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2 **HEAVY METAL SOLUBILISATION DURING THE**
3 **HYDROTHERMAL TREATMENT OF SLUDGE**

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23 **Abstract**

24 The present study analyses the combined effects of temperature (from 160 to
25 200 °C), and, for the first time ever, type of atmosphere (oxidising or inert) and pressure
26 (from 60 to 100 bar) on the solubilisation of heavy metals during the hydrothermal
27 treatment of wet no-diluted sewage sludge. Results revealed that Cd, Pb, Al and Fe were
28 hardly affected by neither the atmosphere nor temperature, remained almost completely
29 in the solid phase during all the hydrothermal treatments tested; while Cr, Ni, Cu and Zn
30 were partially solubilised, being this solubilisation favoured by the presence of an
31 oxidising atmosphere. In contrast, initial dissolved Hg was partially precipitated under
32 both types of atmosphere, although it was re-dissolved after 30 min under an inert
33 atmosphere. Regarding the working conditions, the highest temperature (200 °C) caused
34 the greatest metal immobilisation, whereas the range of pressures tested barely had any
35 effect on it. Concerning the reaction time, the lowest concentration of metals in the
36 liquid fraction of the hydrolysed sludge was obtained during the initial 30 min of
37 treatment.

38 **Keywords**

39 Sludge management, heavy metals, wet oxidation, thermal hydrolysis, solubilisation.

40 **1. Introduction**

41 In urban wastewater treatment plants (WWTP), biological methods are widely
42 used to remove the dissolved organic matter because of their simplicity and reliability
43 (Zhang et al., 2014). Due to the continued increase in population and industrial
44 activities, the generation of sewage sludge as a by-product from biological treatments
45 has also steadily increased. Management of this sludge has been and continues to be one

46 of the most complex and costly problems in WWTP, owing to the high volume
47 produced and its very poor dewaterability (Urrea et al., 2014).

48 As legislation becomes more stringent with regard to conventional sludge
49 management options such as incineration, landfilling or land application, new
50 alternatives focused on the reuse and recycling of this sludge are now being opened.
51 These include the application of a wide range of treatments to recover energy and/or
52 different resources from sludge, such as bio-oil, syngas, building materials, proteins,
53 nutrients, heavy metals, adsorbents, bioplastics, enzymes, etc (Gao et al., 2020;
54 Gherghel et al., 2019; Xiao and Zhou, 2020).

55 At this point, it is interesting to stress that, for many of these options to valorise
56 sewage sludge, a preliminary stage of sludge solubilisation is highly recommended or
57 even mandatory. Probably, the most representative scenario for this approach is the
58 sludge pre-treatment before its anaerobic digestion to produce biogas in order to
59 accelerate the digestion of the solid waste and optimise the methanogenic potential, as
60 well as to reduce the final amount of sludge to be disposed (Abe et al., 2013; Carrère et
61 al., 2010; Donoso-Bravo et al., 2011). Nevertheless, there are many other examples of
62 strategies for sludge management where a proper initial solubilisation is crucial, such as
63 for recovering resources. This pre-treatment enables to destroy the cell walls and release
64 the extracellular and intracellular organic compounds. Afterwards, the products of
65 interest can be subjected to a purification process. Examples of these products include
66 the obtaining of phosphorus as struvite, heavy metals, proteins, enzymes, short-chain
67 fatty acids or biofuels (Chen et al., 2019; Gherghel et al., 2019; Ilgi & Onur, 2020;
68 Kumar et al., 2019; Munir et al., 2017; Suárez-Iglesias et al., 2017; Sun et al., 2013; Xu
69 et al., 2019).

70 Different treatments are available for solubilising sludge, such as hydrothermal
71 processes, ozonation, alkaline hydrolysis, enzymatic lysis, freezing and thawing,
72 mechanical disintegration, high-pressure homogenizers, ultrasound, microwave
73 irradiation and photocatalytic pre-treatment (Carrère et al., 2010; Gherghel et al., 2019).
74 Among them, hydrothermal treatments stand out for their advantages to handle sewage
75 sludge. These methods are adequate for destroying toxic compounds, besides obtaining
76 high added value products such as phosphorus, polysaccharides, lipids or carboxylic
77 acids (Park et al., 2019; Suárez-Iglesias et al., 2017). Moreover, during the
78 hydrothermal treatments of biomass and manure, it was found that most heavy metals
79 can be transformed to other less bioavailability fractions, reducing their environmental
80 risk (Li et al., 2020). In addition, taking into account that hydrothermal methods use
81 water as a solvent and reactant, the costs of treatment is reduced since it is neither
82 necessary to remove the moisture of sewage sludge nor to add other chemical reagents
83 (Chen et al., 2020; Park et al., 2019). Furthermore, they require relative mild reaction
84 conditions (150-320 °C and 20-150 bar) and the gaseous stream generated is low-
85 polluting (Munir et al., 2017; Suárez-Iglesias et al., 2017). Apart from that, thermal
86 hydrolysis is the most industrially widespread technology to enhance sludge anaerobic
87 digestion in WWTP, because not only improves the generation of biogas but also
88 reduces the toxicity and the final volume of digestate (Park et al., 2019).

89 At this point, it is important to bear in mind that an important factor during the
90 choice and application of a specific sludge management strategy (with or without a
91 solubilisation pre-treatment) is always the fate of the heavy metals contained in the
92 sludge at the end of the treatment. These compounds can be accumulated in the soil and
93 passed to living beings through the food chain, having toxic, carcinogenic, mutagenic
94 and teratogenic effects (Zhang et al., 2020). For that reason, the increasing attention

95 paid to environmental protection and the strict legislation has led to the consideration of
96 the heavy metals as a critical parameter to be taken into account during the sewage
97 sludge valorisation (Gherghel et al., 2019).

98 Considering that hydrothermal treatments are profusely used as sludge pre-
99 treatments, as has already been discussed, analysing the heavy metals solubilisation
100 from sludge during these treatments may provide useful knowledge for the
101 understanding and the development of either traditional or new management strategies
102 for this by-product. However, to the best of our knowledge, there are only a few studies
103 in the bibliography dealing with the evolution of heavy metals during hydrothermal
104 treatments of sewage sludge. For example, Zhang et al. (2017) analysed the evolution of
105 Al, Cu, Fe, Zn and Cr in a 4% diluted dewatered sewage sludge subjected to wet
106 oxidation at 40 bar and different pH (5,7 and 9) and temperatures (200, 220 and 240 °C)
107 throughout 60 min of the experiment. On the other hand, Sun et al. (2013) researched
108 the solubilisation of Fe, Al, Mn, Pb and Zn in a diluted sludge (50%) during 90 min of
109 thermal hydrolysis at different temperatures (180,200, 220 and 240 °C). Lastly, Zhang
110 et al. (2015) obtained the changes of Hg, Cd, Pb, Cr, As, Cu, Zn and Ni after
111 hydrolysing excess sludge at 170 °C for 30 min. Thereunder, it is interesting to note that
112 most studies about this topic use previously dewatered sewage sludge as a feedstock,
113 needing to dilute it before the experiments, and only analyse the concentration of a few
114 metals at the end of the treatment or over a short period of time. However, what is most
115 outstanding is that the effect of an oxidising atmosphere during the hydrothermal
116 treatment on the fate of the heavy metals has not thoroughly been studied yet, even
117 when this is one of the main operational parameters in hydrothermal treatments.

118 Due to the aforementioned, the aim of this article is to assess the evolution of the
119 main heavy metals (Hg, Cd, Cr, Pb, Ni, Cu, Zn, Al and Fe) during the hydrothermal

120 treatments of wet no-diluted sewage sludge, focusing on the effects of the temperature
 121 (from 160 °C to 200 °C), the pressure (from 60 bar to 100 bar) and, especially, the type
 122 of atmosphere (oxidising or inert) on their fate.

123 2. Materials and methods

124 2.1. Materials

125 Secondary wet sewage sludge, thickened by flotation, was provided by a
 126 municipal wastewater treatment plant located in Asturias (Spain). Once collected, the
 127 sludge was stored at 4 °C until its use (no more than 10 days). The main characteristics
 128 of this feedstock are shown in Table 1.

129 **Table 1.** Heavy metal concentration and physicochemical properties of sewage sludge.

Parameters	Mean values
pH	6.65 ± 0.03
Total Chemical Oxygen Demand (tCOD) (g O ₂ /L)	34 ± 4
Soluble Chemical Oxygen Demand (sCOD) (g O ₂ /L)	2.4 ± 0.5
Colour Number (CN)	0.10 ± 0.03
Soluble Total Organic Carbon (sTOC) (g C/L)	0.67 ± 0.01
Dry matter (DM) (g/L)	48 ± 2
Total Suspended Solids (TSS) (g/L)	45 ± 3
Volatile Suspended Solids (VSS) (g/L)	30 ± 1
Mercury (Hg) (mg Hg/kg dry matter)	0.6 ± 0.1
Cadmium (Cd) (mg Cd/kg dry matter)	0.7 ± 0.1
Chromium (Cr) (mg Cr/kg dry matter)	19 ± 1
Lead (Pb) (mg Pb/kg dry matter)	26 ± 1
Nickel (Ni) (mg Ni/kg dry matter)	28 ± 1
Copper (Cu) (mg Cu/kg dry matter)	150 ± 7

Zinc (Zn) (mg Zn/kg dry matter)	340 ± 20
Aluminium (Al) (mg Al/kg dry matter)	10300 ± 400
Iron (Fe) (mg Fe/kg dry matter)	12800 ± 600

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131 Among the metals present in the sludge, special attention has been paid to Hg,
132 Cd, Cr, Pb, Ni, Cu and Zn, due to the fact that their concentrations are the limiting
133 factors for sludge land application within the European Union (Hudcová et al., 2019).
134 Additionally, Al and Fe were also analysed because they are the majority metals in the
135 sewage sludge and are toxic for plants and humans in high concentrations, which makes
136 them considered as heavy metals by some authors (Jaishankar et al., 2014; Li et al.,
137 2016; Panda et al., 2009; Tchounwou et al., 2012). As expected, the heavy metal
138 concentrations in the raw sludge were much lower than the threshold values imposed by
139 legislation for its use as fertiliser by direct land application (see Table S.1.in
140 Supplementary Material). After centrifuging the sludge (10000 g, 20 min), the heavy
141 metal content was also determined in the supernatant obtained, turning out to be
142 negligible and indicating that heavy metals were not solubilised in the raw sludge, with
143 the exception of Hg. The distribution of this metal in the feedstock was 47% in the
144 liquid phase and 53% in the solid one, although its total concentration in the sludge was
145 low.

