Enhanced SO_2 adsorption and desorption on chemically and physically activated biochar made from wood residues

Flavia Lega Braghiroli [*1,2], Hassine Bouafif [2], Ahmed Koubaa [1]

[1] Research Forest Institute (Institut de recherche sur les forêts - IRF), University of Québec in Abitibi-Témiscamingue (UQAT), 445 Boul. de l'Université, Rouyn-Noranda, QC J9X 5E4, Canada

[2] Centre Technologique des Résidus Industriels (CTRI, Technology Center for Industrial Waste), Cégep de l'Abitibi-Témiscamingue (College of Abitibi-Témiscamingue), 425 Boul. du Collège, Rouyn-Noranda, QC J9X 5E5, Canada

[*] Corresponding author: (F.L. Braghiroli)

Tel: +1 (819)-762-0931 ext. 1748;

Fax: +1 (819)-762-0906;

Email: Flavia.Braghiroli@uqat.ca

Abstract

SO_2, one of the most harmful gases, is generated when oxygen in air combines with sulfur species from anthropogenic sources (e.g., the smelting of mineral ores). Thus, the objectives of this study are to assess the potential use of activated biochar for the removal of SO_2, and to compare the impact of the activation process on the development of porosity and surface chemistry for SO_2 adsorption. Results show that activated biochars develop porosity (with narrow and wide pores) and functional groups connected to their surface, which makes these materials suitable for adsorption of SO_2. However, no linear relationship between textural properties and the amount of SO_2 adsorbed by activated biochars from dynamic adsorption tests were noticed. In addition, the highest SO_2 adsorption capacity was not reached for materials with the highest surface area, or micropore or ultramicropore volume. Specifically, steam-activated biochar had the best performance for the removal of SO_2 due to its optimal surface area (590 m^2 g^{-1}); volume of ultra- (0.22 cm^3 g^{-1}), micro- (0.23 cm^3 g^{-1}), and mesopores (0.11 cm^3 g^{-1}); its basic character (not from nitrogenated groups); and the low percentage of acid-oxygenated functional groups connected to its surface. After six thermal regeneration cycles, activated biochar exhibited high SO_2 removal capacity and high regenerability. Based on these findings, activated biochar made from forest wood residues has promising potential for the removal of gas contaminants.

Keywords: Activated biochar, SO_2 removal, adsorption, porosity, surface chemistry

1. Introduction

Researchers have been working to develop efficient technologies that will reduce toxic pollutants in the air. A colorless gas with a strong odor, SO_2 is produced when oxygen in air combines with sulfur gas emissions. It is one of the world's major air pollutants and can also easily react with other substances to form harmful components (e.g., sulfuric acid, sulfurous acid, and sulfate particles) (He et al., 2003). The majority of this gas in air comes from human sources, apart from the natural emissions from volcanoes. SO_2 is the major air pollutant produced by industrial activities, especially from the burning of fossil fuels (coal, oil, and gas) for the generation of electricity or the smelting of mineral ores (i.e., aluminum, copper, zinc, lead, and iron) that contain sulfur (Fioletov et al., 2016). The SO_2 generated by industry contributes to urban air pollution that affects human health and well-being and life expectancy (Khaniabadi et al., 2017). Several international agreements aim to reduce emissions of air pollutants. For instance, the Canada–United States Air Quality Agreement of 1991 aims to reduce the impact of transboundary air pollution (Environment and Climate Change Canada, 2018), whereas the 1994 Oslo Protocol on Further Reduction of Sulfur Emissions, signed by Canada and several European countries, intends not only to take effective measures for the reduction of sulfur but also to use renewable energy and efficient technologies to deal with air pollution (UNECE, 2018).

The techniques used in industry for SO_2 removal are based on the principle of gas–liquid reactions, using liquid alkaline solutions (e.g., $Mg(OH)_2$, $Ca(OH)_2$) (Slack et al., 1972; Li and Zhu, 2016), or solid–gas reactions, using carbon-derived materials (e.g., activated carbon) (Shafeeyan et al., 2010; Abdulrasheed et al., 2018; Bamdad et al., 2018). The first procedure generates considerable by-products, whereas the adsorption of SO_2 over carbon materials has been the most viable and effective alternative because of the ease of installation and operation of gas adsorption

