Performance of physically and chemically activated biochars in copper removal from contaminated mine effluents

Flavia Lega Braghiroli[1,2], Hassine Bouafif [2], Carmen Mihaela Neculita[3], 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

[3] Research Institute on Mines and Environment (RIME), University of Québec in Abitibi-Témiscamingue (UQAT), 445 Boul. de l'Université, Rouyn-Noranda, QC J9X 5E4, Canada

[*] Corresponding author: (F.L. Braghiroli); Tel: +1 (819)-762-0931 ext. 1748; Fax: +1 (819)-762-0906; Email: Flavia.Braghiroli@uqat.ca

Abstract

The increasing global demand for metals and minerals justifies the intensive study of treatment options for contaminated mine effluents. The present study evaluated the conversion of wood residues into physically and chemically activated biochars, and their subsequent use in the treatment of Cu in synthetic and actual contaminated mine drainage. First, wood residues were converted into biochar by fast pyrolysis. Then, physical (using steam or CO_2) or chemical (using KOH) activation was carried out in a homemade pilot-scale furnace. After activation, highly microporous (KOH materials) and micro/mesoporous activated biochars (CO_2 and steam materials) were obtained. Batch adsorption testing was first conducted with synthetic effluents. Results showed that CO_2-activated biochar was the most Cu effective adsorbent (99% removal) at low concentrations (5−20 mg L^{-1}). The mechanisms of Cu^{2+} adsorption involved physical and chemisorption for biochars and CO_2-activated biochar, while chemisorption for KOH-activated biochars was probably due to the high proportion of functional groups connected to their surface. In multi-metal acid mine drainage, metal adsorption capacities deteriorated for most of the materials, probably due to effects of ion competition. However, KOH-activated biochar decreased Cu^{2+} concentrations to below the authorized monthly mean allowed by Canadian law (0.3 mg L^{-1}), and decreased Co, Pb, and Mn concentrations up to 95%. These findings indicate that high porosity and oxygenated functional groups connected to the surface of activated biochars are important properties for the enhancement of interactions between carbon materials and metals from mine effluents, as well as for their performance improvement in mine drainage treatment.

Keywords: Activated biochar, adsorption, copper removal, water treatment, actual mine effluents

1. Introduction

Current mining activities, which exploit low-grade ore, generate large amounts of waste. The subsequent contamination is associated with air pollution by gases (CO_2, SO_2, NO_x, etc.) and particulate matter emissions, solid waste that deteriorates the soil, and contaminated effluents that may reach drinking water systems and pose a risk to humans and wildlife (Dudka and Adriano 1997). The main issue is the exposure of geochemically reactive minerals to air and water, which leads to contaminated mine drainage, either acidic (AMD) or contaminated neutral (CND), as well as to surface and underground water pollution (Nordstrom et al. 2015). Cu mining and smelting are one of the major sources of mine waste. Although Cu is an essential element required for living organisms, its divalent form (Cu^{2+}) is potentially toxic and carcinogenic when ingested by aquatic organisms and humans. An excess of Cu leads to vomiting, headache, nausea, liver/kidney failure, and respiratory problems (Akar et al. 2009), and can be harmful to soil biota, plants (Lamb et al. 2012), and aquatic ecosystems (Lee et al. 2010).

Several regulators monitor the levels of Cu in wastewater treatment plants, drinking water, and industrial effluents to certify that the maximum contaminant level should be below a value at which there is no known or expected risk to health. In drinking water, Health Canada fixed the threshold at less than 1 mg L^{-1} (Health Canada 1992), whereas the maximum authorized monthly mean concentration of Cu should be below 0.3 mg L^{-1} according to metal mining effluent regulations (Environment and Climate Change Canada 1999). Several options are available for the treatment of Cu in water: chemical precipitation, ion exchange, membrane filtration, coagulation/flocculation, electrolytic recovery, reverse osmosis, and adsorption. Each technology has its advantages and limits for an efficient Cu removal from wastewater, but high costs are a common drawback. However, adsorption is an attractive technique due to the availability of cost-effective, sustainable, and eco-friendly bioadsorbents (Sekhula et al. 2012).

75 Literature reveals that activated carbons are the most appropriate bioadsorbents between algal,
76 bacterial, agriculture and forest, and fungal and yeast biomass for Cu uptake in water media
77 (Bilal et al. 2013).

78 Several inexpensive waste precursors have been used for the production of activated
79 carbons, including wood residues, fruit shells, stones, husks, and hulls (Tan et al. 2017).
80 Recently, biochar, a by-product carbon-rich material produced from the thermochemical
81 conversion processes of biomass (e.g., torrefaction, slow to fast pyrolysis, and gasification) has
82 also been tested (Lehmann and Joseph 2015). Although biochar has high carbon content and a
83 high proportion of oxygenated functional groups, it is often characterized by low surface area
84 with a small amount of micropores (Liu et al. 2015). Activation is a widely used technique in
85 which a selective gasification of carbon atoms by physical agents (CO_2 or steam) or chemicals
86 (KOH or H_3PO_4) is performed at increasing temperature (e.g., 900 °C) for the development of
87 materials' porosity (Marsh and Rodríguez-Reinoso 2006). The feedstock, pyro-gasification, and
88 activation operating conditions have significant influence on the resultant activated biochar,
89 while highly porous materials with properties similar to activated carbons (e.g., surface areas
90 up to 2500 $m^2\ g^{-1}$) can be produced. However, an optimization study of the operating conditions
91 for the preparation of activated biochars to improve the material porosity is required (Braghiroli
92 et al. 2018a).

