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2 Impact of oxy-fuel combustion gases on mercury retention  
3 in activated carbons from a macroalgae waste: effect of  
4 water

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17

18 **Abstract**

19 The aim of this study is to understand the different sorption behaviours of mercury  
20 species on activated carbons in the oxy-fuel combustion of coal and the effect of high  
21 quantities of water vapour on the retention process. The work evaluates the interactions  
22 between the mercury species and a series of activated carbons prepared from a  
23 macroalgae waste (algae meal) from the agar-agar industry in oxy-combustion  
24 atmospheres, focussing on the role that the high concentration of water in the flue gases  
25 plays in mercury retention. Two novel aspects are considered in this work i) the impact  
26 of oxy-combustion gases on the retention of mercury by activated carbons and ii) the  
27 performance of activated carbons prepared from biomass algae wastes for this  
28 application. The results obtained at laboratory scale indicate that the effect of the  
29 chemical and textural characteristics of the activated carbons on mercury capture is not  
30 as important as that of reactive gases, such as the SO<sub>x</sub> and water vapour present in the  
31 flue gas. Mercury retention was found to be much lower in the oxy-combustion  
32 atmosphere than in the O<sub>2</sub>+N<sub>2</sub> (12.6% O<sub>2</sub>) atmosphere. However, the oxidation of  
33 elemental mercury (Hg<sup>0</sup>) to form oxidized mercury (Hg<sup>2+</sup>) amounted to 60%, resulting  
34 in an enhancement of mercury retention in the flue gas desulphurization units and a  
35 reduction in the amalgamation of Hg<sup>0</sup> in the CO<sub>2</sub> compression unit. This result is of  
36 considerable importance for the development of technologies based on activated carbon  
37 sorbents for mercury control in oxy-combustion processes.

38

39 **Keywords:** mercury; activated carbons; industrial macroalgae waste; oxy-combustion

## 40 1. Introduction

41 Oxy-coal combustion is a promising technology in the field of CO<sub>2</sub> capture and  
42 sequestration (CCS). The basic principle behind this technology is to burn coal in a  
43 mixture of O<sub>2</sub> and recycled gas so that the resulting flue gas is mainly CO<sub>2</sub> and H<sub>2</sub>O  
44 which simplifies the process of separation of CO<sub>2</sub> from the flue gas for further storage  
45 or beneficial use. Although this gas also contains small quantities of O<sub>2</sub>, N<sub>2</sub> and minor  
46 concentrations of SO<sub>x</sub> and NO<sub>x</sub>, the CO<sub>2</sub> can be relatively easily separated before its  
47 capture (Buhre et al., 2005; Wall et al., 2013). The new oxy-combustion conditions may  
48 lead to certain changes with respect to conventional combustion conditions, which  
49 might involve modifications not only in the composition of the reactive gases (Normann  
50 et al., 2009; Liémans et al., 2011; Stanger and Wall, 2011; Ting et al., 2013), but also in  
51 the fate of the trace elements (Roy and Bhattacharya, 2014). Of the trace elements,  
52 mercury is the one of greatest concern because coal combustion is one of the major  
53 anthropogenic sources of mercury to the environment (Zhuang et al., 2011b; Roy et al.,  
54 2013).

55 Mercury is a highly toxic element whose environmental impact is widely recognised,  
56 which is why governments and several organizations have introduced measures to bring  
57 it under control (USEPA, 2011). In particular, one of the UNEP (United Nations  
58 Environment Programme) targets is to protect human health from the release of mercury  
59 and its compounds (UNEP, 2013), and a priority in this field, is the mercury released  
60 from coal combustion. However, in the case of oxy-combustion, mercury is not only an  
61 environmental problem but also a technological one since Hg<sup>0</sup> can accumulate in the  
62 CO<sub>2</sub> compression units and damage the aluminium heat exchangers due to  
63 amalgamation of mercury with aluminium (Santos, 2010).

64 There are basically two ways to capture mercury during coal combustion processes. One  
65 of them is to install purpose-designed systems for mercury capture in power stations,  
66 and the other is to make use of already installed systems intended for the capture of  
67 other contaminants for the co-removal of mercury. A large number of the purpose-  
68 designed systems for capturing mercury species in gas phase are based on solid  
69 sorbents. Of these, activated carbons that are capable of physically or chemically  
70 adsorbing this element, are the most common (Sjostrom et al., 2010). The effectiveness  
71 of activated carbons, which have been evaluated not only at laboratory and pilot level,  
72 but also at industrial scale (Pavlish et al., 2010), depends on particle size, surface area,  
73 porosity, etc. (Lopez-Anton et al., 2002), and gas composition, since reactive gases can  
74 influence mercury speciation and mercury sorption mechanisms.

75 Numerous studies have already been performed on the application of activated carbons  
76 for mercury capture in gases from combustion, and to refer to all of them is outside the  
77 scope of this paper. However, the knowledge accumulated by these studies constitutes a  
78 solid basis to address the emerging problems associated with oxy-combustion that,  
79 given the current state of the art, are far from being understood. To achieve a solution to  
80 these problems it is first necessary to identify the mechanisms of heterogeneous  
81 mercury oxidation on the carbon surface and to determine how the gas composition may  
82 modify these mechanisms (Liu and Vidic, 2000; Miller et al., 2000; Granite and Presto,  
83 2008). To achieve these goals, the effects of reactive gases need to be considered.