apparatus, as well as simple carbon's regeneration. Indeed, activated carbon is the most widely used material for the removal of gaseous pollutants at various concentrations (Mohamad Nor et al., 2013). However, a SO_2 removal mechanism is not well established due to the complexity of the surface porous structure of activated carbons made from abundant low-cost biomass residue precursors. It is known that during the process of SO_2 adsorption in O_2 atmosphere and in presence of H_2O in the gas phase, several reactions may be performed (Eqs. 1–5). These elements will be first adsorbed (ads.) onto the carbon material (Eq. 1–3), and then oxidation of SO_2 to SO_3 (Eq. 4) and the formation of H_2SO_4 (Eq. 5) on the surface of carbon material will be accomplished (Lisovskii et al., 1997; Bagreev et al., 2002):

$$SO_2\ (gas) \rightarrow SO_2\ (ads.) \quad (1)$$

$$O_2\ (gas) \rightarrow 2O_2\ (ads.) \quad (2)$$

$$SO_2\ (gas) + O\ (ads.) \rightarrow SO_3\ (ads.) \quad (3)$$

$$H_2O\ (gas) \rightarrow H_2O\ (ads.) \quad (4)$$

$$SO_3\ (ads) + H_2O\ (ads.) \rightarrow H_2SO_4\ (ads.) \quad (5)$$

The surface chemistry of activated carbons plays a major role on their performance for SO_2 adsorption. It was reported that basic and acid groups connected to the surface of carbon material can improve SO_2 uptake. For some researchers, the presence of basic groups strengthens the bond of H_2SO_4 to the materials' surface (Raymundo-Piñero et al., 2000; Davini, 2001; Bagreev et al., 2002), whereas for others, acid groups weaken the adsorption energy for H_2SO_4, improving the extractability of H_2SO_4 by water (Lisovskii et al., 1997) and, consequently, enhancing SO_2 adsorption. The porous structure of the activated carbon can also have an effect on the SO_2 adsorption, but this process is still controversial. Karatepe et al. (2008) stated that the porous structure, rather than specific surface area, of chemically and physically activated carbons

89 contributed to SO_2 adsorption. They also reported a linear relationship between the micropore
90 volume and the amount of SO_2 adsorbed. For Zhu et al. (2012), the highest SO_2 adsorption capacity
91 does not exist at the largest micropore volume, while a linear relationship was found between the
92 ultramicropore volume of CO_2-activated carbons and SO_2 adsorbed. For Raymundo-Piñero et al.
93 (2000), SO_2 adsorption capacity is related to narrow micropore volume; thus, oxidation of SO_2 to
94 SO_3 (Eq. 3) occurs in pores lower than 0.7 nm independent of the nature and surface chemistry of
95 the material.

96 Other materials such as biochar, a by-product carbon-rich material produced from the
97 thermochemical conversion (i.e., torrefaction, slow to fast pyrolysis, and gasification) of biomass
98 waste materials (Rangabhashiyam and Balasubramanian, 2019), have been recently studied for SO_2
99 removal. According to Xu et al. (2016), biochars made from dairy manure, sewage sludge, and rice
100 husk presented SO_2 sorption capacities of up to 64 mg g^{-1}. Materials had a basic character but low
101 specific surface area (up to 42 m^2 g^{-1}); thus, SO_2 sorbed was due to mineral components in biochar
102 that could react with SO_2 to form various sulfate minerals on its surface. This result could be also
103 improved with the activation of biochars, but few studies reported its use for SO_2 removal. Shao et
104 al. (2018) has recently shown that CO_2 activation of corncobs biochar improved its porosity (755
105 m^2 g^{-1}) and SO_2 adsorption capacity to up to 58 mg g^{-1}. In addition, amine impregnation onto
106 activated biochar has found to develop a surface chemistry basicity, with an increase of nitrogen
107 content, that has a strong interaction with SO_2 contaminant (Shao et al., 2018).

108 Thus, the objectives of the present study are investigating the role of the porous structure and
109 surface chemistry of activated biochars made from wood residues and pilot-scale technologies of
110 fast pyrolysis and activation on their performance for SO_2 adsorption capacity and thermal
111 regeneration.