146 **2.2. Experimental setup**

147 A 1 L 316 SS semi-batch reactor (Parr Instrument Co., Moline, IL.) stirred by
148 two six-bladed magnetically driven turbine agitators (150 rpm) was employed to carry
149 out the hydrothermal experiments. The experimental setup (see Figure S.1. in
150 Supplementary Material) was also equipped with temperature and pressure controllers
151 and indicators, as well as bursting discs, a sampling system and a heating jacket. The

152 gas flow (1800 mL/min of oxygen for wet oxidation or nitrogen for thermal hydrolysis),
153 which was previously saturated with water by a 2 L humidifier, was provided since the
154 beginning of the experiment by a compressed cylinder. Both humidifier and reactor
155 were loaded to 70% of their total volume before starting to ensure safe operation.
156 Subsequently, samples were periodically withdrawn through a condenser and stored in
157 the refrigerator until their centrifugation and analysis.

158 The following operational conditions were tested: temperatures ranging between
159 160 °C and 200 °C, total pressures from 60 bar to 100 bar and the use of inert or
160 oxidising atmospheres. These low conditions were used because they promote good
161 degrees of solubilisation of high added value compounds and were commonly tested in
162 previous research (Barber, 2016; Suárez-Iglesias et al., 2017). More severe conditions
163 imply higher breakage of these biomolecules and more expensive operating costs.

164 **2.3. Analytical methods**

165 pH and tCOD were directly determined in the samples taken from the reactor
166 according to the Standard Methods (APHA et al., 2005). After carrying out these
167 analyses, the samples were centrifuged at 10000 g for 20 min in order to separate the
168 liquid and the solid phase. The following parameters were measured in the supernatant:
169 sCOD according to the Standard Methods (APHA et al., 2005); colour number (CN)
170 according to Urrea et al. (2014) with a T80 UV/VIS spectrophotometer (PG Instruments
171 Ltd, UK) and sTOC using a TOC-V CSH analyser (Shimadzu, Japan). Apart from that,
172 TSS and VSS were measured in the precipitate according to the Standard Methods
173 (APHA et al., 2005).

174 The concentrations of solubilised heavy metals (Hg, Cd, Cr, Pb, Ni, Cu, Zn, Al
175 and Fe) were determined in the supernatant by means of an ICP-MS (Agilent 7700x,

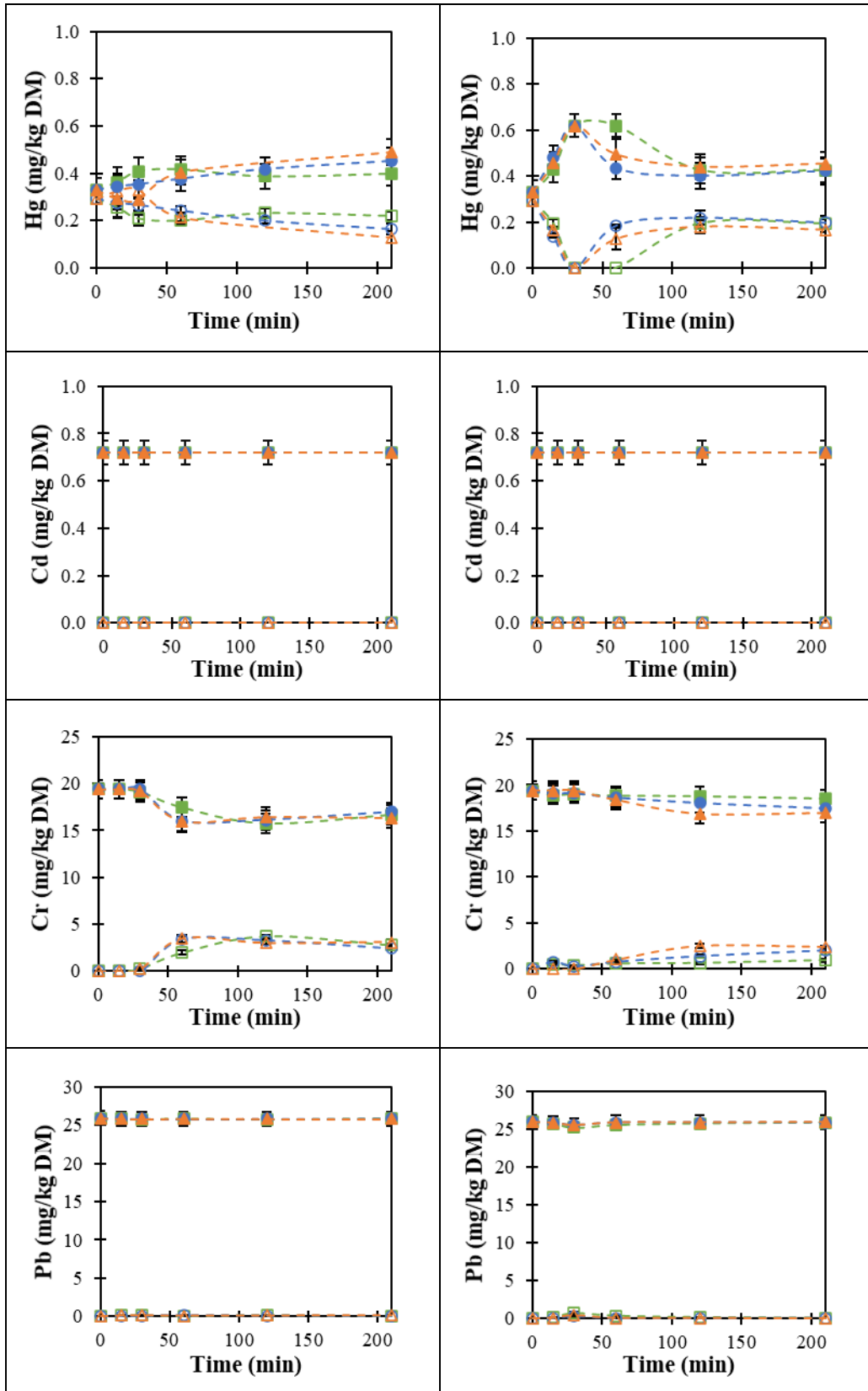
176 Agilent Technologies, CA, USA), equipped with an integrated I-AS autosampler. The
177 collision/reaction cell used 4.3 mL/min of He to eliminate the interferences. The
178 standards used for the metals analysed were Sc (to determine Al, Cr, Fe, Ni, Cu and
179 Zn), Rh (for Cd) and Ir (for Hg and Pb). The same method was used to determine the
180 total heavy metal content in the raw sludge but, before this analysis, a sample of raw
181 sludge was previously dried at 105 °C for 24 h and subsequently digested using the
182 microwave acid digestion method (6 mL of HNO₃ and 2 mL of a 30% H₂O₂ dissolution
183 and microwave equipment (Ethos One, Milestone Systems, Denmark)).