84 Although the effect of SO<sub>2</sub> on mercury adsorption is of great importance, it has not yet  
85 been fully clarified even in conventional combustion plants. Some authors (Uddin et al.,  
86 2008; Diamantopoulou et al., 2010; Morris et al., 2012) have concluded that SO<sub>2</sub> favors  
87 mercury adsorption, particularly in the presence of O<sub>2</sub>, due to the formation of HgSO<sub>4</sub>  
88 on the surface. Other studies (Presto and Granite, 2007; Granite and Presto, 2008;

89 Sjostrom et al., 2009; Morris et al., 2010; Zhuang et al., 2011a; His and Chen, 2012),  
90 however, suggest that the  $\text{SO}_3$  in flue gases leads to the formation of  $\text{H}_2\text{SO}_4$  on the  
91 surface of the activated carbon which leads to pore blockage, inhibiting the adsorption  
92 of  $\text{Hg}^0$ . The role of water in mercury retention by activated carbons during conventional  
93 combustion is another variable whose influence on the adsorption mechanism has been  
94 explained in various ways. However, in the case oxy-combustion the role of water needs  
95 to be fully clarified because in this particular process, water vapor can be expected to be  
96 present in significantly higher concentrations. Apparently, the presence of water in the  
97 flue gas, even in the range of 5-10%, seriously impedes the removal of mercury  
98 (Cudahy and Helsel, 2000; Richards, 2005; Presto and Granite, 2007), probably due to  
99 the adsorption of water molecules into the micropore structure of the activated carbon,  
100 which reduces the number of the active sites available for mercury (Zheng et al., 2012).  
101 However, Li et al. (2002) found that moisture on activated carbon surfaces favours  $\text{Hg}^0$   
102 adsorption at room temperature.

103 To stress the importance of flue gas composition for mercury retention on activated  
104 carbon is not to imply that the characteristics of the activated carbon itself are not  
105 important. Typical activated carbons may capture  $\text{Hg}^{2+}$ , but in general they are not good  
106 sorbents for  $\text{Hg}^0$ . The retention of  $\text{Hg}^0$  can be significantly enhanced by using activated  
107 carbons impregnated with sulfur, chlorine, bromine or iodine that chemically interact  
108 with  $\text{Hg}^0$  (Assian and Kaghazchi, 2013; Rupp and Wilcox, 2014). The limitation that is  
109 often attributed to these impregnated materials is the cost of the preparation (Pacyna et  
110 al., 2010). This explains why the use of solid wastes as precursors for the preparation of  
111 activated carbons has emerged as a competitive way to produce these materials (Klasson  
112 et al., 2010). Satisfactory results for mercury retention have been obtained using  
113 renewable sources of carbon such as bamboo charcoal, poultry manure, waste tires,

114 chicken waste, etc (Skodras et al., 2007; Yaji et al., 2008; Tan et al., 2011). Although  
115 some of these sorbents have been tested at industrial scale (De et al., 2013), most of the  
116 studies have so far been focused on the development of good textural and chemical  
117 properties of the activated carbons with very little attention being paid to the effect that  
118 the gases in a full coal combustion atmosphere have on mercury retention. In addition,  
119 the results may be very different in an oxy-combustion atmosphere and in one of air  
120 combustion due to their different gas compositions.

121 In view of these considerations this work focuses on the interactions between mercury  
122 species and a series of activated carbons prepared from a waste from the agar-agar  
123 industry in an oxy-combustion atmosphere, paying special attention to the role that the  
124 high concentration of water in the flue gases can play in the retention of mercury.

## 125 2. **Experimental**

126 The activated carbons used in this work were prepared from two types of precursor i) a  
127 macroalgae waste (algae meal) from the agar-agar industry (AM) and ii) a char (AMP)  
128 obtained by pyrolysis of AM at 750°C. The conditions for obtaining both samples have  
129 been previously described (Ferrera-Lorenzo et al., 2014a). These precursors (AM and  
130 AMP) were chemically activated with KOH, in precursor/KOH proportions of 0.5:1 and  
131 1:1. The activation temperatures used were 750 and 900°C and the heating rate and N<sub>2</sub>  
132 flow rate were 5°C/min and 150 ml/min, respectively (Ferrera-Lorenzo et al., 2013,  
133 2014a). The activated carbons obtained from AM and AMP were labelled AMA and  
134 AMPA followed by the precursor/KOH proportions and the activation temperatures  
135 used (Table 1). These materials were washed with HCl 5M and deionized water, and  
136 dried before testing. A commercial sulphur-impregnated activated carbon developed for