2. Materials and methods

2.1 Synthesis of activated biochar

In this study, black spruce (BS) and white birch (WB) residues were sampled from sawmills and converted into biochars (BBS and BWB) by fast pyrolysis at 454 °C through CarbonFX fast pyrolysis technology (Airex Energy, Bécancour, QC, Canada). Biochars were then milled at 1–2 mm (Grinder: Ro-tap RS-29, WS Tyler, Mentor, OH, USA) and activated in a homemade pilot oven in presence of three types of activating agents: KOH, CO_2, and superheated steam. In chemical activation, 100 g of biochar was mixed with 200 g of water and 100 g KOH pellets. The mixture was left in the fume hood for 2 h and then, continue drying in an oven at 120°C overnight. Then, the impregnated material was activated at 900 °C for approximately 67 min in N_2 atmosphere. The same procedure was carried out in physical activation, in which the flowing gas of CO_2 (3 L min^{-1}) or steam (0.3 L min^{-1}) was introduced when the temperature reached 900 °C for approximately 67 min. The activated biochars were labeled KOHBWB, KOHBBS, CO2BWB, CO2BBS, H2OBWB and H2OBBS, depending on the type of activation agent and wood residue.

2.2 Physicochemical characterization

The prepared biochars and activated biochars were characterized by pH, elemental composition (C, H, N, S, O), surface chemistry, specific surface area and pore volume. The pH of the resultant filtrate, obtained by mixing 0.4 g of biochar-derived material with 20 mL of distilled water overnight, before (pH_i), and after (pH_f) SO_2 adsorption, was measured using a SevenMulti, Mettler Toledo (Greifensee, Switzerland) equipped with Inlab Routine Pro electrode. Perkin Elmer 2400 CHNS/O Analyzer (Waltham, MA, USA) was used for the determination of C, H, N, S, O elements, whereas Kratos AXIS ULTRA X-ray photoelectron spectroscopy (XPS) (Wharfside, MA, UK) was used for analyzing the surface chemistry of the prepared materials.

The pore texture parameters of biochars and activated biochars were obtained by CO_2 adsorption at 0 °C and N_2 adsorption at -196 °C, respectively, using a Micromeritics ASAP 2460 automatic apparatus (Norcross, GA, USA). After treatment of N_2 adsorption-desorption isotherms, the most important parameters were obtained: i) surface area: S_{BET} ($m^2\ g^{-1}$) (Brunauer et al., 1938); ii) micropore volume: $V_{\mu N_2}$ ($cm^3\ g^{-1}$) (Dubinin, 1989); iii) total pore volume: V_t ($cm^3\ g^{-1}$) (Gregg and Sing, 1991); iv) mesopore volume: V_m ($cm^3\ g^{-1}$); and v) average pore width calculated by the Stoeckli-Ballerini equation (Stoeckli and Ballerini, 1991). Ultramicroporosity ($V_{\mu CO_2}$) and pore size distribution (PSD) (Tarazona, 1995) were obtained through CO_2 and N_2 adsorption isotherms, respectively.

2.3 SO_2 adsorption and materials' regeneration tests

Dynamic tests were carried out at room temperature (~ 20 °C) to evaluate the capacity of biochars and activated biochars for SO_2 adsorption. The apparatus and conditions used for determining SO_2 breakthrough capacity were chosen according to the standard test method: *ASTM D6646-03 (2008)* (ASTM Standard D6646-03, 2008). Materials were placed into a glass column (27 cm length, 2.5 cm diameter) at different weighs (10–25 g) due to their various densities. Then, 50 ppm of SO_2 with moist air passed through the column at 30 mL min^{-1}. The outlet concentration of SO_2 was measured using a GazBadger®Pro flue gas meter (Industrial Scientific, Pittsburgh, USA), and the test was stopped when the outlet concentration equaled the inlet concentration. The SO_2 efficiency removal was calculated by Eq. 6:

$$SO_2 \text{ removal efficiency} = \frac{C_{0\,SO2} - C_{SO2}}{C_{0\,SO2}} \cdot 100\% \qquad (6)$$

where $C_{0\,SO_2}$ and C_{SO_2} were the inlet and outlet SO_2 concentration, respectively, measured by the flue gas meter. SO_2 saturation capacities were calculated by integrating the area above the saturation curves and saturation time. The saturation tests were repeated at least five times to make sure that

158 the textural properties and consequently, the SO_2 adsorption capacities of activated biochars
159 prepared in a prototype pilot activation furnace were reproducible. During the regeneration cycle,
160 the saturated material was placed in the activation furnace at 600 °C for 1 h in N_2 atmosphere. The
161 adsorption–desorption cycle was repeated six times, and the SO_2 adsorption capacity (mg g^{-1}) after
162 each regeneration cycle was then calculated.