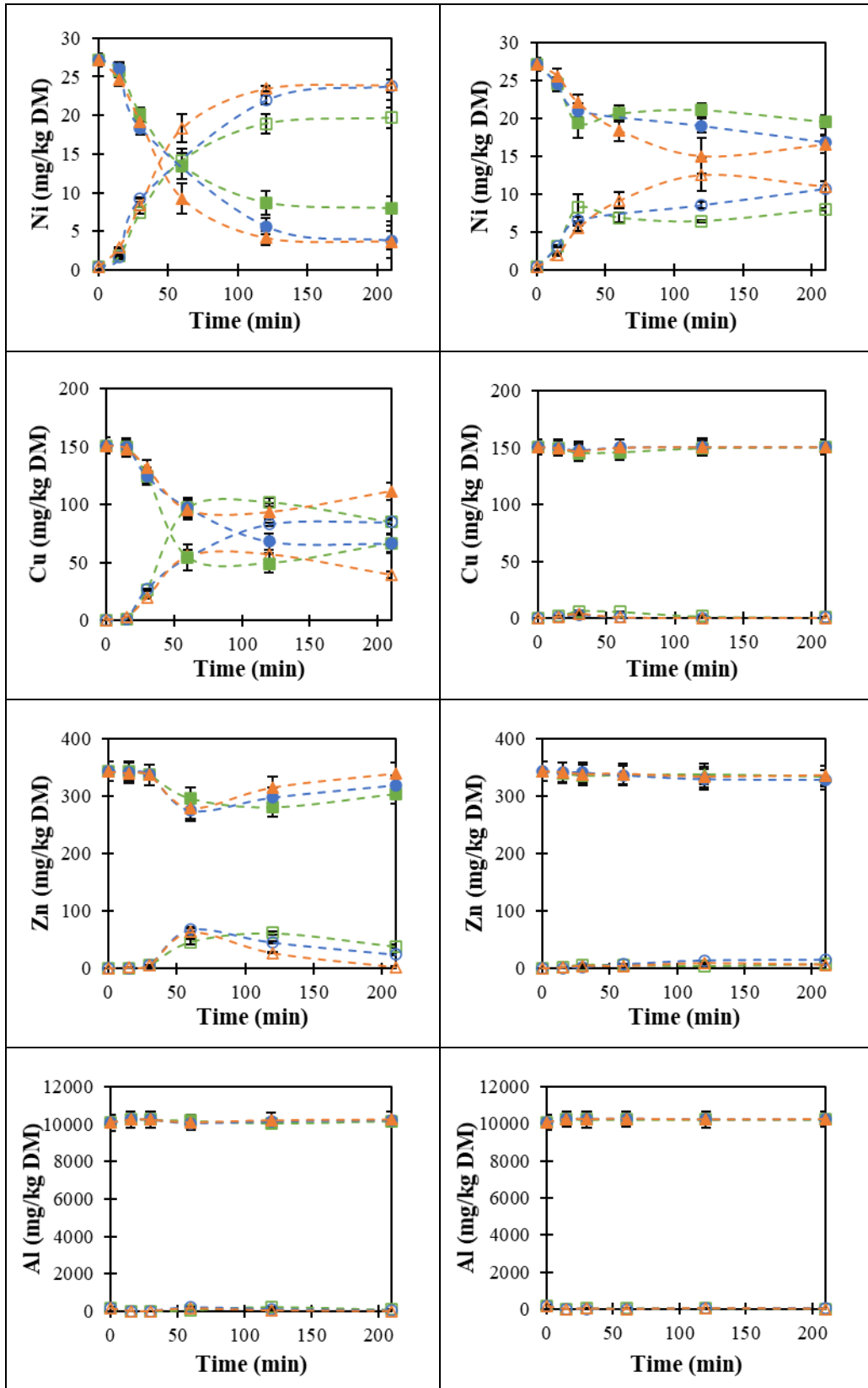
184 **3. Results and discussion**

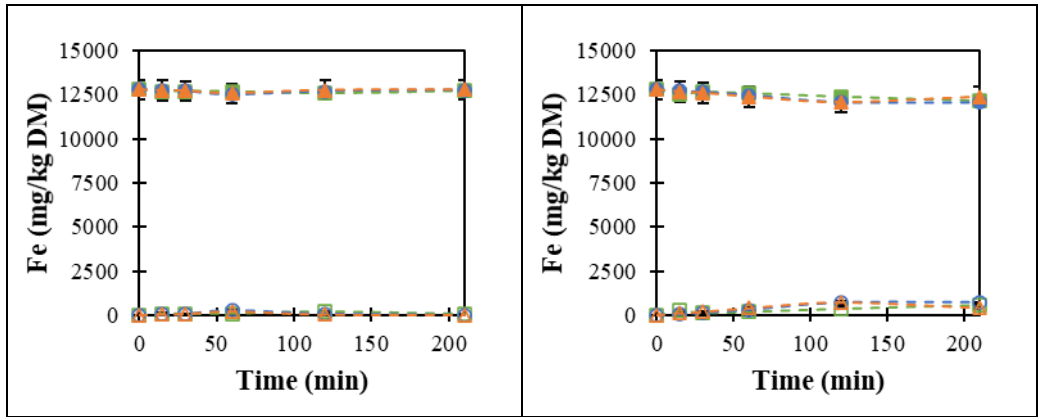
185 **3.1. Effect of type of atmosphere and temperature**

186 Firstly, the effect of the type of atmosphere (oxidising or inert) and temperature
187 on the concentrations of heavy metals (Hg, Cd, Cr, Pb, Ni, Cu, Zn, Al, Fe) during the
188 hydrothermal treatment of the secondary sewage sludge at 80 bar was studied, as shown
189 in Figure 1. To this purpose, different hydrothermal treatments were carried out at three
190 different temperatures (160, 180 and 200 °C) either in presence (wet oxidation) or
191 absence (thermal hydrolysis) of oxygen, measuring the concentrations of heavy metals
192 obtained after centrifuging each sample (solubilised metals). The fraction of non-
193 solubilised metal was easily calculated as the difference between the total amount of the
194 corresponding heavy metal in the raw sludge (see table 1) and the solubilised one for
195 each treatment time.

Wet oxidation (WO)	Thermal hydrolysis (TH)
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197 **Fig. 1.** Effect of temperature (160 (■), 180 (●) and 200 °C (▲)) on the concentration of
 198 solubilised (○) and non-solubilised (●) heavy metals during the hydrothermal treatment
 199 of sewage sludge in presence of an oxidising (left column) or inert (right column)
 200 atmosphere. In all cases: pressure, 80 bar; stirrer speed, 150 rpm; gas flow rate, 1800
 201 mL/min.

202 Focusing firstly on the effect of the atmosphere, most of these heavy metals (Hg,
 203 Cr, Ni, Cu, Zn and Fe) were significantly affected by the presence of oxygen during the
 204 hydrothermal treatments, observing that the oxidation promoted a greater solubilisation
 205 of the metals. Specifically, the most remarkable differences observed due to the type of
 206 atmosphere used were in the behaviours of Hg, Ni and Cu. In the case of Hg, during the
 207 wet oxidation, the concentration of dissolved metal gradually decreased throughout 210
 208 min of reaction, being this precipitation more noticeable at higher temperatures. Hence,
 209 the percentages of total Hg in the liquid phase at the end of the treatment (210 min)
 210 were 35.7% (0.22 ± 0.02 mg/kg DM) at 160 °C, 26.9% (0.17 ± 0.02 mg/kg DM) at 180
 211 °C and 21.0% (0.13 ± 0.02 mg/kg DM) at 200 °C. Nevertheless, in absence of oxygen,
 212 the concentration of dissolved Hg drastically decreased, being completely removed in
 213 less than 30 min, but after this time it was re-solubilised, being this solubilisation rate
 214 slower at the lowest temperature (160 °C). In fact, this metal almost reached again its

215 initial percentage in the liquid phase (from 47% to 30%) at the end of the treatment (210
216 min), regardless of the temperature tested. This re-dissolution could be caused by the
217 role of short organic molecules and the reduced sulphur as Hg ligands, reducing the
218 content of Hg in the solid phase (Zhang et al., 2015). Concerning Ni, this metal was
219 partially solubilised during both treatments and this mainly happened throughout the
220 first hour of treatment, but the absence of oxygen and/or the use of lower temperatures
221 reduced this solubilisation. Initially, only around 1.5% (0.42 ± 0.07 mg/kg DM) of the
222 total Ni was in the liquid phase for the raw sewage sludge, whereas this percentage
223 increased up to 71.2% (20 ± 1 mg/kg DM) at 160 °C, 86.2% (24 ± 1 mg/kg DM) at 180
224 °C and 86.7% (24 ± 2 mg/kg DM) at 200 °C after 210 min of treatment under an
225 oxidising atmosphere. Nevertheless, after the thermal hydrolysis, the percentage of this
226 metal in the liquid was around 45% lower than the one reached in the presence of
227 oxygen, with percentages of 29.1% (8.0 ± 0.2 mg/kg DM) at 160 °C, 38.9% (10.7 ± 0.1
228 mg/kg DM) at 180 °C and 39.9% (11.0 ± 0.7 mg/kg DM) at 200 °C. This fact could be
229 associated with the oxidation and mineralisation of the intermediate compounds formed
230 during the wet oxidation, reducing the possibilities of the complex formation, so the
231 metal concentration in the liquid phase increased. In contrast, during the thermal
232 hydrolysis, these compounds were not decomposed, so there could be a balance
233 between the solubilisation and the formation of complexes. Finally, the behaviour of Cu
234 during the wet oxidation was similar to the previously explained for Ni, although the
235 effect of temperature on their concentrations in the liquid phase was diametrically
236 opposed, with a negative impact of the temperature on the solubilisation rate of Cu.
237 Thus, the proportion of solubilised Cu increased from an initial value of 0.2% ($0.34 \pm$
238 0.01 mg/kg DM) to 56.0% (85 ± 4 mg/kg DM), 56.1% (85 ± 2 mg/kg DM) and 26.1%
239 (40 ± 3 mg/kg DM) at 160, 180 and 200 °C, respectively, after 210 min of wet

240 oxidation. On the contrary, this metal remained almost entirely in the solid phase during
241 the sludge thermal hydrolysis, a fact that radically contrasts with its trend during wet
242 oxidation. During the hydrolysis, solubilised Cu only slightly increased during the first
243 30 min of reaction, being this rise higher at the lowest temperature (from 0.2% to 3.9%).
244 Then, the concentration of Cu in the liquid phase under an inert atmosphere was
245 progressively reduced to almost the initial value, being this decrease faster at higher
246 temperatures. Hence, at the end of the thermal hydrolysis of the sludge, the proportions
247 of total Cu in the liquid were negligible for all the temperatures tested: 0.4% ($0.59 \pm$
248 0.02 mg/kg DM) at 160 °C, 0.3% (0.56 ± 0.04 mg/kg DM) at 180 °C and 0.2% ($0.39 \pm$
249 0.04 mg/kg DM) at 200 °C. This behaviour can be linked to the Maillard reactions that
250 occur at temperatures above 170 °C and the formation of H^+ during the thermal
251 hydrolysis. In fact, for temperatures lower than 170 °C, the Cu was solubilised while the
252 organic matter was hydrolysed into shorter molecules and the intra and extracellular
253 compounds were released, so solubilised Cu was combined with them. For higher
254 temperatures, the Maillard reactions consumed the small molecules and the H^+ formed
255 was accumulated in the surface of the oxides, so Cu remained in the solid phase in more
256 stable states than the one formed with these oxides (Sun et al., 2013; Wu et al., 2016).