93 The effective sorption of metals by activated biochars made by using different operating
94 conditions and feedstock have been reported in the literature. According to a very recent review
95 (Braghiroli et al. 2018b), the surface functional groups (e.g., carboxylic, phenolic, amino
96 groups), specific surface area, and pore volume (narrow and wide micropores), as well as the
97 optimum pH, are the most important factors in potentially providing more bonding sites for
98 heavy metals interactions with activated biochars. The overall metal removal mechanisms
99 include physical adsorption, electrostatic attraction between positive charges (metals) and

negative charges (surface of activated biochar), ion exchange, surface complexation, and metal precipitation (Chowdhury et al. 2012; Adebisi et al. 2017a, 2017b). Hence, the removal of up to 18 mg g^{-1} of Cu (C_0 from 50 to 100 mg L^{-1}) was reported using KOH-activated fruit peel of mangostene biochar (Hamid et al. 2014). Then, up to 96% of Cu (C_0 = 63.5 mg L^{-1}) elimination using steam-activated soybean straw biochars was published by Lima et al. (2010). The improved efficiency compared to biochars (96 vs. 85%) was associated with increased surface area (up to 793 m^2 g^{-1}), which eventually facilitated the access of functional groups connected to the surface of activated biochars. High adsorption capacity of Cu (203 mg g^{-1}; C_0 from 0.1 to 600 mg L^{-1}) was also attributed to the presence of both carboxylic and phenolic groups on steam-activated date pit biochars, improving cation exchange and complexation of adsorbent surface-metal interactions, as well as greater surface area (1467 m^2 g^{-1}) for physical sorption (Bouchelta et al. 2012). In another study, steam-activated manure biochar showed high Cu sorption capacity (104 mg g^{-1}; C_0 = 1270 mg L^{-1}) due to the presence of inorganics (e.g., P, S, Ca, Na) that played an important role in the development of specific surface functionalities and of multiple interactions between activated biochar' surface and Cu^{2+} ions. It was also reported that metals sorption were favored at low pH level (fixed at 4.8), whereas at pH higher than 6, Cu precipitation occurred (Lima et al. 2014).

Based on the authors' best knowledge, this study is the first to examine the use of wood residues (white birch and black spruce) for the production of activated biochars in pilot-scale technologies for the treatment of Cu in synthetic and actual mine effluents. Most previous studies evaluated the performance of activated biochars in the removal of very high concentrations of Cu from synthetic solutions, but very few studies focused on the use of activated biochar for the removal of multi-metal contaminants from actual mine effluents. According to the circular economy principle (recover and recycle, instead of "take, make, and discard"), the use of wood residues in mine effluent treatment appears to be a winning formula

for both the mining and forestry industries, such as in Abitibi-Témiscamingue, the region of Québec, Canada, where the present study was conducted.

In this context, the objective of the present study is to evaluate the removal efficiency of physically and chemically activated biochars made from wood residues for the treatment of Cu in synthetic effluent and actual AMD.

2. Materials and methods

2.1 Material sampling and synthesis of biochar and activated biochar

White birch (WB) and black spruce (BS) residues were sampled from sawmills located in the Abitibi-Témiscamingue region, Québec, Canada. More details on wood residues preparation, CarbonFX fast pyrolysis technology, and pilot-scale activation furnace are available elsewhere (Braghiroli et al. 2018a). In summary, biochars were produced at 454 °C in an oxygen-free environment using the CarbonFX fast pyrolysis technology developed by Airex Energy Inc. (Bécancour, QC, Canada). The resulting biochars made from WB and BS residues were activated in a homemade pilot oven. Three types of activating agents were used for the production of activated biochars: KOH, CO_2, and steam. In chemical activation, 100 g of each biochar were mixed with 200 g of distilled water and 100 g of KOH, and left in the fume hood for 2 h. Then, the mixture was left in an oven at 120 °C overnight. The impregnated biochar was then placed in the feed hopper; and when the furnace reached 900 °C in a N_2 atmosphere, the material was transported into the furnace by a screw conveyor (driven by an electronic engine) to the recovery hopper. 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. The raw biochars were labelled BWB and BBS, while activated

148 biochars depending on the type of activation agent, were labelled as e.g., CO2BWB, KOHBWB,
149 or H2OBBS.