163 **3. Results and discussion**

164 3.1 SO_2 adsorption

165 Significant differences in the performance of biochars and activated biochars can be seen in
166 SO_2 breakthrough curves (Fig. 1) and the calculated SO_2 capacities (Table 1). H2OBWB obtained
167 the highest adsorption capacity of 76.9 mg g^{-1}, followed by CO2BWB (56.9 mg g^{-1}), KOHBWB
168 (35.3 mg g^{-1}), CO2BBS ~ KOHBBS ~ H2OBBS (~ 25.0–26.5 mg g^{-1}), and finally both biochars (~
169 20.4 mg g^{-1}). Activated biochars had a basic character (pH of between 8.2 and 10.3); after SO_2
170 adsorption, however, their pH was reduced to between 2.1 and 3.3, whereas biochars had an acid-
171 neutral and acid character before (pH 5.9–7.1) and after (pH 4.1–4.4) SO_2 adsorption, respectively.
172 This physical characteristic may explain the formation of H_2SO_4 (Eqs. 1–5) during SO_2 adsorption.
173 It implies that SO_2, O_2, and H_2O were adsorbed on the internal surface of biochar-derived materials
174 close enough and in appropriate steric configuration to react and form H_2SO_4 that was then
175 transported to accessible inner pores (Izquierdo et al., 2003).

176 To explain the differences in SO_2 adsorption capacity of activated biochars, both porosity and
177 surface chemistry were considered. First, analysis of the textural properties of biochars shows that
178 they are highly ultramicroporous, with surface areas of 177 and 208 m^2 g^{-1} for BWB and BBS,
179 respectively. The modification of biochar structure is an alternative for improving the pore
180 structure, surface area, and its surface chemistry, determinant characteristics for enhancing SO_2

adsorption over carbon materials. Thus, after activation, birch-activated biochars presented highly developed porosity with surface areas in the presence of KOH, CO_2, and steam of 1700, 881, and 590 $m^2\ g^{-1}$, respectively, while spruce materials had slightly lower surface areas of 1662, 735, and 412 $m^2\ g^{-1}$, respectively. Indeed, activation of biochars in the presence of CO_2 or superheated steam agents promoted the removal of carbon atoms that generated a porous structure (Marsh and Rodríguez-Reinoso, 2006; Giudicianni et al., 2017; Gargiulo et al., 2018). In the case of chemical activation in the presence of KOH, the mechanism is more complex due to the presence of several reactions that contribute to pore development. First, the reaction of carbon with KOH produces K_2CO_3, H_2, and K, which enlarges material's pore size through intercalation with carbon sheets. Then, carbon is consumed by K_2CO_3 to produce CO; at higher temperatures (> 800°C), K_2CO_3 is decomposed into CO_2 and K_2O, which are further broken down into K and CO (Dehkhoda et al., 2016). The resultant gases also contribute as physical agents during chemical activation, and, for this reason, the highest porosity development was found in KOH-activated biochars.

N_2 adsorption–desorption isotherms of birch- and spruce-activated biochars are presented in Figs. 2 a) and b), respectively. KOH-activated biochars and H2OBBS had an isotherm of Type I, according to IUPAC classification (Sing, 1985), typical of microporous materials presenting an elbow at P/P_0 at 0.05 followed by a horizontal plateau. Whereas a combination of isotherms Type I and IV is typical of the existence of narrow microporosity and mesoporosity with the presence of a narrow hysteresis loop for CO_2-activated biochars and H2OBWB (Braghiroli et al., 2018). PSDs obtained by application of density functional theory (DFT) (Fig. 2 c) and d)) were in good agreement with results obtained from N_2 isotherms. Activated birch biochars presented the highest proportion of CO_2 adsorbed in ultramicropores compared to spruce materials (Figs. 2 e) and f)), while KOH activation produced the highest proportion of ultramicropores, followed by CO_2 and

steam. Figs. 2 g) and h) show the PSD calculated by application of the DFT model to CO_2 isotherms. The DFT curves of birch-activated biochars and H2OBBS show pores between 0.4 and 0.8 nm and from 0.8 to > 1 nm, while CO2BBS and H2OBBS showed three peaks; one from 0.4 to 0.7 nm, another between 0.7 and 0.8 nm, and the last between 0.8 and 0.9 nm.