257 Concerning Cr, Zn and Fe concentrations, the effect of the type of atmosphere
258 was less marked on these metals than on the previous ones. In the presence of oxygen,
259 the percentage of total Cr in the liquid phase mainly increased between 30 and 60 min
260 (from 0% to approximately 14%), being the solubilisation rate lower at the lowest
261 temperature (160 °C). After the first hour of reaction, the concentrations reached ($3.3 \pm$
262 0.3 mg/kg DM) remained constant until the end of the treatments. This solubilisation
263 was due to the transformation of the Cr^{3+} compounds, which were insoluble, into
264 soluble Cr^{6+} compounds at high temperatures (Zhang et al., 2017). Under an inert

265 atmosphere, Cr had a less pronounced but more continuous tendency towards its
266 solubilisation, which was greater when the temperature was increased. For instance, the
267 percentages of this metal in the liquid phase at the end of the thermal hydrolysis were
268 4.7% (0.9 ± 0.2 mg/kg DM), 10.2% (2.0 ± 0.1 mg/kg DM) and 12.5% (2.4 ± 0.1 mg/kg
269 DM) of the total amount of Cr in sludge at 160, 180 and 200 °C, respectively, obtaining
270 slightly lower solubilisation degrees than after wet oxidation. On its part, Zn was also
271 partially solubilised during the first hour of oxidation (from 0% to up to 19%), but then
272 its concentration in the liquid phase decreased, especially at high temperatures. At the
273 end of the wet oxidation, the net effect of the treatment was a partial solubilisation of
274 this metal, whose proportions in the liquid after 210 min of treatment at 160 °C, 180 °C
275 and 200 °C were 11.2% (38 ± 3 mg/kg DM), 7.0% (24 ± 2 mg/kg DM) and 0.8% ($2.7 \pm$
276 0.4 mg/kg DM), respectively, of the total amount of Zn in the sludge. Nonetheless, Zn
277 was hardly solubilised under an inert atmosphere (from 0% to 2% after 210 min). This
278 trend was caused by the solubilisation and volatilisation of part of the organic
279 complexes that were combined with Zn (Wu et al., 2016). Lastly, Fe was initially in the
280 solid phase of the raw sludge but its concentration in the liquid steadily increased until
281 60 min of oxidation at 180 and 200 °C, delayed to 120 min at the lowest temperature
282 (160 °C), being solubilised around 2% of the total Fe. After that maximum, the
283 concentration of solubilised Fe decreased again, being the higher the temperature, the
284 higher the precipitation. In the end, the percentages of Fe in the liquid phase were
285 insignificant: 0.6% (78 ± 5 mg/kg DM) at 160 °C, 0.2% (19 ± 1 mg/kg DM) at 180 °C
286 and 0.0% (0 ± 0 mg/kg DM) at 200 °C. On the other hand, when an inert atmosphere
287 was employed, the effect of temperature on solubilised Fe was analogous to that found
288 under an oxidising atmosphere but more marked. Hence, the Fe solubilisation at 160 °C
289 was continuous during the thermal hydrolysis, increasing its concentration in the liquid

290 phase from 0% to 4.8% (610 ± 20 mg/kg DM) after 210 min of treatment. However, at
291 higher temperatures, a peak of solubilised Fe (5.6% of the total Fe) was reached after
292 120 min, which is 4% higher than the achieved by wet oxidation. This concentration
293 (700 ± 100 mg/kg DM) remained constant at 180 °C until the end of the treatment (210
294 min) but decreased up to 3.1% (400 ± 20 mg/kg DM) at 200 °C for the same time. The
295 lower proportion of Fe in the liquid phase under an oxidising atmosphere could be
296 related to the oxidation of soluble Fe^{2+} to Fe^{3+} , which forms precipitates (Wu et al.,
297 2015).

298 Finally, focusing on the rest of metals (Cd, Pb and Al), their trends have shown
299 similarities during both thermal hydrolysis and wet oxidation treatments. Cd was the
300 only heavy metal that remained completely insoluble during both hydrothermal
301 treatments, regardless of temperature and type of atmosphere. In the case of Pb and Al,
302 although it cannot be perceived in the graphs due to the very low concentrations in the
303 liquid phase in comparison with the corresponding values to the solid one, the
304 temperature did have a slight effect on the soluble concentrations of these metals.
305 Regarding Pb, this was solubilised until reaching a maximum after 30 min, instead of
306 after 60 min as in the case of Fe, under both types of atmosphere. However, this peak of
307 solubilisation was more pronounced at the lowest temperature and higher in absence of
308 oxygen. Particularly, the proportion of total Pb in the liquid increased from 0.0% (0 ± 0
309 mg/kg DM) in the beginning to 2.7% (0.7 ± 0.1 mg/kg DM) at 160 °C, 1.4% ($0.38 \pm$
310 0.04 mg/kg DM) at 180 °C and 1.6% (0.40 ± 0.01 mg/kg DM) at 200 °C after 30 min of
311 treatment under an inert atmosphere, while the proportion never was higher than 0.5%
312 in presence of oxygen. After passing that time, the concentration of solubilised Pb was
313 reduced up to similar values, even though the temperature seemed to have an opposite
314 effect depending on the presence or absence of oxygen. Thus, during the wet oxidation

315 treatments, the higher the temperature, the lower the precipitation of the solubilised Pb.
316 As an example, the solubilised fraction of total Pb after 210 min of wet oxidation were
317 0.0% (0 ± 0 mg/kg DM) at 160 °C, 0.2% (0.06 ± 0.01 mg/kg DM) at 180 °C and 0.5%
318 (0.12 ± 0.01 mg/kg DM) at 200 °C. By contrast, at the end of the thermal hydrolysis,
319 greater Pb solubilities were obtained at lower temperatures, being the presence of this
320 metal in the liquid reduced to 0.3% (0.07 ± 0.01 mg/kg DM), 0.2% (0.04 ± 0.01 mg/kg
321 DM) and 0.0% (0 ± 0 mg/kg DM) at 160, 180 and 200 °C, respectively, of the total
322 amount in the sludge. This behaviour could be explained in a similar way that the
323 others. At lower temperatures and short reaction times, a higher proportion of Pb was
324 dissolved, particularly, the part of this metal that was in a form more sensitive to
325 changes in water composition. After that, at higher temperatures and longer times, the
326 solubilised metal was combined with the organic monomers, forming insoluble
327 complexes (Sun et al., 2013). Finally, 98.2% of the total Al was initially present in the
328 solid phase, but during the first 30 min of treatments, the small fraction of soluble Al
329 was also completely precipitated whereas, for higher reaction times, the presence of
330 oxygen and the temperature affected its trend. Under an oxidising atmosphere, its
331 concentration in the liquid phase was recovered after 60 min of treatment at 180 and
332 200 °C, delayed to 120 min at the lowest temperature (160 °C), to decreased again. So,
333 at the end of the oxidation (210 min) the distribution of the total Al in the liquid phase
334 was 0.9% (90 ± 3 mg/kg DM), 0.4% (36 ± 3 mg/kg DM) and 0.0% (0 ± 0 mg/kg DM)
335 after 210 min of treatment at 160 °C, 180 °C and 200 °C, respectively. Nevertheless,
336 under an inert atmosphere, Al did also precipitate during the first hour of thermal
337 hydrolysis, but then, the re-dissolution was much lower than that obtained by wet
338 oxidation and the concentrations reached were maintained during the treatment without
339 being affected by temperature, as was not the case during wet oxidation. Thus, the

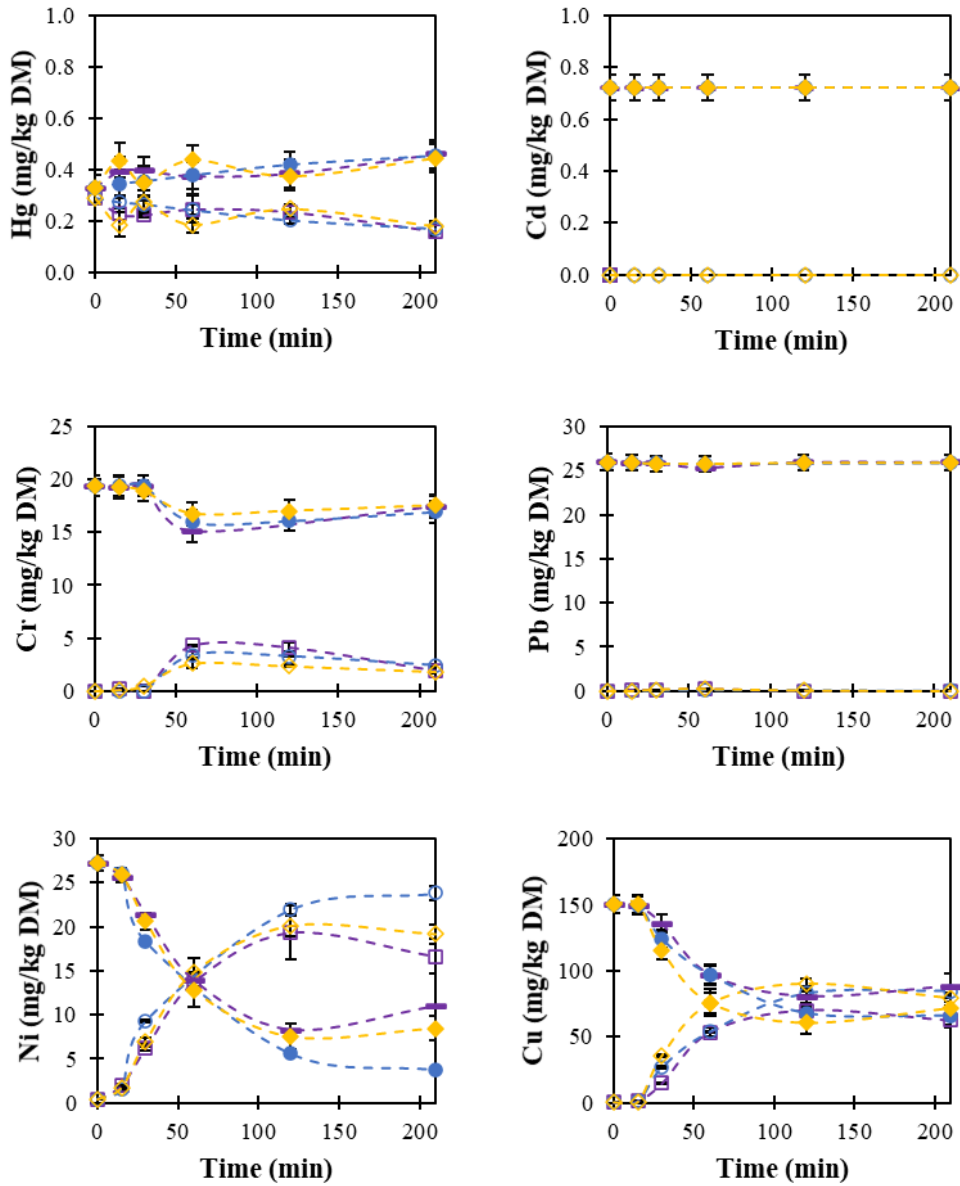
340 presence of Al in the liquid was reduced from 1.8% (190 ± 10 mg/kg DM) of the total
341 Al in the raw sludge to 0.2% (25 ± 3 mg/kg DM) at the end of the hydrolysis (210 min).