150 2.2 Physical and chemical characterization of biochar and activated biochar

151 Biochars and activated biochars were characterized for their physicochemical parameters:
152 pH, elemental composition (C, H, N, S, O), morphology, surface chemistry, specific surface
153 area, and pore volume. The pH of activated biochars was determined according to a standard
154 test method (ASTM D3838 - 05(2017)) using a SevenMulti, Mettler Toledo (Greifensee,
155 Switzerland) equipped with Inlab Routine Pro electrode. Elemental composition of all materials
156 was determined in a CHNS elemental analyzer, Perkin Elmer 2400 CHNS/O Analyzer
157 (Waltham, MA, USA), by combustion of the samples in a stream of pure O_2. The morphology
158 of biochars and activated biochars was investigated with a JEOL JSM-5500 (JEOL USA, Inc.,
159 Peabody, MA, USA) Scanning Electron Microscope (SEM), after metallization. X-ray
160 photoelectron spectroscopy (XPS) spectra were recorded with a Kratos AXIS ULTRA system
161 (Wharfside, MA, UK) equipped with a channel electron multiplier detector. The XPS core level
162 spectra were analyzed with Casa software.

163 Micromeritics ASAP 2460 automatic apparatus (Norcross, GA, USA) was used for
164 obtaining N_2 adsorption/desorption isotherms of porous materials at -196 °C. The data were
165 then treated for measuring surface area, S_{BET} ($m^2\ g^{-1}$), calculated by the Brunauer-Emmett-Teller
166 (BET) model (Brunauer et al. 1938); micropore volume, $V_{\mu, N2}$ ($cm^3\ g^{-1}$), determined by the
167 Dubinin–Radushkevich (DR) equation (Dubinin 1989); total pore volume, V_t ($cm^3\ g^{-1}$),
168 calculated from the amount of nitrogen adsorbed at the relative pressure of 0.97 (Gregg and
169 Sing 1991); and mesopore volume, V_m ($cm^3\ g^{-1}$), calculated by the difference $V_t - V_{\mu, N2}$.
170 Ultramicroporosity was obtained by CO_2 adsorption at 0 °C ($V_{\mu, CO2}$ ($cm^3\ g^{-1}$)) and the pore size
171 distribution (PSD) was determined by application of density functional theory (DFT) using N_2
172 adsorption isotherms (Tarazona 1995).

2.3 Adsorption kinetics experiments

Kinetic experiments were conducted in 100 mL beakers containing 0.05 g of adsorbent material and 50 mL of synthetic effluent with Cu^{2+} concentration of 100 mg L^{-1}. The supernatants were sampled after predefined intervals at 2, 4, 6, 8, 10, 12, 18, 24, and 48 h. The beakers were placed on a multi-position stirring plate, at 500 rpm, and at room temperature (20 ±2 °C). The pH, potential redox (Eh), and dissolved oxygen (DO) of the supernatant were measured in the beginning and on each sample collected. DO and Eh were measured using LDO Hatch and ORP Hach (London, ON, Canada) meters, respectively, with a double junction Ag/AgCl reference electrode. The supernatants were filtered, and the residual metal trace was determined by using microwave plasma atomic emission spectroscopy (MP-AES 4200, Agilent Technologies, Mississauga, ON, Canada). This procedure was carried out for all 8 materials, including 2 biochars (BWB and BBS) and 6 activated biochars (CO2BWB, KOHBWB, H2OBWB, CO2BSB, KOHBSB, and H2OBSB).

Sorption capacity q_t (mg g^{-1}) was calculated with the application of Eq. 1:

$$q_t = [C_0 - C_t] \cdot \frac{V}{m} \quad (1)$$

where C_0, C_t, V, and m represent, respectively, the concentrations of Cu in solution (mg L^{-1}) at the initial and at t moment, the total volume of solution (L), and the amount of the material used (g).

The equations of pseudo-first (Eq. 2) and pseudo-second (Eq. 3) order model (Lagergren 1898), and Elovich (Eq. 4) were employed to describe Cu adsorption kinetics.

$$\log(q_e - q_t) = \log(q_e) - k_1 \cdot \frac{t}{2.303} \quad (2)$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2\, t \quad (3)$$

$$q_t = \frac{1}{b} \cdot \ln(ab) + \frac{1}{b} \cdot \ln(t) \quad (4)$$

where q_e and q_t refer to the amount of Cu adsorbed (mg g^{-1}) at equilibrium and at any time, t (h), respectively, and k_1 is the equilibrium rate constant of pseudo-second order adsorption (h^{-1}), and k_2 is the kinetic constant of pseudo-first order adsorption (g (mg h)$^{-1}$), a is the initial adsorption rate (mg (g h)$^{-1}$), and the parameter $1/b$ is related to the number of sites available for adsorption.

2.4 Adsorption equilibrium experiments

The tests of isotherm adsorption were conducted at different initial Cu concentrations (5, 10, 20, 50, 100, 200, 500, and 1000 mg L^{-1}) under the same conditions as the kinetic experiments. Equilibrium was carried out for 48 h adsorption testing. Sorption capacity q_e (mg g^{-1}) was calculated with Eq. 5, where C_0, C_e, V, and m represent, respectively, the concentrations of Cu (mg L^{-1}) at the initial and equilibrium solutions, the total volume of solution (L), and the amount of the material used (g). The adsorption (%) was calculated with Eq. 6:

$$q_e = [C_0 - C_e] \cdot \frac{V}{m} \quad (5)$$

$$Adsorption\ (\%) = [C_0 - C_e] \cdot \frac{100}{C_0} \quad (6)$$

The equations of Langmuir (Langmuir 1918) and Freundlich (Freundlich 1906) represented by Eq. 7 and 8, respectively, were employed to describe Cu sorption:

$$\frac{C_e}{q_e} = \frac{1}{b \cdot q_{max}} + \frac{C_e}{q_{max}} \quad (7)$$

$$\log q_e = \log k_f + n \cdot \log C_e \quad (8)$$

where C_e and q_e have the same meaning for both equations, q_{max} is the maximum uptake per unit mass of adsorbent (mg g^{-1}), and b is the Langmuir constant related to the adsorption energy (L mg^{-1}) while k_f and n are Freundlich coefficients.