137 Hg<sup>0</sup> retention (Norit RBHG3), was employed as a reference material (Lopez-Anton et  
138 al., 2002).

139 The moisture content of the macroalgae waste was obtained following the UNE 32002  
140 norm, on the basis of weight loss at 105°C over a period of 1 hour, and the ash content  
141 was determined by calcining the sample in a muffle at 815°C for 1 hour in the presence  
142 of oxygen, according to the UNE 32004 norm. The carbon, hydrogen and nitrogen  
143 contents of the samples were determined using LECO CHN-2000 equipment. The  
144 sulphur content was measured on a LECO S-144-DR equipment. The chlorine  
145 concentration was measured by means of an ion selective electrode after combustion in  
146 a calorimetric bomb. Textural characterization was performed by measuring the N<sub>2</sub>  
147 adsorption at -196 °C on an automatic apparatus (Micromeritics ASAP 2420).  
148 Isotherms were employed to calculate the specific surface area, S<sub>BET</sub>, and Total Pore  
149 Volume, V<sub>TOT</sub>, at a relative pressure of 0.95. The micropore and mesopore size  
150 distributions were calculated on the basis of the density functional theory (DFT). The  
151 narrow microporosity (pore width smaller than 0.7 nm) was estimated from the CO<sub>2</sub>  
152 adsorption isotherms at 0°C, taking 1.023 g cm<sup>-3</sup> as the density of adsorbed CO<sub>2</sub> and  
153 0.36 as β parameter (the affinity factor that characterizes each adsorbate). The CO<sub>2</sub>  
154 isotherms were used in conjunction with the Dubinin-Raduskevich equation to  
155 calculate the micropore volume, W<sub>0</sub>, micropore size (L<sub>0</sub>), and energy characteristic (E<sub>0</sub>).  
156 The water vapour adsorption isotherms were determined at 25°C for water activity (a<sub>w</sub>)  
157 using a scale of 0 to 1. The equilibrium moisture content was expressed in grams per g  
158 of dry solid.

159 The laboratory device used for the retention of mercury is shown in Figure 1. The  
160 experimental device consisted of a glass reactor heated by a furnace and fitted with a  
161 thermocouple. The sorbent bed was prepared by mixing 30 mg of sample with 500 mg

162 of sand.  $\text{Hg}^0$  in gas phase obtained by means of a permeation tube was passed through  
163 the sorbent bed at a rate of  $0.5 \text{ L min}^{-1}$  in a concentration of  $100 \mu\text{g m}^{-3}$ . A synthetic gas  
164 mixture consisting of 4%  $\text{O}_2$ , 1000ppm  $\text{SO}_2$ , 1000ppm  $\text{NO}$ , 100 ppm  $\text{NO}_2$ , 25 ppm  $\text{HCl}$ ,  
165 12%  $\text{H}_2\text{O}$ , 64%  $\text{CO}_2$  and 20%  $\text{N}_2$  was employed as the simulated oxy-combustion  
166 atmosphere. To evaluate the effect of water vapour and reactive gases a series of  
167 experiments were carried out in the same atmosphere without water,  $\text{O}_2+\text{N}_2$  (12.6%  $\text{O}_2$ )  
168 and  $\text{N}_2$  atmospheres. The temperature of the sorbent was  $150^\circ\text{C}$ . The gas lines were  
169 heated to avoid possible condensation. The mercury adsorption curves were obtained  
170 using a continuous  $\text{Hg}^0$  emission monitor (VM 3000). A dilution flow rate of  $2 \text{ L min}^{-1}$   
171 with air was added before the VM 3000. The mercury content after the retention  
172 experiments was determined by means of an automatic mercury analyzer (AMA). The  
173 duration of the mercury experiments was the time needed for the samples to reach  
174 maximum retention capacity. The oxidation of the mercury was evaluated by capturing  
175 the  $\text{Hg}^{2+}$  in an ion exchanger resin (Dowex<sup>®</sup> 1x8), especially designed for the selective  
176 extraction of  $\text{Hg}^{2+}$  species (Fuente-Cuesta et al., 2014). The resin was placed at the exit  
177 of the reactor prior to the  $\text{Hg}^0$  continuous analyzer (Figure 1). The  $\text{Hg}^{2+}$  in the resin at  
178 the end of the retention experiments was determined by AMA. The resin had previously  
179 been conditioned with a mixture of  $\text{HCl}:\text{H}_2\text{O}$  (1:1) at  $90^\circ\text{C}$  for 30 minutes and then  
180 filtered and dried. The content of  $\text{Hg}^{2+}$  condensate in the water and collected during the  
181 experiments prior to the analyzer was determined by AMA.

### 182 3. Results and discussion

183 The chemical analysis data for the precursors and activated carbons from algae wastes  
184 used in the present study have been detailed in previous works (Ferrera-Lorenzo et al.,  
185 2013, 2014b). The activated carbons obtained from wastes of the agar-agar industry had



186 low ash (2.2-7.3%) and high carbon (83-91%) contents. The nitrogen content was  
187 higher than 3% whereas for RBHG3 (0.47%) and other activated carbons reported in the  
188 literature (Bermúdez et al., 2010) it is much lower. The important difference is the sulfur  
189 content which was 1% in the activated carbons and 6% in the impregnated RBHG3  
190 carbon. Chlorine, which can also play an important role in mercury capture, varies in  
191 the different samples as a consequence of the efficiency of the washing process after  
192 activation. It is 0.02% in AMA0.5:1-750, 0.03% in AMPA1:1-900, 0.09% in  
193 AMPA1:1-750 and AMPA0.5:1-900 and 0.22% in AMPA0.5:1-750.