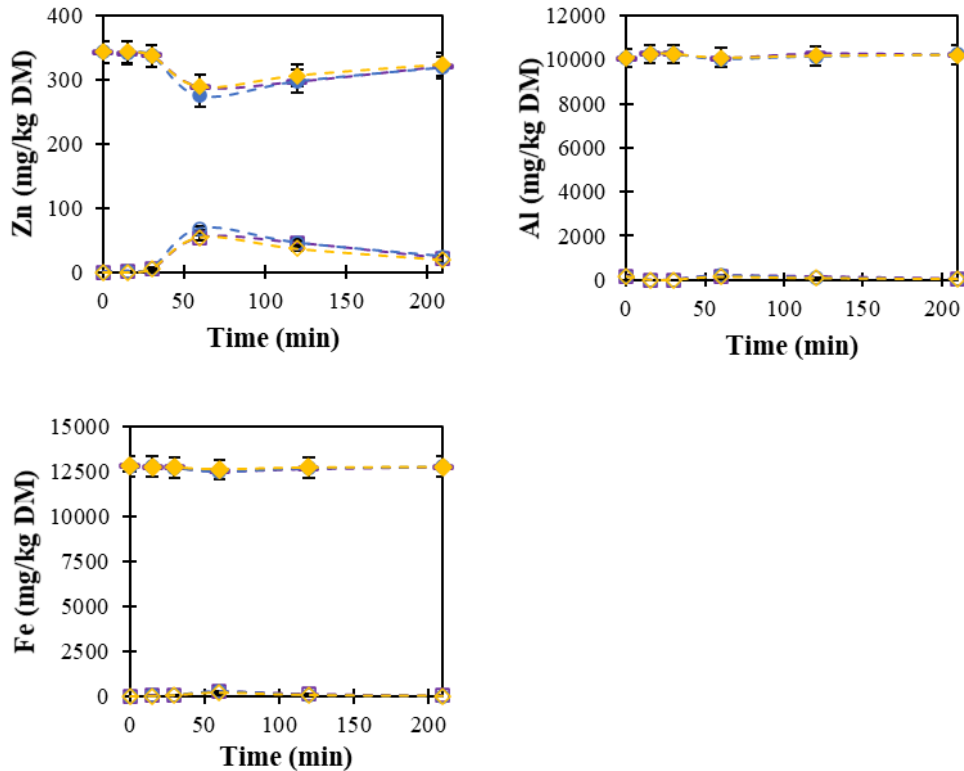
342 Therefore, in the view of the experimental results, it can be concluded that the
343 use of an inert atmosphere during the hydrothermal treatment of the sludge allows a
344 higher immobilisation of heavy metals in the solid phase than under an oxidising
345 atmosphere, except for Fe, which was solubilised to a greater extent under an inert one.
346 However, this metal was the most abundant one, so its solubilisation had a considerable
347 impact, causing that the total percentage of the sum of solubilised heavy metal in the
348 sewage sludge after the wet oxidation was lower than after thermal hydrolysis. Thus, the
349 proportion of heavy metals in the liquid phase of the sludge went from 0.8% (190 ± 10
350 mg/kg DM) to 1.3% (313 ± 8 mg/kg DM) at 160 °C, 0.8% (191 ± 5 mg/kg DM) at 180
351 °C and 0.3% (69 ± 3 mg/kg DM) at 200 °C after 210 min under an oxidising atmosphere
352 and to 2.7% (640 ± 20 mg/kg DM), 3.3% (780 ± 10 mg/kg DM) and 1.9% (440 ± 20
353 mg/kg DM), respectively, under an inert one.

354 Concerning the other operational parameter, the highest temperature produced
355 the greatest immobilisation of heavy metals, regardless of the atmosphere employed. In
356 addition, the lowest solubilised concentrations were obtained throughout the first 30
357 min of reaction. During this period of time, the second majority heavy metal in the
358 sludge (Al) precipitated and remained in the solid phase, which reduced the total
359 concentration of heavy metals in the liquid phase. Moreover, the low increase in the
360 metal concentration in the liquid phase is linked to the behaviour of the organic matter,
361 according to the explanations given for each metal. As can be seen in Figure S.2.
362 (Supplementary Material), throughout this time, the organic compounds had barely
363 reacted, nor have they solubilised in the liquid phase. Therefore, the bonds of the heavy
364 metals in the solid phase with these compounds had not been broken significantly.

365 **3.2. Effect of pressure**

366 In order to better understand the role of oxygen in the fate of the heavy metals
367 during the hydrothermal treatments of sludge, a set of wet oxidation experiments were
368 carried out at different pressures (see Figure 2).





369

370 **Fig. 2.** Effect of pressure (60 (—), 80 (●) and 100 bar (◆)) on the concentration of
 371 solubilised (○) and non-solubilised (●) heavy metals during the wet oxidation treatment
 372 of sewage sludge. In all cases: temperature, 180 °C, stirrer speed, 150 rpm; oxygen flow
 373 rate, 1800 mL/min.

374 Results revealed that, in general, the pressure effect on the distribution of heavy
 375 metals was less important than the temperature one, at least in the range tested. This can
 376 be easily deduced from the fact that the evolutions of heavy metals during the sludge
 377 wet oxidation under different pressures were similar one to another. In fact, the trends in
 378 the physicochemical properties of sludge (see Figure S.3. in Supplementary Material),
 379 being these linked to the solubilisation of the metals as explained throughout the
 380 previous section, behaved similarly regardless the pressure tested. Similar results were
 381 achieved by Urrea et al. (2014), who obtained only a slight increase in the oxidation rate
 382 at higher pressures due to cellular lysis is a hydrolytic process, so pressure hardly

383 affects it. Applied to the heavy metals, as higher pressure means more dissolved oxygen
384 and, therefore, the reactions are accelerated (Debellefontaine and Foussard, 2000), there
385 will be a greater presence of sulphates, phosphates and other compounds with which
386 metals form complexes (Shi et al., 2013; Zhang et al., 2017). For this reason,
387 solubilisation and precipitation could be compensated, causing that little effect was
388 observed.

389 As in the case of the temperature, Cd, Pb, Al and Fe mainly remained in the
390 solid phase throughout the experiments for all the pressures of oxygen tested, being in
391 the liquid phase in very small concentrations, with the exception of Cd, which was
392 again completely insoluble. The percentage of solubilised Pb increased from 0% (0 ± 0
393 mg/kg DM) to almost 1% (0.19 ± 0.05 mg/kg DM) in the liquid during the first 60 min
394 of treatment under oxygen, but then that proportion decreased below 0.2% (0.03 ± 0.02
395 mg/kg DM), regardless of the pressure chosen. In the case of Al, it experienced, as
396 previously commented, an initial precipitation, although the initial concentration of
397 metal in the liquid was again recovered after 60 min of experiments. Then, it decreased
398 until the end of the treatments, equally for all pressures tested, so the proportion in the
399 liquid phase was reduced from 1.8% (190 ± 10 mg/kg DM) to 0.4% (45 ± 7 mg/kg
400 DM). Similarly, Fe reached a peak of solubilisation after 60 min of treatment, being
401 slightly lower at the highest pressure (from 0% (0 ± 0 mg/kg DM) to 2.0% (256 ± 10
402 mg/kg DM), 2.1% (268 ± 3 mg/kg DM) and 1.4% (180 ± 20 mg/kg DM) respectively, at
403 60, 80 and 100 bar). Then, its decrease in the liquid phase was continuous until the end
404 of the treatment, achieving the same final concentration in the liquid (0.2% of the metal
405 or 27 ± 5 mg/kg DM), regardless of the pressure tested.

406 Regarding Hg, its trend was a continuous precipitation during the treatments. For
407 instance, after 210 min of wet oxidation, the percentage of total Hg in the liquid phase

408 was reduced from 47% (0.29 ± 0.02 mg/kg DM) to 25.7% (0.16 ± 0.03 mg/kg DM),
409 26.9% (0.17 ± 0.02 mg/kg DM) and 28.4% (0.18 ± 0.2 mg/kg DM) at 60, 80 and 100
410 bar. Contrary to that trend, Ni and Cu were progressively solubilised from the sludge
411 during wet oxidation, remaining at the end around 70% (20 ± 3 mg/kg DM) and 50%
412 (75 ± 6 mg/kg DM) of total metal in the liquid phase, respectively. Finally, Cr and Zn
413 experienced a peak of solubilisation after 60 min, with this being slightly greater at the
414 lowest pressure. Nevertheless, at the end of wet oxidation, 10% (2.1 ± 0.3 mg/kg DM)
415 of the total Cr and 6% (22 ± 2 mg/kg DM) of the total Zn remained in the liquid phase,
416 regardless of the pressure tested.