The surface area of carbon materials is often related to their adsorption capacity. For Atanes et al. (2012), the highest SO_2 uptake on cork-powder-activated carbon was consistent with its large surface area; but the adsorption behavior for CO_2-lignite-activated carbon, which had the highest surface area, did not follow this trend (Karatepe et al., 2008). The plots of the amount of SO_2 adsorbed from dynamic tests versus the surface area, different pore volumes (micropore, mesopore and ultramicropore volume) and the average pore width of activated biochars (Fig. 3 a), b), c), d) and e)) reveal that there is no linear relationship between them. The dependence between SO_2 sorbed and textural properties is usually obtained at equilibrium test conditions. Therefore, in this study, it might have some kinetic limitations during SO_2 adsorption at dynamic test conditions. In addition, similar to Karatepe et al. (2008), the highest surface area obtained for KOH-activated biochars does not mean that they presented the highest SO_2 adsorption. Notably, rather optimal textural properties – e.g., S_{BET}, V_t, average pore width, $V_{\mu\ N2}$ and $V_{\mu\ CO2}$ of 590 $m^2\ g^{-1}$, 0.34 $cm^3\ g^{-1}$, 0.80 nm, 0.23 $cm^3\ g^{-1}$, and 0.22 $cm^3\ g^{-1}$, respectively – are associated with H2OBWB and SO_2 sorbed.

Micropore volume in carbon materials was found to be the most important parameter to affect gas pollutant adsorption (Lua and Guo, 2000). However, the material with the highest micropore or ultramicropore volumes (Fig. 3 b) and d), respectively) did not adsorb the highest proportion of SO_2. The relationship between mesopore volume (Fig. 3 c) and SO_2 uptake is not obvious, even though materials with 0 % of mesopores, such as KOHBWB and KOHBBS, had the lowest SO_2

adsorption capacity. Raymundo-Pinero et al. (2000) noticed a linear relationship between ultramicropore volume and adsorbed SO_2, even though activated carbons with a ultramicropore volume higher than 0.4 cm^3 g^{-1} deviated from the trend. In this work, SO_2 adsorption was diminished for materials having ultramicropore volume in the range of 0.20 cm^3 g^{-1} as well as at higher than 0.30 cm^3 g^{-1}. In the first case, similar to Karatepe et al.'s (2008) findings, the narrow micropores, which comprised between 0.14 and 0.18 cm^3 g^{-1}, were unfavorable to SO_2 adsorption because materials could have different pore geometries that restricted the diffusion of SO_2 molecules. In the second case, similar to Raymundo-Piñero et al.'s (2000) findings, materials with a wide microporosity showed less SO_2 adsorption simply because the ability for oxidation of SO_2 into SO_3 inside the micropores did not take place.

The SO_2 adsorption behavior for the most porous activated biochars (i.e., KOHBWB and KOHBBS) do not follow the general trend. Their performance for SO_2 uptake was not consistent with their textural properties, but it could be related with surface functional groups that might be responsible for inhibiting SO_2 adsorption. Therefore, oxygenated functional groups connected to the surface of biochar-derived materials were examined by XPS analysis. The primary C1s peak was divided into five peaks at different binding energies of < 285eV, 285.7 < BE < 287.1, 286.1 < BE < 288, 288 < BE < 289.4 and BE > 290 corresponding to C--C, C–OH, C=O or O–C–O, O=C–O and $\pi \rightarrow \pi^*$, respectively. The peak area percentage shown in Table 1 indicates the content of each functional group. Activated biochars presented the highest percentage of graphitic sp^2 carbon followed by C–OH, C=O or O–C–O and O=C–O groups. KOH-activated biochars presented the highest proportion of these oxygenated groups (25.4 %) followed by CO_2 and steam-derived materials (13.4 % for H2OBBS).