194 The specific surface area ( $S_{\text{BET}}$ ) ranged from 813 (AMPA0.5:1-750) to 1982 m<sup>2</sup>/g  
195 (AMA0.5:1-750), and the total volume ( $V_{\text{TOT}}$  [p/p<sup>0</sup>=0.95], from 0.364 (AMPA0.5:1-  
196 750) to 0.914 cm<sup>3</sup>/g (AMA0.5:1-750) (Ferrera-Lorenzo et al., 2014b). Most of the  
197 adsorbents were microporous materials with a certain degree of mesoporosity  
198 development. The microporosity varied from 29% to 68% in the case of  
199 ultramicroporosity (<0.7 nm) and from 20% to 57% in the case of medium-size  
200 microporosity (0.7-2 nm). Mesoporosity development (2-50 nm) ranged from 10% to  
201 14%. The ultramicroporosity volume was higher in the activated carbons obtained from  
202 AMP, whereas medium microporosity and mesoporosity was greater in the activated  
203 carbons obtained from AM. RBHG3 has a similar porosity distribution with a  
204 prominent microporous development. The activated carbon which presents the highest  
205 micropore volume calculated by CO<sub>2</sub> isotherms is AMPA1:1-900 ( $W_0=0.586 \text{ cm}^3\text{g}^{-1}$ )  
206 followed by AMA0.5:1-750 ( $W_0= 0.514\text{cm}^3\text{g}^{-1}$ ), AMPA1:1-750 ( $W_0=0.449 \text{ cm}^3\text{g}^{-1}$ ),  
207 AMPA0,5:1-900 ( $W_0= 0.410 \text{ cm}^3\text{g}^{-1}$ ), AMPA0,5:1-750 ( $W_0=0.332 \text{ cm}^3\text{g}^{-1}$ ) and RBHG3  
208 ( $W_0=0.266 \text{ cm}^3\text{g}^{-1}$ ).

209 Special attention has been paid in the present work to the H<sub>2</sub>O adsorption at 25°C.  
210 Figure 2 shows the water vapour adsorption-desorption isotherms for samples

211 AMPA1:1-750, AMPA0.5:1-900, AMA0.5:1-750 and RBHG3. As can be seen, the  
212 water vapour adsorption isotherms are of type V or S-shaped, which is typical of  
213 microporous materials. The process of water adsorption is due to both physical  
214 adsorption and chemical interaction with the surface groups. The activated carbons  
215 obtained from the algae meal and carbonized algae meal exhibit a higher water vapour  
216 adsorption than that of the commercial activated carbon (RBHG3). If the slopes of the  
217 isotherms in the lower  $P/P^0$  are carefully examined, it can be seen that all the isotherms  
218 have a convex shape, which suggests the presence of hydrophilic surface groups. At low  
219 relative pressure the macroalgae activated carbons present a higher water vapour  
220 adsorption than commercial activated carbon (RBHG3) which suggests a greater  
221 presence of hydrophilic groups in these materials capable of forming hydrogen bonds  
222 with water molecules. The sample activated at 900°C shows a lower adsorption capacity  
223 at low pressure, suggesting that at a high activation temperature, the surface groups  
224 disappear. As the pressure increases the influence of the textural development becomes  
225 more important. The isotherm which presents the highest adsorption capacity at  
226 moderate pressures corresponds to the activated carbon from the algae meal  
227 (AMA0.5:1-750), whereas RBHG3 displays the lowest adsorption capacity.

228 Table 2 shows the mercury retention capacities and the percentages of  $Hg^{2+}$  resulting  
229 from heterogeneous (gas-solid interaction) oxidation. The homogeneous (gas-gas  
230 interaction) mercury oxidation in the same flue gas composition has been studied  
231 previously (Fernández-Miranda et al., 2014). The confidence limit of the results is given  
232 as the standard deviation. To determine which characteristics of the activated carbon  
233 influence mercury retention all the sorbents were first tested in an atmosphere made up  
234 just of  $O_2$  and  $N_2$ . The mercury retention capacities range from 1000-1600  $\mu g g^{-1}$  for all  
235 the activated carbons in this simple atmosphere. The char AMP shows the lowest