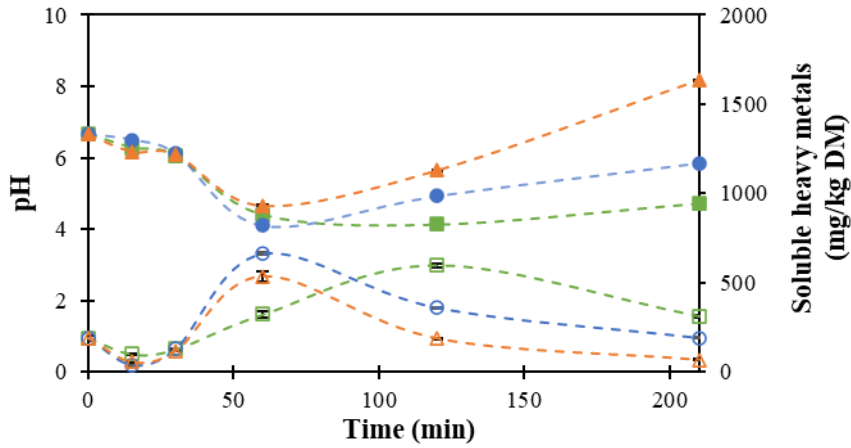
417 Lastly, analysing the overall effect of pressure on the total amount of solubilised
418 heavy metals, it is proved that pressure is not a determining factor in their fate,
419 obtaining percentages of 0.78% (187 ± 9 mg/kg DM) at 60 bar, 0.79% (191 ± 5 mg/kg
420 DM) at 80 bar and 0.80% (192 ± 5 mg/kg DM) at 100 bar after 210 min. Furthermore,
421 as in the case of the temperature, during the first 30 min of reaction, the lowest
422 percentages of heavy metals in the liquid fraction of sludge were registered.

423 In addition, it is important to note that the initial percentage of solubilised metals
424 in the raw sewage sludge (0.81%) is similar to that after 210 min of wet oxidation.
425 However, the oxidised sludge contains more products of high added value in the liquid
426 phase, while the volume of the solids is reduced and, therefore, heavy metals are more
427 concentrated in this phase than before the treatment. In fact, the total concentration of
428 heavy metals in the solid phase increased from 27 ± 1 g/kg TSS to 126 ± 8 g/kg TSS at
429 the end of the treatment.

430 **3.3. Discussion**

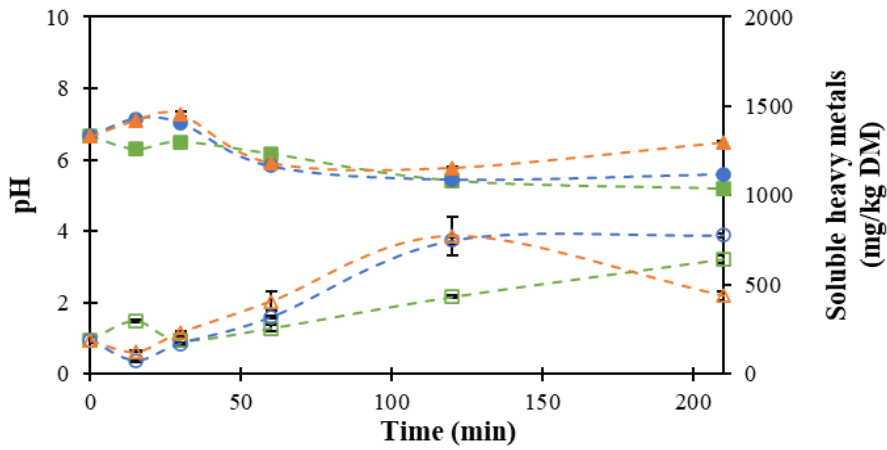
431 In order to better understand the fate of the heavy metals, Figure 3 shows the
 432 evolution of their total concentration in the liquid phase during the different treatments
 433 and working conditions alongside the pH evolutions.

434 **a.1)**



435

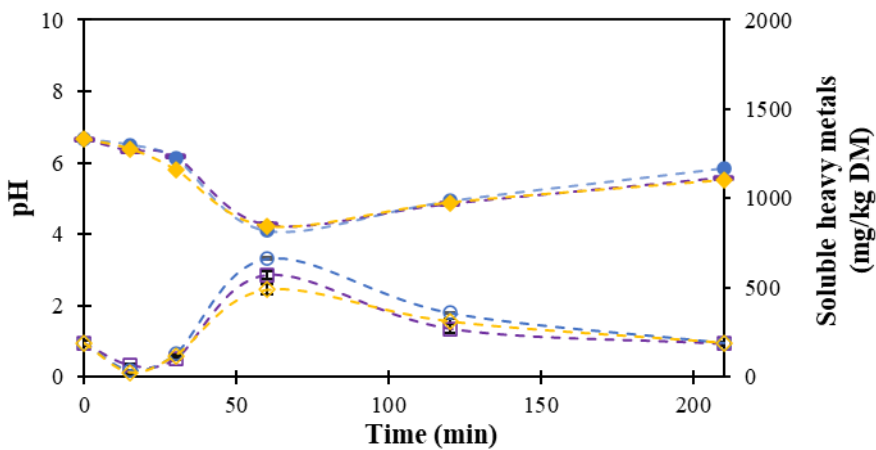
436 **a.2)**



437

438

b)



439

440 **Fig. 3.** a) Effect of temperature (160 (■), 180 (●) and 200 °C (▲) at 80 bar) on the
441 concentration of heavy metals in the liquid phase (○) and pH (●) during the wet
442 oxidation (1) and thermal hydrolysis (2) of sewage sludge; b) effect of pressure (60
443 (—), 80 (●) and 100 bar (◆) at 180 °C) during the wet oxidation of sewage sludge. In all
444 cases: stirrer speed, 150 rpm; oxygen flow rate, 1800 mL/min.

445 As previously explained, the solubilisation of the heavy metals is highly related
446 to the changes in the physicochemical properties of the sludge during the hydrothermal
447 treatments (see Figure S.2. in Supplementary Material). In this sense, it is well known
448 that extracellular polymeric substances (EPS) play a very important role in biosorption
449 of heavy metals. EPS comprise a mixture of, mainly, polysaccharides and proteins that
450 contain ionizable functional groups such as carboxyl, phosphoric, amine and hydroxyl
451 groups, which enable EPS to sequester heavy metals. Ion exchange, complexation with
452 negatively charged functional groups, adsorption and precipitation are the mechanism
453 involved in this metal biosorption onto EPS (Nouha et al., 2018). These EPS, which
454 remain attached to the outer surface of the cell, are the first solubilised fraction of the
455 sludge, even at moderate temperatures (Urrea et al., 2018). This would also involve a
456 high release of heavy metals into the liquid phase as the temperature increased, owing to
457 the loss of the bonds (Wu et al., 2016). Once solubilised, these heavy metals are
458 immersed in a hydrolysate composed by a complex pool of proteins, carbohydrates,
459 humic acids, organic acids... All these different substances can also be transformed into
460 shorter-chain compounds during the treatment and interact with the dissolved heavy
461 metals by adsorption, depending on the pH of the medium. This produce, mainly in
462 form of phosphates, the precipitation and immobilisation of a fraction of the heavy
463 metals in the solid phase for longer times of treatment (Shi et al., 2013; Sun et al., 2013;
464 Zhang et al., 2015; Zhang et al., 2017).

465 In this sense, although the mechanisms of reaction are significantly different
466 depending on the type of atmosphere employed during the hydrothermal treatment, no
467 release of metals was observed during the first minutes of reaction (see Figure 3), when
468 the operational conditions (temperature and pressure) had not yet been reached and the
469 oxidation reactions had not been well developed. After that, both types of treatments
470 (wet oxidation and thermal hydrolysis) produced an increase in sCOD and,
471 consequently, in sTOC, due to the release of extra and intracellular compounds to the
472 liquid phase (Suárez-Iglesias et al., 2017), with a maximum of solubilisation after 60
473 min of treatment (see Figure S.2. in Supplementary Material). However, whereas the
474 soluble organic load did not change after this time using an inert atmosphere, the
475 presence of an oxidising atmosphere during the wet oxidation involved that the organic
476 matter was firstly oxidised to intermediate compounds and then, these to CO₂ and water
477 (Oulego et al., 2016; Urrea et al., 2014), so both tCOD and sCOD decreased after that
478 60 min of reaction. For this reason, the reaction medium was firstly acidified by the
479 presence of these acidic intermediates that were subsequently degraded (Urrea et al.,
480 2014). Some intermediates, such as oxidised phenol-like compounds, as well as other
481 coloured cellular compounds solubilised from the sludge, were indirectly measured by
482 the colour number (Urrea et al., 2018), which also registered a maximum after 60
483 minutes of treatment. In contrast, during the thermal hydrolysis, the oxidation of the
484 organic load did not occur due to the absence of oxygen, so tCOD and pH remained
485 almost unaltered throughout the treatment (Urrea et al., 2018). Despite this, the colour
486 number also increased, but to a greater extent than in presence of oxygen, which was
487 probably due to the formation of melanoidins by the Maillard reactions between the
488 solubilised proteins and carbohydrates (Dwyer et al., 2008).

489 Due to the impossibility of obtaining a detailed description of each compound in
490 the hydrolysate and the high complexity of the interactions between these and the
491 different metals, explaining the fate of a specific metal during the hydrothermal
492 treatment of sludge is difficult. Nevertheless, some fundamental aspects can indeed be
493 concluded.

494 The first one is that low pH values had a positive effect on the solubilisation of
495 heavy metals in the liquid phase, as can be seen in Figure 3. In fact, the maximum
496 concentration of dissolved metals (between 60 and 120 min) coincided with the lowest
497 pH values observed. The decrease in pH value during the first hour of hydrothermal
498 treatment had a double positive effect on the initial solubilisation of heavy metals
499 because the acidic medium increased the EPS solubilisation and improved the metal
500 stability in aqueous phase. However, as the pH increased again by the hydrolysis and,
501 mainly, the oxidation reactions of the organic compounds, the presence of dissolved
502 heavy metals was noticeably reduced. In this sense, Boardman et al. (2004) reported a
503 minimum in the solubility of metal hydroxides at pH values ranging from 8 to 10,
504 depending on the metal considered. This pH effect on the fate of the heavy metals
505 during the hydrothermal treatment of sludge was linked to the type of atmosphere
506 employed. As previously explained, carrying out the sludge solubilisation under an
507 oxidising atmosphere provoked a higher acidification of the hydrolysate at the
508 beginning of the treatment, as well as a faster VSS disintegration, which involved a
509 higher concentration of dissolved metal in comparison with the hydrothermal process
510 under an inert one. However, for longer reaction times, the oxidation of the dissolved
511 organic matter provoked a re-alkalinisation of the hydrolysate to values even higher
512 than the initial one. This caused a higher removal of dissolved metals at the end of the

513 treatment (210 min) than the obtained under an inert atmosphere, where pH values
514 hardly fluctuated during the treatment.