The constant b allows the determination of the R_L equilibrium parameter (Eq. 9) that indicates the shape of the isotherm (at $R_L = 0$, the adsorption is irreversible; $0 < R_L < 1$, the

adsorption is favorable; at R_L = 1, the adsorption is linear; and at R_L > 1, the adsorption is unfavorable):

$$R_L = \frac{1}{1 + b \cdot C_0} \quad (9)$$

2.5 Adsorption of Cu in actual mine effluent

The actual effluent, containing Cu and other metals, was collected from an operating gold mine located in Abitibi-Témiscamingue, QC, Canada, and preserved at 4 °C, prior to testing. The same testing conditions for the kinetics and isotherms studies of Cu in synthetic effluents were also applied for this effluent. The supernatants were filtered, and the residual metals were measured by MP-AES equipment while the pH, Eh, and DO were measured using the same multimeter. Anions (NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}) were determined using the ion chromatography Dionex ICS-5000 with a capillary column Ionpac AS18 (ThermoFisher Scientific, Waltham, USA).

2.6 Geochemical modelling

The thermodynamic geochemical equilibrium model Visual MINTEQ (VMINTEQ) version 3.1 (Visual MINTEQ 2018) was applied to calculate saturation indices (SI) of potential mineral phases present in the AMD. The data on the effluent (e.g., pH, contaminant concentrations) was used to calculate equilibrium distribution of chemical species according to geochemical processes (e.g., precipitation, complexation, ion exchange). If SI < 0, minerals are undersaturated or in a dissolved form; if SI = 0, minerals are at equilibrium; and finally if SI > 0, minerals are oversaturated and might precipitate.

2.7 Activated biochar regeneration

Chemical regeneration tests were performed with an activated biochar for six cycle adsorption-desorption tests. Adsorption tests were conducted under the same conditions as the isotherm experiments. After sorption, 0.1 g of dried adsorbent was mixed and shaken with 20

mL eluents of 0.1 M HNO_3, 0.5 M H_2SO_4, and 1 M HCl, according to Kołodyńska et al. (2017). The desorption was determined using Eq. 10:

$$\%D = \frac{C_{des}}{C_0} \times 100\% \quad (10)$$

where C_0 and C_{des} (mg L^{-1}) are the initial Cu concentration and the concentration of Cu ions in solution after desorption, respectively.

3. Results and discussion

3.1 Physicochemical characterization of the activated biochars

SEM images of activated biochars (Fig. 1) show a typical morphology of wood-derived carbons where the original wood structure is maintained. Fast pyrolysis followed by activation leads to the formation of various sizes of pits, holes, and cave-type openings on the carbon structure for all three types of activating agents. The development of narrow and wide pores was noticed, but no clear structural differences were identified across materials physically or chemically activated. The physicochemical properties of biochar and activated biochars are presented in Table 1. Notably, the carbon content of materials made by fast pyrolysis and activation substantially increased, whereas oxygen and hydrogen contents decreased. During the thermal treatment of lignocellulosic and biochar-derived materials, various carbon compounds (e.g., H_2O, CO_2, CO, NH_3, HCN, $C_xH_yO_z$) are released. With further increase in temperature, compounds with less carbon (e.g., CO_2, CO, NO_x) are continuously released, leading to increased material's carbon content and pore development (Liu et al. 2015).

Biochar activation involves mostly a reaction between the carbon (in biochar molecular structure) and injected CO_2 or steam as seen in Eq. 11 (Boudouard reaction) (Calo and Perkins 1987) and Eq. 12, respectively. In fact, the physical agents will promote the removal of carbon atoms (burn off) from the structure of biochar at high temperatures, causing the development of

pores. In chemical activation, the main reaction mechanism (Eq. 13), as proposed by Radovic and Rodriguez-Reinoso (1997), involves the following steps: KOH dehydration to form K_2O; K_2O reduction to metallic potassium (K); K oxidation to form K_2O; and K_2O hydration to form KOH. Chemical activation is considered efficient because different potassium compounds and gases (physical agents) are formed as well as K that penetrates into the biochar structure to expand its framework and porosity. Therefore, before and after activation, materials showed an acid and basic character, respectively. At any type of activation, pH ranged from 8.2 to 10.3 (Table 1).