236 mercury retention capacity ( $20 \mu\text{g g}^{-1}$ ), which is well below that of the activated  
237 samples. AMP has a BET surface area value of  $4 \text{ m}^2/\text{g}$  (Ferrera-Lorenzo et al., 2014b)  
238 while the activated samples range from 800 to  $2000 \text{ m}^2/\text{g}$ . Therefore, the development  
239 of texture is another factor to take into consideration for mercury retention. However, an  
240 examination of the different textural characteristics of the activated carbons reveals that  
241 there is no clear relationship between surface area, pore distribution and mercury  
242 capture. Varying the activation temperature and the proportion of precursor/activating  
243 agent leads to materials with different textural characteristics, but no correlation can be  
244 established between the surface area, ultramicropore volume, medium-microporous  
245 volume, mesoporous volume and mercury retention capacity. Therefore, the textural  
246 development is not the only factor affecting mercury retention. In the atmosphere  
247 formed by  $\text{O}_2$  and  $\text{N}_2$ , the differences observed in the mercury adsorption curves (Figure  
248 3) can be attributed mainly to variations in the chlorine content remaining in the  
249 material after washing. It is worth noting that the activated carbon with the highest  
250 chlorine content (AMPA0.5:1-750) shows the highest mercury retention capacity which  
251 is similar to that of the commercial carbon impregnated with sulfur. The positive  
252 influence of the presence of chlorine in carbon materials for mercury retention is well  
253 known. Chlorine species can generate chemisorption sites on carbon surfaces favoring  
254 the adsorption of mercury.

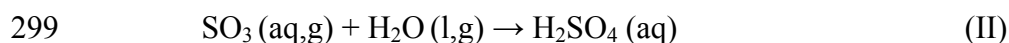
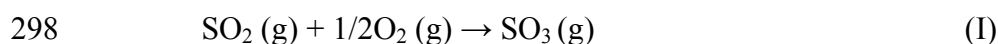
255 It must be emphasized that the activated carbons prepared from algae meal and algae  
256 meal carbonized in the atmosphere of  $\text{O}_2+\text{N}_2$  can reach retentions of the order of the  
257 activated carbon impregnated with sulfur RBHG3 (Table 2). In an inert atmosphere ( $\text{N}_2$ )  
258 the retentions are much lower ( $<400 \mu\text{g g}^{-1}$ ), in agreement with previous studies (Morris  
259 et al., 2012; Karatza et al., 2013) which demonstrates that  $\text{O}_2$  plays a critical role in  
260 mercury sorption on carbon surfaces. In the absence of other oxidizing species the

261 presence of O<sub>2</sub> increases the mercury uptake. It has been suggested that mercury  
262 bonding on the carbon surface is associated with oxygenated groups, in particular, with  
263 lactone and carbonyl groups (Li et al., 2002, 2003).

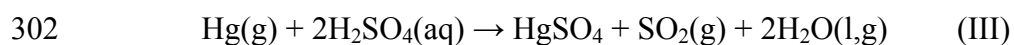
264 The behaviour of mercury on a selection of the activated carbons where the gas  
265 composition simulates that of coal oxy-combustion is completely different (Table 2). It  
266 can be seen that, on the one hand, the mercury retention capacity is much lower in the  
267 reactive atmospheres than in O<sub>2</sub> and N<sub>2</sub> and that, between 20 and 60% of Hg<sup>2+</sup> results  
268 from heterogeneous oxidation in the oxy-combustion atmosphere. Figure 4 shows the  
269 mercury adsorption curves for a series of representative samples of activated carbons  
270 from algae meal in a simulated oxy-combustion flue gas (Figure 4a) and in the same  
271 atmosphere when it is dry (Figure 4b). The mercury analyzer, which only detects Hg<sup>0</sup>,  
272 recorded that the mercury signal did not reach the baseline (22±3 µg m<sup>-3</sup>). This could be  
273 because mercury was retained in the activated carbon and/or because of mercury  
274 oxidation.

275 A high concentration of water vapour in an oxy-fuel atmosphere has a considerable  
276 impact on the process and on all gas cleaning systems, the behaviour of mercury being  
277 no an exception. Mercury capture on solid sorbents may decrease as a consequence of  
278 the presence of water vapour in the atmosphere (Cudahy and Helsel, 2000; Richards,  
279 2005; Presto and Granite, 2007; Zheng et al., 2012). In the particular case of the  
280 sorbents evaluated in this work, it can be seen (Table 2) that retention increased in the  
281 dry flue gas. This could have been a consequence of the high water vapour adsorption of  
282 the materials obtained from the algae waste, as can be seen from Figure 2. If the  
283 activated carbons from the algae waste are compared, those with the highest water  
284 adsorption capacity present the lowest mercury retention capacity in the oxy-  
285 combustion atmosphere (Figure 2, Table 2). The same conclusion can be drawn from

286 the results with the activated carbon RBHG3 which present the lowest water adsorption  
287 capacity (Figure 2) and have the highest mercury retention capacity in the atmosphere  
288 with water (Table 2). However, retention improves in the dry oxy-combustion  
289 atmosphere for all activated carbons, where the retentions are of the same order, and  
290 comparable to that of the reference activated carbon RBHG3. Previous results obtained  
291 by the authors in similar conditions (Fernández-Miranda et al., 2014) demonstrated that  
292 the presence of water vapor in the flue gas results in the formation of sulfuric acid  
293 according to reactions I and II, reaction I being favored in the presence of CO<sub>2</sub>. This  
294 might lead to lower mercury retentions in the presence of water (Table 2), since the high  
295 concentration of H<sub>2</sub>SO<sub>4</sub> could result in almost complete pore blockage. It should be  
296 noted that the formation of sulphuric acid is a consequence of reaction in the gas stream  
297 and is not influenced by the sulfur content in the activated carbons.