515 Regarding the temperature, it had opposite effects on the solubilisation of heavy
516 metals from sludge. On one hand, the higher the temperature, the faster the EPS
517 solubilisation and the release of heavy metals, which involved a higher mobilisation of
518 these. On the other hand, the higher the temperature, the largest the degradation of the
519 organic matter, especially under oxidising atmospheres, which produced a higher final
520 re-alkalinisation of the hydrolysate and a lower stability of the dissolved heavy metals.

521 Finally, the oxygen pressure was not a determining factor neither for the
522 solubilisation of heavy metals nor for the evolution of the physicochemical properties of
523 sludge (see Figure S.3. in Supplementary Material) due to cellular lysis is a hydrolytic
524 process, as previously commented. Moreover, the higher the pressure, the faster the
525 oxidation rate, which means that the greater the presence of sulphates and phosphates,
526 among others, which can form complexes with metals (Debellefontaine and Foussard,
527 2000; Shi et al., 2013; Zhang et al., 2017). For these reasons, solubilisation and
528 precipitation could be balanced. In this case, the pressure only affected the colour
529 number. Regarding its evolution, it seemed that 80 bar was the optimal pressure for
530 coloured intermediate formation, as 60 bar did not promote it and 100 bar accelerated
531 their decomposition.

532 In any case, it is important to note that the previous discussion has been carried
533 out in terms of total dissolved heavy metals (see Figure 3), as the sum of the dissolved
534 concentration of each heavy metal for a specific reaction time, so the overall trend of
535 heavy metals was highly influenced by the behaviour of the predominant metals, that is
536 to say, Al and Fe. Nonetheless, almost all heavy metals analysed described to a greater
537 or lesser extent the trends shown in Figure 3, except for Cd, Hg and Ni. In fact, Cd

538 remained immobilised in the solid phase, while Hg followed a downward trend and Ni
539 remained in the liquid phase after being solubilised in presence of oxygen.

540 **4. Conclusions**

541 As heavy metal concentrations are considered critical parameters for the sewage
542 sludge valorisation, this study assesses the effect of the operational conditions on the
543 fate of the main heavy metals during the hydrothermal treatment of wet no-diluted
544 sewage sludge. In this sense, the election of an inert atmosphere led to a higher
545 immobilisation of heavy metals in the solid phase than an oxidising one, with the
546 exception of Fe. In addition, the total amount of heavy metals that were solubilised in
547 the liquid phase after both treatments (210 min) represents less than 4% of their total
548 amount in the sludge, while their total concentration in the solid phase increased around
549 5 times due to the volatile suspended solids disintegration. Concerning the operational
550 conditions, the higher the temperature, the greater the immobilisation of heavy metals
551 was, regardless of the atmosphere employed, while the pressure was not a determining
552 factor on the fate of the heavy metals. Finally, regarding the time of reaction, the lowest
553 solubilised concentration of heavy metals was obtained throughout the first 30 min of
554 hydrothermal treatments.

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683

Supplementary Material

HEAVY METAL SOLUBILISATION DURING THE HYDROTHERMAL TREATMENT OF SLUDGE

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INDEX

- Table S.1.** Limit heavy metal concentrations as a function of soil pH in Spain (Hudcová et al., 2019) and their concentration in the raw sludge employed in this work. 3
- Figure S.1.** Scheme of the experimental setup: (B1) compressed bottle of oxygen or nitrogen, (H1) humidifier, (R1) reactor with heating jacket, (C1) condenser, (E1) PID controller (gas flow, humidifier and reactor temperature, stirrer speed and pressure). Streams: (1) gas, (2) saturated gas, (3) gas outlet, (4) sample outlet. 4
- Figure S.2.** Effect of temperature (160 (■), 180 (●) and 200 °C (▲)) on the main physicochemical properties (pH, CN, tCOD, sCOD, sTOC, TSS and VSS) during the hydrothermal treatment of sewage sludge in presence of an oxidising (left column) or inert (right column) atmosphere. In all cases: pressure, 80 bar; stirrer speed, 150 rpm; gas flow rate, 1800 mL/min. 4
- Figure S.3.** Effect of pressure (60 (—), 80 (●) and 100 bar (◆)) on the main physicochemical properties (pH, CN, tCOD, sCOD, sTOC, TSS and VSS) during the wet oxidation treatment of sewage sludge. In all cases: temperature, 180 °C; stirrer speed, 150 rpm; oxygen flow rate, 1800 mL/min. 6

Table S.1. Limit heavy metal concentrations as a function of soil pH in Spain (Hudcová et al., 2019)* and their concentration in the raw sludge employed in this work.

Heavy metal	Soils with pH < 7 (mg/kg dry matter)	Soils with pH > 7 (mg/kg dry matter)	Raw sewage sludge (mg/kg dry matter)
Mercury (Hg)	16	25	0.6 ± 0.1
Cadmium (Cd)	20	40	0.7 ± 0.1
Chromium (Cr)	1000	1500	19 ± 1
Lead (Pb)	750	1200	26 ± 1
Nickel (Ni)	300	400	28 ± 1
Copper (Cu)	1000	1750	150 ± 7
Zinc (Zn)	2500	4000	340 ± 20
Aluminium (Al)	-	-	10300 ± 400
Iron (Fe)	-	-	12800 ± 600

* Hudcová, H., Vymazal, J., Rozkošný, M., 2019. Present restrictions of sewage sludge application in agriculture within the European Union. *Soil Water Res.* 14, 104–120. <https://doi.org/10.17221/36/2018-SWR>

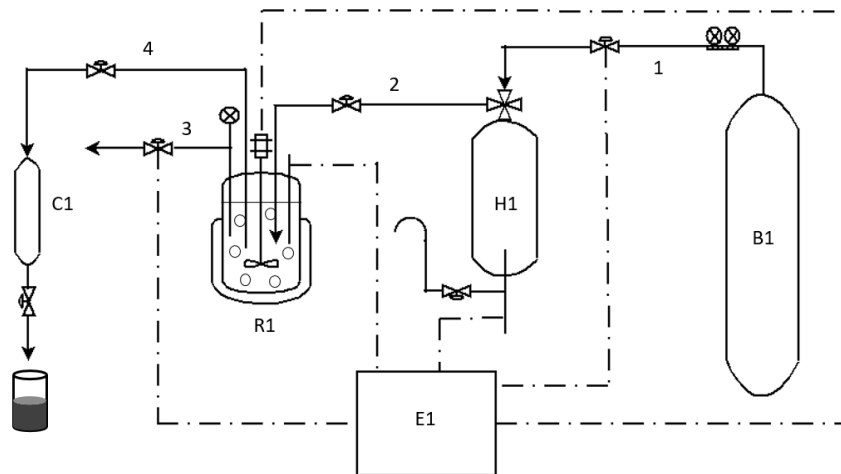
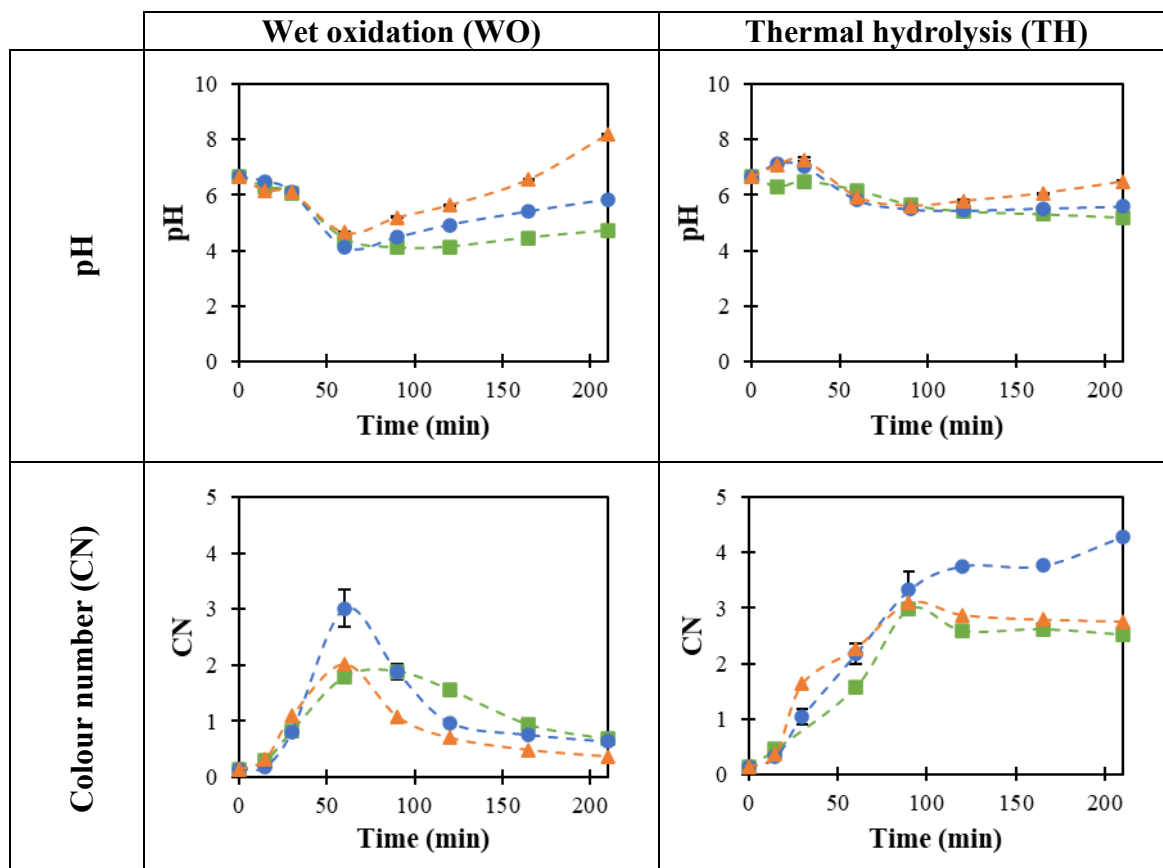


Fig. S.1. Scheme of the experimental setup: (B1) compressed bottle of oxygen or nitrogen, (H1) humidifier, (R1) reactor with heating jacket, (C1) condenser, (E1) PID controller (gas flow, humidifier and reactor temperature, stirrer speed and pressure).