$$C + CO_2 \leftrightarrow 2\,CO \quad (11)$$

$$C + H_2O \leftrightarrow CO + H_2 \quad (12)$$

$$6KOH + 2C \rightarrow 2K + 3H_2 \uparrow + 2K_2CO_3 \quad (13)$$

The oxygen functional groups present on the surface of biochars and activated biochars were investigated by XPS. After deconvolution of C1s peaks, the relative proportions of the functional groups were estimated (Supplementary Material, Table 1S). The two most predominant peaks measured for most of all materials were related to aliphatic/aromatic carbon (C–C, C–H, and C=C), at BE lower than 285 eV (62−76%), and the C–O bond, at BE in a range 285.7–287.1 (18−8%). The other peaks (at 286.1−288, and 288–289.4 eV) were then attached to the oxygen-containing moieties, i.e., C=O or O−C−O, and O–C=O, respectively (Lazzarini et al. 2016). KOH-activated biochars had the highest proportion of total oxygenated groups: 22.4 and 25.4% for KOHBBS and KOHBWB, respectively, followed by CO2BWB (19.5%), H2OBWB (17.9%), CO2BBS (17.5%), and H2OBBS (13.4%). In addition, KOHBBS had a more evenly divided proportion of oxygenated groups—8.1% (C–O bond), 7.9% (C=O or O−C−O), and 6.4% (O–C=O) relative to CO2BWB, 12.8, 4.5, and 2.2%, respectively—which can have more distinct and abundant interactions with metals.

Analysis of the textural properties of biochars shows that they are highly ultramicroporous, as evidenced by the CO_2 adsorption analysis with low surface areas: 177 and 208 $m^2\ g^{-1}$ for BWB and BBS, respectively. After activation, birch-activated biochars presented highly developed surface areas in presence of KOH, CO_2, and steam, 1700, 881, and 590 and $m^2\ g^{-1}$, respectively. However, these materials had a porous structure highly different from each other. According to the IUPAC classification (Sing 1985), N_2 adsorption/desorption isotherms at -196 °C for KOH-activated biochars are of Type I, characteristic of microporous solids with a narrow elbow at $P/P_0 = 0.05$ and a horizontal plateau (Fig. 1S a). For the other materials, the N_2 isotherms are a combination of Type I and Type IV, with an important nitrogen uptake at relative pressures $P/P_0 < 0.01$. This indicates the existence of a well-developed narrow microporosity, and a slight slope up to $P/P_0 = 0.9$. The development of wider microporosity and mesoporosity with the presence of a narrow hysteresis loop is hence confirmed. PSDs obtained by DFT (Fig. 1S b) are in good agreement with results obtained from N_2 isotherms. No pics higher than 2 nm were observed for highly microporous KOH-activated biochars (i.e., 0% mesoporosity), whereas the other materials presented two pics: one in micropore range (< 2 nm), and the other in mesopores (10–50 nm).

3.2 Adsorption kinetics

The kinetics of adsorption describe the rate of Cu^{2+} ions uptake on biochar-derived materials. The adsorption capacity of Cu^{2+} increased with time for all materials (Fig. 2). The adsorption equilibrium was reached for most of materials at 24 h testing. Thereafter, it reached a plateau, which indicates that no additional Cu^{2+} was removed from the synthetic effluent at 100 mg L^{-1}. The Cu^{2+} adsorption capacity for CO2BWB increased 5 times (~49 mg L^{-1}) compared to biochars (~10 mg L^{-1}). The adsorption capacities of biochar-derived materials for Cu^{2+} varied according to the following sequence: CO2BWB < KOHBBS < H2OBWB < KOHBWB ~ CO2BBS < H2OBBS < BBS ~ BWB.

316 The experimental data for the adsorption of Cu^{2+} onto biochar-derived materials were
317 interpreted with the kinetic models (pseudo-first and pseudo-second order, and Elovich's
318 equation) to evaluate the controlling mechanism of adsorption process. The derived kinetic
319 parameters of these models (Table 2) show that experimental data obtained from biochars and
320 activated biochars do not follow the pseudo-second kinetic model as evidenced by R^2
321 coefficients between 0.02 and 0.72. Biochars and CO_2-activated biochars best fit the pseudo-
322 first (R^2 = 0.79–0.99) and Elovich models (R^2 = 0.82–0.97), whereas steam and KOH-activated
323 biochars best defined the adsorption process of the Elovich kinetic model as evidenced by R^2
324 coefficients: 0.67–0.95. These results are in agreement with several other metal adsorption
325 systems that have been described by the Elovich equation (Wu et al. 2009).

326 Pseudo-first model is based on the assumption that physisorption limits the rate of
327 adsorption of Cu^{2+} onto the adsorbent (Lagergren 1898), whereas the Elovich model gives a
328 good correlation on highly heterogeneous surfaces and chemisorptive interaction onto
329 materials' surface (Aharoni and Tompkins 1970). These results suggest that physical and
330 chemical interactions may simultaneously contribute and control Cu^{2+} uptake onto biochars and
331 CO_2-activated biochars surfaces, whereas chemisorption is the main adsorption interaction
332 between Cu^{2+} metal ions and activated biochars made with steam and KOH. Physisorption
333 involves Van der Waals or electrostatic forces as confirmed by the effect of optimum pH (4.5),
334 while chemisorption involves covalent forces (Xie et al. 2017), which can be formed with active
335 oxygenated functional groups as observed by XPS analysis in the prepared materials structure
336 (Chowdhury et al. 2015).