249 The comparison of SO_2 uptake and the total oxygenated groups (%) measured by XPS analysis
250 and the nitrogen content (%) from elemental analysis (already reported in (Braghiroli et al., 2018))
251 are given in Fig. 4 a) and b), respectively. The material that showed the highest proportion of SO_2
252 sorbed (H2OBWB) had one of the lowest percentage of acid-oxygenated groups (17.9 %), i.e.,
253 phenolic, lactonic, and carboxylic acid. Although an important amount of acid groups appeared on
254 the surface of activated biochars, the measured pH indicated that the material had a basic character,
255 and therefore, most functional groups had a basic character in their composition. Indeed, SO_2 is a
256 Lewis acid in which S is an acceptor atom that will strongly interact with basic surface materials to
257 form stable complexes (Rezaei et al., 2015). According to Shafeeyan et al. (2010), the basicity of
258 carbon materials are primary related to delocalized π-electrons of graphene layers that attract
259 protons as well as basic surface functionalities, i.e., nitrogen-containing groups or oxygen-
260 containing surface functionalities such as chromene, ketone, and pyrone. Fig. 4 b) shows that little
261 amount of nitrogen (0.2 %) is present in H2OBWB; thus, its basic character (pH = 8.6) does not
262 come from nitrogenated groups connected to their surface. Although KOHBBS had one of the
263 highest percentage of nitrogen (2.7 %), acid-oxygenated groups (16.2 %), surface area (1662 m^2 g^{-1}),
264 and micropore volume (0.72 cm^3 g^{-1}), its SO_2 sorption capacity was one of the lowest (26.4 mg
265 g^{-1}). As mentioned earlier, this result can be explained by the incapability of SO_2 oxidation into
266 SO_3 inside micropores (Raymundo-Piñero et al., 2000).

267 The comparative SO_2 sorption capacity of carbon-derived materials in the available literature
268 is presented in Table 2. For most of materials listed, the porosity and surface area created after a
269 thermal treatment or activation (Atanes et al., 2012; Davini, 2001), and the presence of mineral
270 components and mostly nitrogen content, have created complexes with SO_2 (Xu et al., 2016) and a
271 basic character (Sun et al., 2016), respectively, which played a major role in their performance of

SO_2 adsorption. Also, the impregnation of nitrogenated groups on the surface of activated biochars showed an enhancement of SO_2 adsorption (Shao et al., 2018). However, this procedure could be an extra expenditure in industry during the production of activated carbons. An option that is currently under study is the use of wood from construction waste that contains some amount of resin or nitrogenated compounds that could improve the basicity of steam-activated biochar and consequently the interactions with SO_2.

3.2 Activated biochar regeneration

Regeneration of activated biochars is an important asset necessary for industrial applications so that sorbents can be reused in successive adsorption–desorption cycles (Braghiroli et al., 2018). To investigate the regeneration and stability of activated biochars, six regeneration cycles were performed. Materials were regenerated under thermal treatment at 600 °C for 1 h in an inert atmosphere. Throughout the thermal regeneration of activated biochars after SO_2 adsorption, H_2SO_4 sorbed on the materials' structure is removed by the reduction of carbon, following the Eq. 7 (Knoblauch et al., 1981). These gas products (SO_2, CO_2, and H_2O) may also further react to produce elemental sulfur, SO_2 or H_2SO_4 (Knoblauch et al., 1981; Richter, 1990). According to Cui et al. (2018), the higher temperature (from 400 to 600 °C), the better desulfurization activity of coke materials after regeneration. At 600 °C, the interactions established between the adsorbate and adsorbent are able to break.

$$2H_2SO_4 + C \rightarrow 2SO_2 + 2H_2O + CO_2 \qquad (7)$$

The regeneration efficiency of H2OBWB was evaluated due to its better performance for SO_2 uptake comparing to the other activated biochars. SO_2 breakthrough curves and SO_2 adsorption capacity of H2OBWB before and after six adsorption−desorption cycles are illustrated in Fig. 5 a) and b), respectively. As can be seen in Fig. 5, after each cycle, the SO_2 removal capacity of H2OBWB decreases (approx. 60 mg g^{-1}) compared to cycle 0 (76.9 mg g^{-1}), but it then increases to

up 85.3 mg g^{-1} (cycle 5). PSD curves of H2OBWB and H2OBWB after four, five and six adsorption-desorption cycle experiments are presented in Fig. 6. It is clearly seen that the pore structure of activated biochar was altered after these regeneration cycles, which led to a slight increase in its surface area and micropore volume with a reduction of mesopores that in turn favored the storage capacity of H_2SO_4 and therefore the SO_2 adsorption capacity. Indeed, the surface area and micropore volume have increased to approximately 680 m^2 g^{-1} and 0.26 cm^3 g^{-1}, respectively (cycle 6), compared to 590 m^2 g^{-1} and 0.23 cm^3 g^{-1} (cycle 0). After SO_2 adsorption test, the acid surface (pH = 3.2) of H2OBWB increased but then decomposed at 600 °C during the SO_2 desorption test, leaving a new basic surface (pH = 8.3) that favored SO_2 sorption capacity. Consequently, it is possible that the surface chemistry of the regenerated material is more suitable for SO_2 adsorption than that of the original H2OBWB.