300 In contrast, other authors (Morris et al., 2012) have observed that the formation of  
301 H<sub>2</sub>SO<sub>4</sub> on the carbon surface favors mercury retention through reaction III.



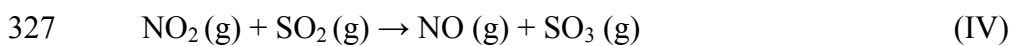
303 Mechanism (III) assumes that after being physically adsorbed onto the surface, Hg<sup>0</sup> will  
304 be oxidized to Hg<sup>2+</sup>. The Hg<sup>2+</sup> will then become bound to Lewis base surface sites either  
305 in carbon-oxygen or carbon-sulfur functional groups. In the present study and in both  
306 the activated carbons from the algae waste and the activated carbon impregnated with  
307 sulfur, the mercury was oxidized. However, Hg<sup>2+</sup> was not retained in any significant  
308 amount by the activated carbons, this mercury remaining in the gas phase or being

309 condensed in the water. Therefore, the factors that play a role against the retention of  
310 mercury by activated carbons in oxy-combustion processes can be summed up as  
311 follows:

312 i) The formation of a large amount of H<sub>2</sub>SO<sub>4</sub> due to the high concentration of  
313 water vapour produced in oxy-combustion (up to 30%), which would block the mercury  
314 adsorption sites on the carbon surface.

315 ii) The slow kinetics of mercury adsorption from HgSO<sub>4</sub> due to the short contact  
316 time between the activated carbons and gas, which is less than 1 second (similar to the  
317 contact times in the injection of activated carbon in coal-fired power plants).

318 It should also be noted that even in a dry atmosphere, the mercury retention capacities  
319 of the activated carbons decrease in the presence of reactive gases compared to retention  
320 in an O<sub>2</sub>+N<sub>2</sub> atmosphere. It is well known that NO<sub>x</sub> can promote mercury oxidation  
321 (Miller et al., 2000; Niksa et al., 2001; Fuente-Cuesta et al., 2012; Rodríguez-Pérez et  
322 al., 2013; Wu et al., 2013), but it can also favor SO<sub>2</sub> sulfation through reaction IV  
323 below. This reaction has been observed by the authors of the present study in previous  
324 experiments carried out under the same experimental conditions (Fernández-Miranda et  
325 al., 2014). The formation of SO<sub>3</sub> would then compete with the mercury for the same  
326 binding sites.



328

329 **4. Conclusions**

330 The results of this study confirm the essential role of O<sub>2</sub> in mercury capture by activated  
331 carbons. The activated carbons obtained from biomass algae waste showed a mercury  
332 retention capacity of the same order as the activated carbon impregnated with sulphur in  
333 an atmosphere free of reactive gases. The presence of reactive gases, mainly SO<sub>2</sub>/SO<sub>3</sub>,  
334 and vapor water enhanced mercury oxidation. The Hg<sup>2+</sup> produced was retained to a  
335 limited extent in the carbons. These results need to be taken into consideration when  
336 developing technologies for mercury control in oxy-combustion processes, where the  
337 presence of a large amount of water vapor may result against to mercury adsorption.  
338 The results also make it clear that such minor differences in the textural properties of  
339 activated carbons as those reported in this work are eclipsed by the chemical properties  
340 (CI) of the materials and by the composition of the flue gas.

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483 **Figure captions**

484 **Figure 1.** Schematic diagram of the experimental device for mercury retention

485 **Figure 2.** Water vapour adsorption isotherms (at 25°C) of the materials

486 **Figure 3.** Mercury adsorption curves corresponding to the carbon samples in an O<sub>2</sub>+N<sub>2</sub>  
487 atmosphere

488 **Figure 4.** Mercury adsorption curves corresponding to the activated carbons in a) oxy-  
489 combustion and b) oxy-combustion water vapour-free atmospheres

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498 Table 1.- Activated carbons obtained in the experimental conditions used

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Sample	Activation agent/precursor	Activation temperature (°C)	N <sub>2</sub> flow rate (ml/min)
AMA0.5:1-750	0.5:1	750	150
AMPA0.5:1-750	0.5:1	750	150
AMPA0.5:1-900	0.5:1	900	150
AMPA1:1-750	1:1	750	150
AMPA1:1-900	1:1	900	150

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**Nomenclature:** AMA: Activated carbon from algae meal (AM); AMPA: Activated carbon from algae meal carbonized (AMP)

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506 **Table 2.** Mercury retention capacities and heterogeneous oxidation percentages of the507 activated carbons in O<sub>2</sub>+N<sub>2</sub>, oxy-combustion and oxy-combustion water vapour-free

508 atmospheres.