337 3.3 Adsorption isotherms

338 Biochars and activated biochars were tested for their ability to adsorb Cu in synthetic
339 effluent. Comparative adsorption isotherms of Cu show that activated biochars (e.g., CO2BWB)
340 exhibited almost fivefold higher Cu sorption relative to biochars (Fig. 3 a). The efficiency of

341 Cu removal in synthetic effluents (C_0 = 5–20 mg L^{-1}) was up to 50%, for biochars, whereas it
342 varied from 95 to 99%, for activated biochars (Fig. 3 b). In addition, Cu removal for all materials
343 deteriorated with increases in initial concentrations. For example, CO2BWB decreased more
344 than four times (from 99 to 24%), when initial concentrations increased (from 5 to 200 mg L^{-1},
345 respectively).

346 Langmuir and Freundlich, two widely used isotherm models, were applied to describe the
347 sorption of Cu by biochars and activated biochars (Table 3). The Langmuir model describes the
348 monolayered adsorbents on the homogeneous surface (Langmuir 1918), whereas the Freundlich
349 model indicates that the adsorption would take place on a heterogeneous surface (Freundlich
350 1906). According to the correlation coefficients (R^2) listed in Table 3, the experimental data fit
351 Freundlich (R^2 = 0.77–0.94) better than Langmuir (R^2 = 0.15–0.92), although the separation
352 factor (R_L) lower than 1 suggests that Cu^{2+} adsorption on biochar-derived materials is a
353 favorable process. This result is consistent with the kinetic studies, in which data matched the
354 Elovich model, i.e., based on chemisorption process.

355 With an increase of Cu concentration to up to 1000 mg L^{-1}, KOHBBS showed the greatest
356 adsorption capacity: q_{exp} and q_{max} obtained from experiments and predicted based on Langmuir
357 model, respectively, were 137 and 132 mg g^{-1}. Ion exchange and complexation are the most
358 important mechanisms associated with Cu uptake by adsorbents (Baccar et al. 2009; Bouchelta
359 et al. 2012; Bilal et al. 2013). Hamid et al. (2014) reported that Cu was mainly adsorbed by
360 chemical interactions with active functional groups present on the surface of the KOH-activated
361 fruit peel of mangostene biochar. Indeed, KOHBBS presented a great and evenly divided
362 proportion of oxygenated groups (phenolic, carboxylic, aldehyde or ether), which improve the
363 cation exchange capacity and complexation properties of these adsorbents in addition to the
364 greater specific surface area and microporosity.

A comparison of adsorption capacity of Cu^{2+} on different activated biochars in the available literature (Table 4) shows that higher adsorption capacities of activated biochar (even better than commercial activated carbon) are attributed to several factors, as mentioned before, such as physicochemical properties (high specific surface area, pore size, type of functional groups connected to the materials surface), high affinity between carbon material and Cu^{2+}, optimum pH, increasing carbon (g): contaminant (mL) ratio, and high initial Cu concentration used. The comparable adsorption capacity of materials made in this study with other adsorbents reveals that physical and chemical activated biochar made from wood residues is suitable for the removal of Cu^{2+} since it has a relatively high adsorption capacity.

3.4 Cu removal in actual AMD

The initial concentration of Cu^{2+} in actual AMD (1.75 mg L^{-1}) collected from an operating mine site largely exceeded the maximum authorized monthly mean concentration of Cu (0.3 mg L^{-1}) allowed by the Canadian law (Environment and Climate Change Canada 1999). For most of biochar-derived materials, the removal of Cu^{2+} was not significant, and varied from 17 to 56% (Fig. 4). The only material for which Cu removal topped 99% was KOHBBS. The sorption of the activated biochar seems to be unaffected by the nature of the precursor (WB or BS). Rather, it is associated with increased surface area (highly porous materials) and improved access of functional groups connected to the surface of activated biochars that may have improved the interactions between Cu and the surface of the material. KOHBBS also exhibited the highest adsorption capacity in synthetic effluents at very high Cu concentrations.

Comparing the composition of AMD before and after adsorption onto KOHBBS (Table 5), it was noticed that pH, Eh, and DO of the effluent did not vary significantly, but metal adsorption capacities were reduced (Fig. 4) relative to single-metal synthetic effluent, probably due to multi-metal competition from an actual effluent onto KOHBBS (Mohan and Chander 2001, 2006). In addition to Cu removal, other metals were also removed in presence of KOHBBS,

390 including Co, Fe, Mn, Na, Pb, and Zn (Table 5). Among these metals, Co and Pb had the highest
391 removal efficiency of 95 and 43%, respectively, although a significant increase of K is probably
392 coming from the KOH activation during the production of activated biochar. Therefore, a
393 decrease of metals concentration was observed in presence of activated biochar, even though a
394 pre- and/or post-treatment is required to reduce the level of metal concentrations (e.g., Mn, Zn,
395 Fe) to meet Canadian regulations (see q_{exp} in Table 3).