4. Conclusion

The capacity of activated biochars to enhance adsorption of SO_2 was investigated according to materials' porous structure and surface chemistry. No linear relationship was observed between surface area; total, micropore, mesopore, and ultramicropore volume of activated biochars; and SO_2 sorbed from dynamic adsorption tests. KOH-activated biochars, the most porous materials (up to 1700 m^2 g^{-1}) with a wide microporosity, had less uptake of SO_2 once their capacity for SO_2 oxidation into SO_3 did not occur. Nitrogen-basic groups of up to 2.5 % were not enough to improve the performance of KOH-activated biochars for SO_2 sorption. On the other hand, steam-activated biochar had an optimal moderate surface area (590 m^2 g^{-1}) and porous structure, a basic character, and a low proportion of acid-oxygenated functional groups connected to its surface, which played an important role on its performance for SO_2 adsorption. After the thermal regeneration of activated biochar, results suggested that H2OBWB had high SO_2 removal capacity and suitability for

successive adsorption–desorption cycles. Therefore, activated biochar made from forest wood residues in the presence of steam at 900 °C is a promising potential adsorbent material for the efficient removal of SO_2 contaminant.

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464 **Captions of tables**

465 **Fig. 1.** SO_2 removal efficiency curves as function of saturation adsorption time for a) BWB- and b)
466 BBS-activated materials.

467 **Fig. 2.** a) and b) N_2 adsorption–desorption isotherms (full and open symbols, respectively) at -196
468 °C; c) and d) PSD determined by the DFT method and N_2 isotherms; e) and f) CO_2
469 adsorption isotherms at 0 °C; g) and h) PSD determined by the DFT method and CO_2
470 isotherms for activated biochars made from birch and spruce, respectively.

471 **Fig. 3.** Relationship between SO_2 uptake and a) surface area, b) micropore volume, c)
472 mesopore volume, d) ultramicropore volume and e) average micropore width of
473 biochars (●) and KOH (♦), CO_2 (■), and steam-activated biochars (▲).

474 **Fig. 4.** Relationship between SO_2 uptake and a) percentage of acid-oxygenated groups measured
475 by XPS and b) percentage of nitrogen measured by elemental analysis of biochars (●) and
476 KOH (♦), CO_2 (■) and steam-activated biochars (▲).

477 **Fig. 5.** a) SO_2 concentration adsorbed as function of breakthrough time, and b) SO_2 adsorption
478 capacity of H2OBWB after six adsorption−desorption cycles.

479 **Fig. 6.** PSD determined by the DFT method and N_2 isotherms for H2OBWB and H2OBWB after
480 four, five and six adsorption-desorption cycle experiments.

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Captions of figures

Table 1. pH, saturation adsorption time, SO_2 saturation capacities, and contributions to the C1s bands in XPS patterns for biochar-derived materials

Table 2: Comparative SO_2 sorption capacity of carbon-derived materials

528 **Table 1.** pH, saturation adsorption time, SO_2 saturation capacities, and contributions to the C1s

529 bands in XPS patterns for biochar-derived materials

	BWB	**BBS**	**KOHBWB**	**KOHBBS**	**CO2BWB**	**CO2BBS**	**H2OBWB**	**H2OBBS**
pH_i	5.9	7.1	9.9	10.2	9.5	10.0	8.6	9.7
pH_f	4.1	4.4	2.5	2.5	2.1	2.9	3.3	3.2
Breakthrough time (min)	21.3	21.2	36.5	27.1	58.3	26.1	78.5	27.5
SO_2 capacity (mg g^{-1})	20.4	20.3	35.3	26.4	56.9	25.0	76.9	26.5
XPS analysis	Binding energy (BE) (eV) and area of the peak (%)							
BE < 285eV (graphitic sp^2 carbon)	68.0	72.0	61.8	65.4	72.1	75.8	67.6	72.8
285.7 < BE < 287.1 (C–OH)	17.1	18.4	14.7	8.1	12.8	11.7	8.1	4.1
286.1 < BE < 288 (C=O or O–C–O)	4.6	3.5	7.3	7.9	4.5	3.4	6.9	6.4
288 < BE < 289.4 (O=C–O)	4.6	2.2	3.4	6.4	2.2	2.4	2.9	2.9
Total oxygenated groups	26.3	24.1	25.4	22.4	19.5	17.5	17.9	13.4
BE > 290 ("Shake-up" satellites)	5.7	3.9	12.8	12.2	8.4	6.7	14.5	13.8

