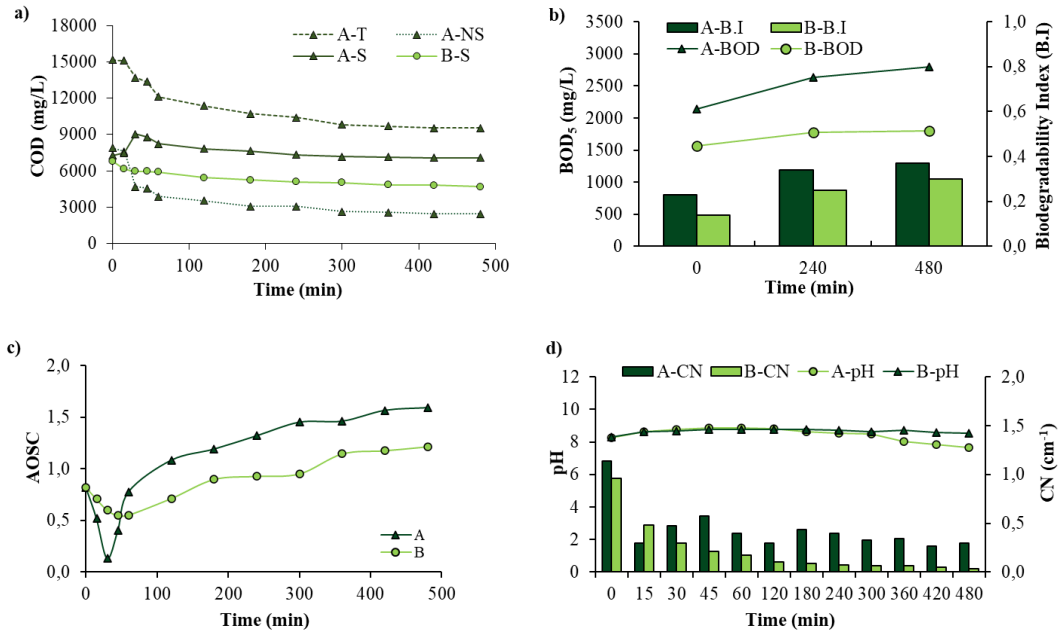

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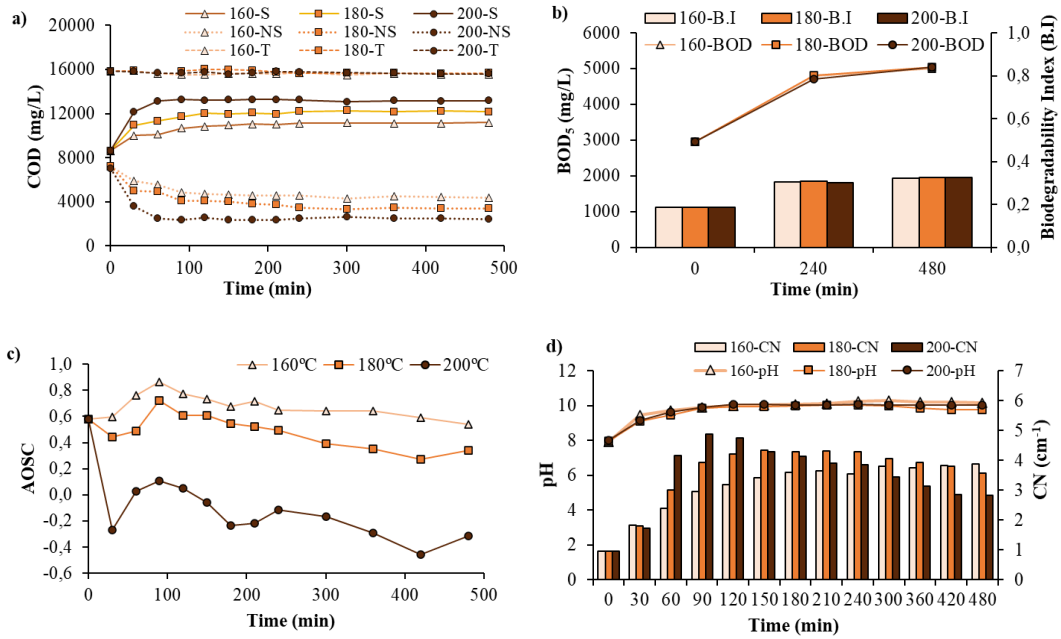