Sample	O <sub>2</sub> +N <sub>2</sub>		Oxy-comb.		Oxy-comb/free H <sub>2</sub> O	
	Hg ret. (µg g <sup>-1</sup> )	Hg <sup>2+</sup> (g) <sub>out</sub> (%)	Hg ret. (µg g <sup>-1</sup> )	Hg <sup>2+</sup> (g) <sub>out</sub> (%)	Hg ret. (µg g <sup>-1</sup> )	Hg <sup>2+</sup> (g) <sub>out</sub> (%)
AMP	20±3	0	---	---	---	---
AMA0.5:1-750	1221±300	0	3.2±0.5	28	200±15	55
AMPA0.5:1-750	1607±100	0	---	---	---	---
AMPA0.5:1-900	1240±200	1	6.5±1.1	22	150±13	54
AMPA1:1-750	1428±200	0	12±2	32	250±18	60
AMPA1:1-900	1037±200	0	---	---	---	---
RBHG3	1649±200	1	127±10	20	250±15	55

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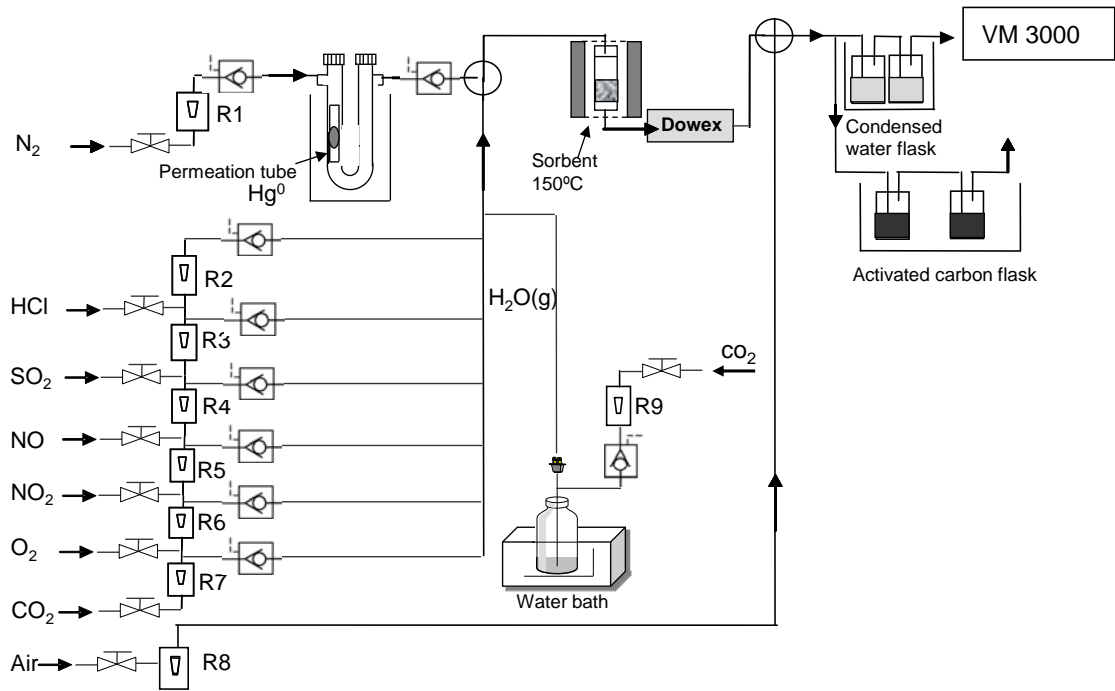
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Oxy-comb.: simulated oxy-combustion flue gas; Hg ret.: mercury retention capacity; Hg<sup>2+</sup>(g)<sub>out</sub>: oxidized mercury by heterogeneous oxidation

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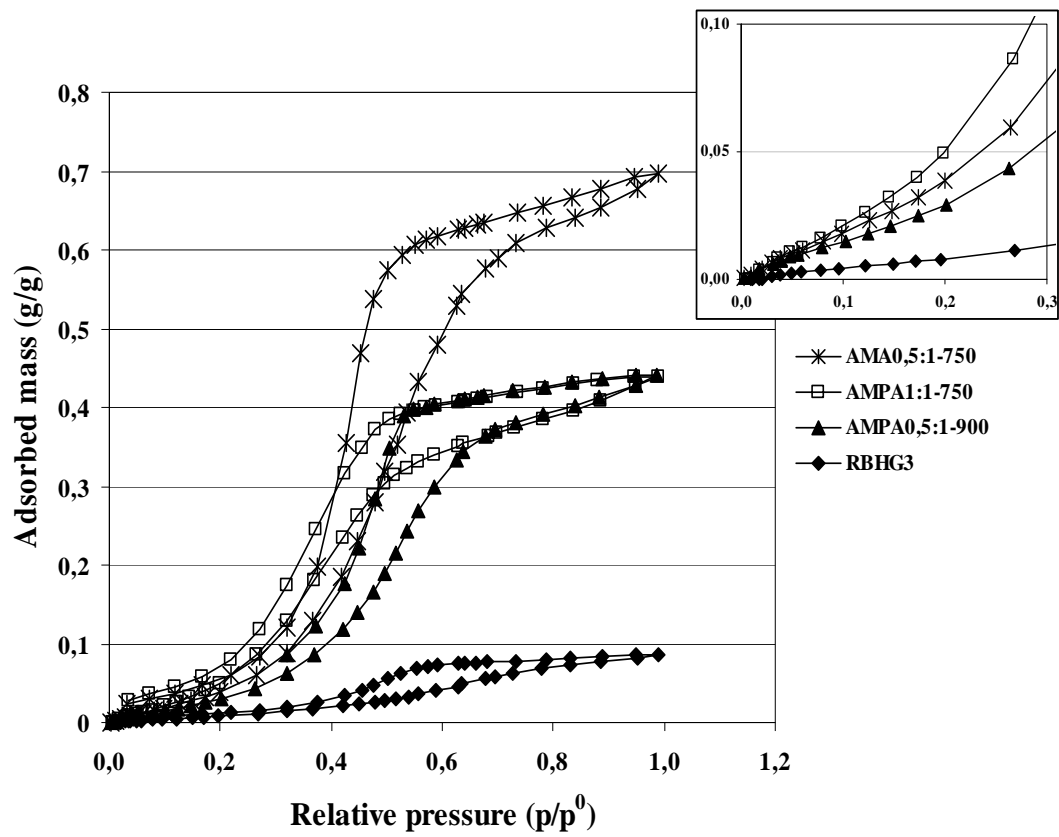
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515 Figure 1