Streams: (1) gas, (2) saturated gas, (3) gas outlet, (4) sample outlet.



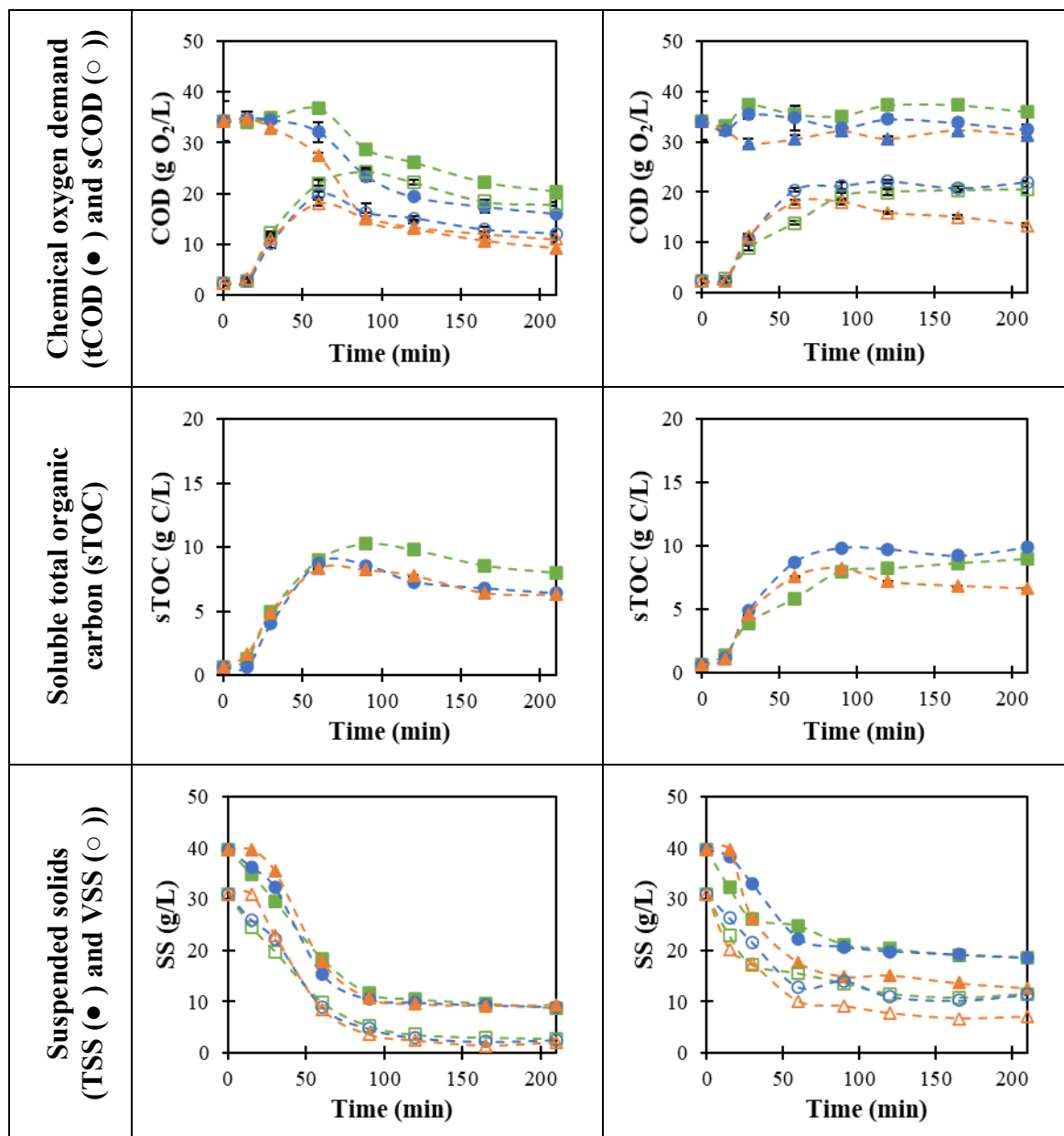
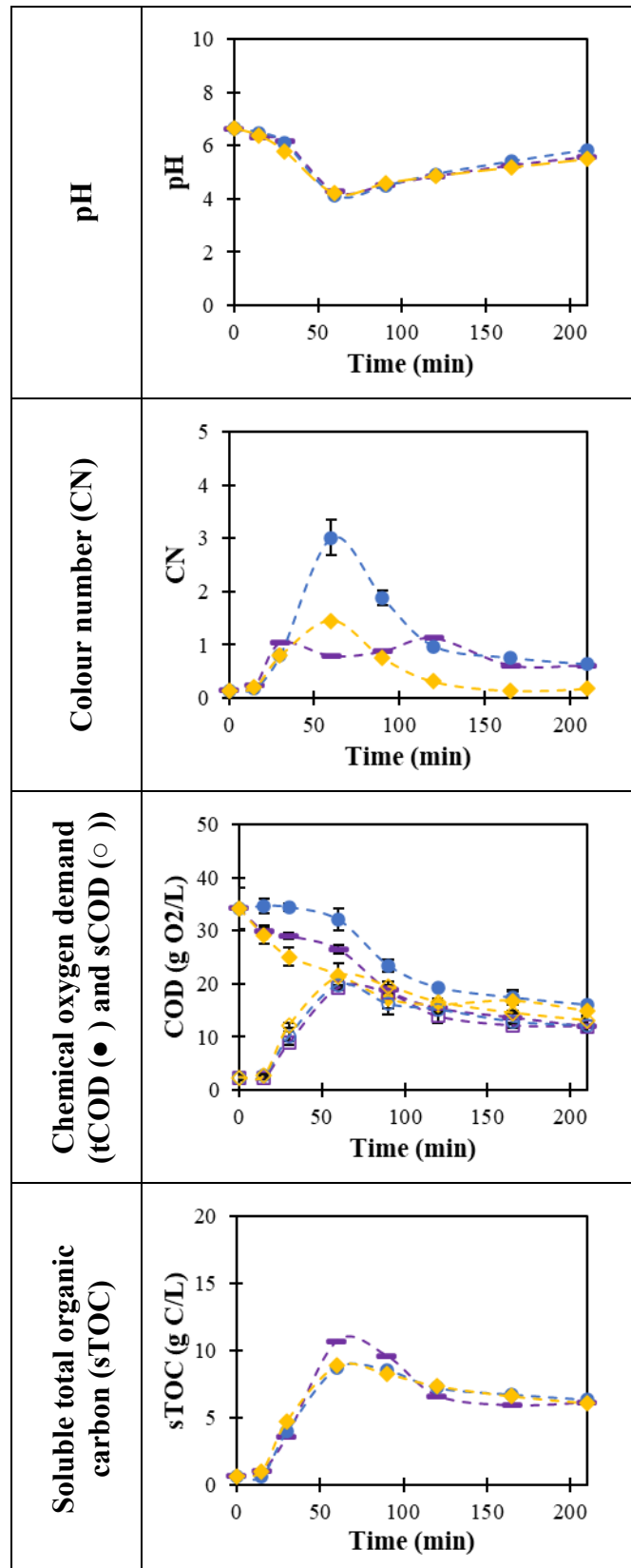


Figure S.2. Effect of temperature (160 (■), 180 (●) and 200 °C (▲)) on the main physicochemical properties (pH, CN, tCOD, sCOD, sTOC, TSS and VSS) during the hydrothermal treatment of sewage sludge in presence of an oxidising (left column) or inert (right column) atmosphere. In all cases: pressure, 80 bar; stirrer speed, 150 rpm; gas flow rate, 1800 mL/min.



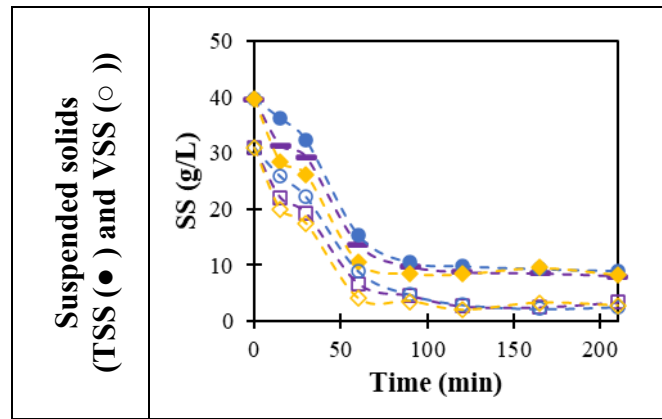


Figure S.3. Effect of pressure (60 (—), 80 (●) and 100 bar (◆)) on the main physicochemical properties (pH, CN, tCOD, sCOD, sTOC, TSS and VSS) during the wet oxidation treatment of sewage sludge. In all cases: temperature, 180 °C; stirrer speed, 150 rpm; oxygen flow rate, 1800 mL/min.