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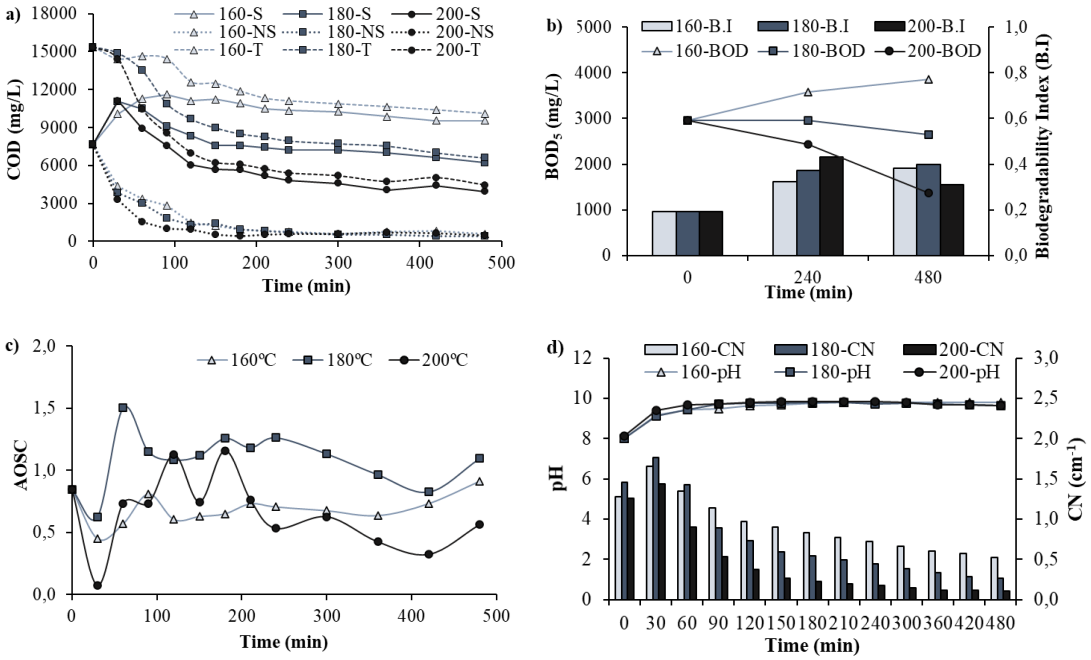

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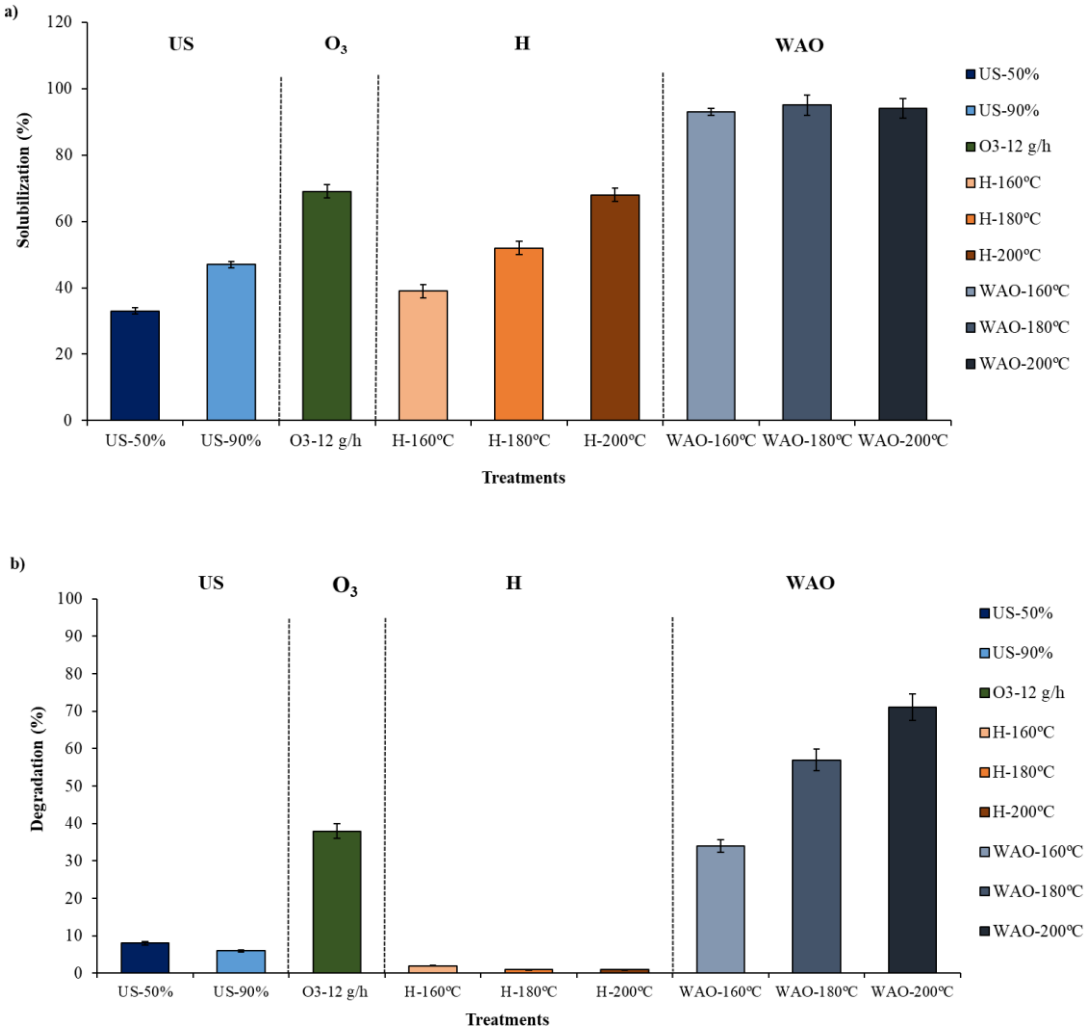

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