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548 **Table 2:** Comparative SO_2 sorption capacity of carbon-derived material

Material precursor	Materials treatment	Experimental conditions	S_{BET} (m^2 g^{-1})	SO_2 adsorption capacity (mg g^{-1})	N (wt.%)	References
Biochar made from dairy manure (DM), sewage sludge (SS), and rice husk (RH)	Pyrolysis at 500 °C	Dynamic tests; Room temperature; Glass column: 25 cm length, 5 cm diameter, 2.5 cm length of sample (3.8─8 g); 0.5% SO_2 (5000 ppm) with ambient air; Flow rate: 1.5 L min^{-1}	DM: 4.8 SS: 10 RH: 41	DM: 64 SS: 35 RH: 13	DM: 2.2 SS: 3.3 RH:0.6	(Xu et al., 2016)
Carbon fibers made from ethylene tar	Activation in presence of steam (S) and ammonia (N) at 800~915 °C	Fixed-bed reactor; 30 °C; SO_2 (2000 ppm) with or without 5% vol. O_2; Total flow rate: 100 mL min^{-1}	S: 1469 N: 1480	S: 11 N: 28	S: 0.01 N: 1.1	(Li et al., 2001)
N-doped carbon made from polymerization of phenol, melamine, and formaldehyde	Pyrolysis at 900 °C	Fixed-bed reactor; 25 °C; 0.1 g sample; SO_2 (500 ppm), N_2 balance; Total flow rate: 200 mL min^{-1}	1013	48	10 (at.%)	(Sun et al., 2016)
Activated pyrolysed bituminous coal	Pyrolysis at 700 °C and further activation in presence of CO_2 at 900 °C	Thermogravimetric analyser; 100 °C; SO_2 (1000 ppm), O_2 (3%), CO_2 (10%), water vapour (10%) in N_2	740	92	-	(Davini, 2001)
Activated biochar made from cork powder	Pyrolysis at 750 °C and further activation in presence of KOH or CO_2 at 750°C	Thermogravimetric analyser; 45 °C; SO_2 (500─10000 ppm), N_2 balance; Total flow rate: 120 mL min^{-1}	KOH: 584 CO_2: 76	KOH: 90 CO_2: 65	KOH: 0.3 CO_2: 1.5	(Atanes et al., 2012)
Activated biochar made from corncobs	Pyrolysis at 600 °C followed by activation in presence of CO_2 at 850 °C and further impregnation with methyldiethanolamine	Fixed-bed reactor; 120 °C; 1% SO_2 (20 mL min^{-1}) and N_2 (80 mL min^{-1})	-	156	6.5 (at.%)	(Shao et al., 2018)
Commercial coconut shell activated carbon	-	Fixed-bed reactor; 150─200 °C; 1 g sample; SO_2 (1000 ppm), N_2 balance; Total flow rate: 1 L min^{-1}	748	21	-	(Sun et al., 2013)
Commercial single wall carbon nanotube	-	Fixed-bed reactor; 150─200 °C; 1 g sample; SO_2 (1000 ppm); N_2 balance; Total flow rate: 1 L min^{-1}	404	4	-	(Sun et al., 2013)
Commercial activated carbon (Panreac)	-	Thermogravimetric analyser; 45 °C; SO_2 (500─10000 ppm), N_2 balance; Total flow rate: 120 mL min^{-1}	752	65	0.2	(Atanes et al., 2012)
Commercial activated coke	-	Fixed-bed reactor; 5 g sample	563	53	0.6	(Sun et al., 2011)

Activated biochar made from wood residues	Pyrolysis at 454 °C and further activation in presence of steam at 900 °C	Dynamic tests; Room temperature; Glass column: 27 cm length; 2.5 cm diameter; 23 cm length of sample (10─25 g); SO_2 (50 ppm) with moist air; Flow rate: 30 mL min^{-1};	590	77	0.2	**This work**

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