396 Metals can form soluble and precipitate complexes, but to precipitate them from water, the
397 pH must range from 6 to 9, although Fe^{3+} can precipitate at pH higher than 3.5 (Ríos et al. 2008).
398 According to VMINTEQ geochemical modelling, oversaturation and possible precipitation for
399 $MnHPO_4$ was performed in initial AMD, whereas all metals in AMD after sorption onto
400 KOHBBS were undersaturation. Ríos et al. (2008) employed a significant zeolite: effluent ratio
401 (5 g:100 mL) for the treatment of AMD, which increased the pH of the system, and,
402 consequently, metal concentrations decreased probably due to precipitation on the surface of
403 zeolite. According to Table 1, all materials, including KOHBBS, exhibited an acid character, so
404 precipitation of certain solid phases on the surface of the ion exchanger might not be promoted.
405 However, precipitation also depends on metal concentration, temperature, the existence of
406 metals and anions, and time to thermodynamic equilibrium (Cuppett 2006). In the study, at such
407 low adsorbent: effluent ratio (0.1 g:100 mL), the pH was maintained at very low value (2.6);
408 thus, the presence of a precipitate was not obvious.

409 3.5 Regeneration of activated biochar

410 The feasibility of the adsorption technology on an industrial scale depends on the
411 reusability of spent activated biochar. In addition, chemical regeneration is largely used for
412 desorbing inorganic contaminants, especially metals. Desorption experiments were carried out
413 in order to estimate the metal releasing capacity of an activated biochar loaded with Cu^{2+}. Three
414 types of acid eluents were applied for Cu desorption: HNO_3, H_2SO_4, and HCl at different

concentrations 0.1, 0.5, and 1 M. By comparing the three eluents, HNO_3 was found to be the most efficient, even if used at the lowest concentration, followed by HCl and, finally, H_2SO_4. Under strong acid condition, the surface of the sorbent is in a protonated form, which allows desorption of positively charged ions. In the first adsorption-desorption cycle, desorption efficiency was found to be 99.6, 99.2, and 98.6%, respectively (Fig 5. a). After the six regeneration cycles (Fig. 5 b), the efficiency of Cu desorption was reduced to 76.2, 51.4, and 36.2% using HNO_3, H_2SO_4, and HCl, respectively. These results suggest that activated biochar made from wood residues has high regenerability, more stable Cu desorption efficiency with HNO_3 compared to the other two acid eluents, and suitability for a minimum of at least six successive adsorption-desorption cycles.

4. Conclusion

Activated biochars were produced from wood residues using physical (steam and CO_2) and chemical (KOH) processes. The experimental data revealed that Cu removal depends on the physicochemical characteristics (e.g., high surface area and porosity, and oxygenated functional groups connected to materials surface) of the sorbent material as well as the effluent type (single or multi-metal) and initial metal concentrations ($C_0 < 2$ mg L^{-1} or $C_0 \geq 5$ mg L^{-1}). CO_2-activated biochar showed better efficiency for Cu in synthetic effluent at up to 200 mg L^{-1}, whereas KOH-activated biochar was the most efficient material for Cu from high concentration synthetic effluent (1000 mg L^{-1}) and from multi-metal actual effluent. Elovich kinetic and Freundlich isotherm models were found to fit the experimental data, indicating that chemical interactions of oxygenated functional groups with Cu on the heterogeneous surface might be occurring. The desorption of Cu ions was successfully carried out through chemical regeneration with HNO_3, which was the most efficient approach, even after six adsorption-desorption cycles, relative to H_2SO_4 and HCl. Therefore, wood residues seem to be an attractive

precursor for the production of activated biochar for remediating Cu present in actual mine effluent. However, a pre- and/or post-AMD treatment would be required to reduce high levels of other metals such as Fe, Al, and Mn according to the fixed Canadian thresholds for mine effluent.

Acknowledgments

This research was funded by the Québec's Ministry of Economy, Science and Innovation (Ministère de l'Économie, de la Science et de l'Innovation du Québec), the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canada Research Chairs Program, the College of Abitibi-Témiscamingue, and the Technology Centre for Industrial Waste (Centre Technologique des Résidus Industriels) through its partners on this project, Airex Energy and Iamgold Corporation. The first author, Dr. Flavia Lega Braghiroli, also sincerely acknowledges NSERC financial support via a Banting Postdoctoral Fellowship (2017–2019). The authors also thank Anne-Marie Marleau Claveau, Félicia Porqueres, Maéva Giasson, Gilles Villeneuve, Mamadou Dia, Nicolas Bergeron and Hélie Jacob Turmel for their assistance with experiments, analysis and testing in the laboratory.

457 **References**

458 Adebisi, G. A., Chowdhury, Z. Z., & Alaba, P. A. (2017a). Equilibrium, kinetic, and
459 thermodynamic studies of lead ion and zinc ion adsorption from aqueous solution onto
460 activated carbon prepared from palm oil mill effluent. *Journal of Cleaner Production*,
461 *148*, 958–968. doi:10.1016/j.jclepro.2017.02.047

462 Adebisi, G. A., Chowdhury, Z. Z., Hamid, S. B. A., & Ali, E. (2017b). Equilibrium isotherm,
463 kinetic, and thermodynamic studies of divalent cation adsorption onto *Calamus*
464 *Gracilis* sawdust-based activated carbon. *BioResources*, *12*(2), 2872–2898.