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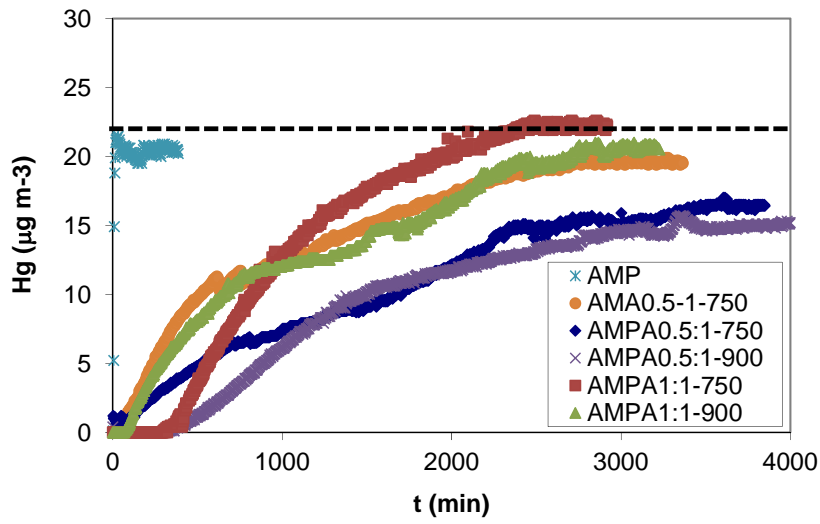
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520 Figure 2

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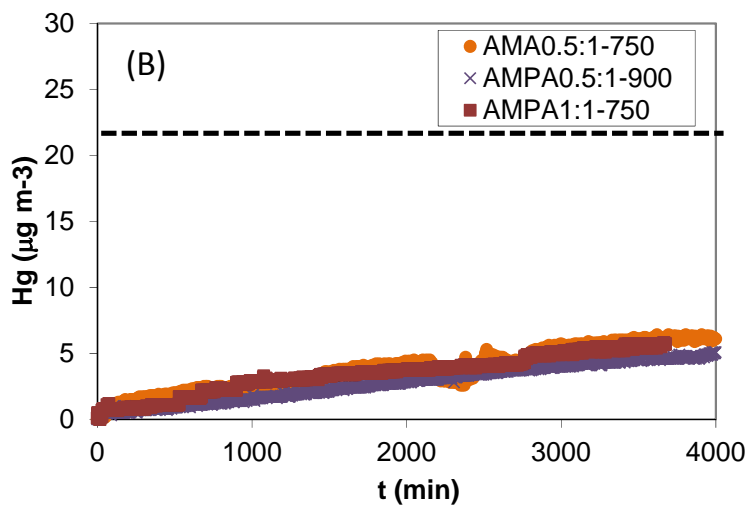
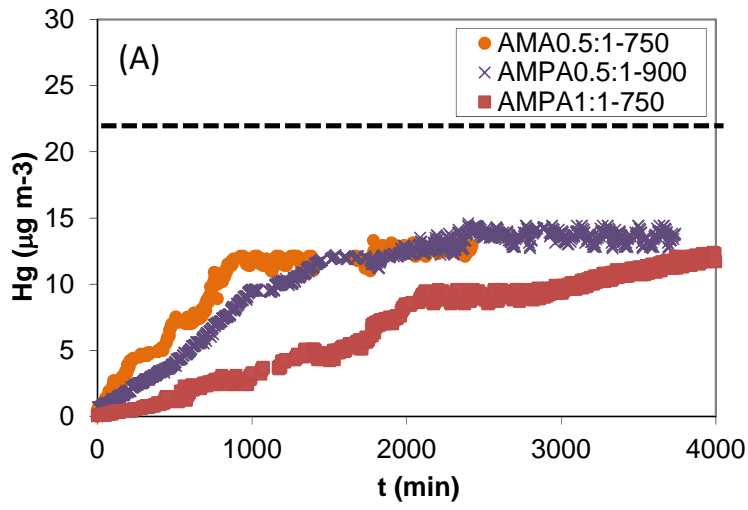
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526 Figure 3

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532 Figure 4