465 Aharoni, C., & Tompkins, F. C. (1970). Kinetics of adsorption and desorption and the Elovich
466 equation. *Advances in Catalysis*, *21*, 1–49. doi:10.1016/S0360-0564(08)60563-5

467 Akar, S. T., Akar, T., Kaynak, Z., Anilan, B., Cabuk, A., Tabak, Ö., et al. (2009). Removal of
468 copper(II) ions from synthetic solution and real wastewater by the combined action of
469 dried *Trametes versicolor* cells and montmorillonite. *Hydrometallurgy*, *97*(1–2), 98–
470 104. doi:10.1016/j.hydromet.2009.01.009

471 Baccar, R., Bouzid, J., Feki, M., & Montiel, A. (2009). Preparation of activated carbon from
472 Tunisian olive-waste cakes and its application for adsorption of heavy metal ions.
473 *Journal of Hazardous Materials*, *162*(2–3), 1522–1529.
474 doi:10.1016/j.jhazmat.2008.06.041

475 Banerjee, S., Mukherjee, S., LaminKa-ot, A., Joshi, S. R., Mandal, T., & Halder, G. (2016).
476 Biosorptive uptake of Fe^{2+}, Cu^{2+} and As^{5+} by activated biochar derived from
477 *Colocasia esculenta*: isotherm, kinetics, thermodynamics, and cost estimation. *Journal*
478 *of Advanced Research*, *7*(5), 597–610. doi:10.1016/j.jare.2016.06.002

479 Bilal, M., Shah, J. A., Ashfaq, T., Gardazi, S. M. H., Tahir, A. A., Pervez, A., et al. (2013).
480 Waste biomass adsorbents for copper removal from industrial wastewater—a review.
481 *Journal of Hazardous Materials*, *263*, 322–333. doi:10.1016/j.jhazmat.2013.07.071

Bouchelta, C., Medjram, M. S., Zoubida, M., Chekkat, F. A., Ramdane, N., & Bellat, J.-P. (2012). Effects of pyrolysis conditions on the porous structure development of date pits activated carbon. *Journal of Analytical and Applied Pyrolysis*, *94*, 215–222. doi:10.1016/j.jaap.2011.12.014

Braghiroli, F. L., Bouafif, H., Hamza, N., Bouslimi, B., Neculita, C. M., & Koubaa, A. (2018a). The influence of pilot-scale pyro-gasification and activation conditions on porosity development in activated biochars. *Biomass and Bioenergy*, *118*, 105–114. doi:10.1016/j.biombioe.2018.08.016

Braghiroli, F. L., Bouafif, H., Neculita, C. M., & Koubaa, A. (2018b). Activated biochar as an effective sorbent for organic and inorganic contaminants in water. *Water, Air, Soil Pollution*, *229*(7). doi:10.1007/s11270-018-3889-8

Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, *60*(2), 309–319. doi:10.1021/ja01269a023

Calo, J. M., & Perkins, M. T. (1987). A heterogeneous surface model for the “steady-state” kinetics of the boudouard reaction. *Carbon*, *25*(3), 395–407. doi:10.1016/0008-6223(87)90011-X

Chowdhury, Z. Z., Hasan, Md. R., Abd Hamid, S. B., Marlina Samsudin, E., Zain, S. Mohd., & Khalid, K. (2015). Catalytic pretreatment of biochar residues derived from lignocellulosic feedstock for equilibrium studies of manganese, Mn(II) cations from aqueous solution. *RSC Advances*, *5*(9), 6345–6356. doi:10.1039/C4RA09709B

Chowdhury, Z. Z., Zain, S. M., Khan, R. A., Rafique, R. F., & Khalid, K. (2012). Batch and fixed bed adsorption studies of lead (II) cations from aqueous solutions onto granular activated carbon derived from *Mangostana Garcinia* shell. *BioResources*, *7*(3), 2895–2915.

507 Cuppett, J. D. (2006). Evaluation of copper speciation and water quality factors that affect
508 aqueous copper tasting response. *Chemical Senses*, *31*(7), 689–697.
509 doi:10.1093/chemse/bjl010
510 Ding, Z., Hu, X., Wan, Y., Wang, S., & Gao, B. (2016). Removal of lead, copper, cadmium,
511 zinc, and nickel from aqueous solutions by alkali-modified biochar: batch and column
512 tests. *Journal of Industrial and Engineering Chemistry*, *33*, 239–245.
513 doi:10.1016/j.jiec.2015.10.007
514 Dubinin, M. M. (1989). Fundamentals of the theory of adsorption in micropores of carbon
515 adsorbents: Characteristics of their adsorption properties and microporous structures.
516 *Carbon*, *27*(3), 457–467. doi:10.1016/0008-6223(89)90078-X
517 Dudka, S., & Adriano, D. C. (1997). Environmental impacts of metal ore mining and
518 processing: a review. *Journal of Environment Quality*, *26*(3), 590.
519 doi:10.2134/jeq1997.00472425002600030003x
520 Environment and Climate Change Canada. (1999). Environmental Code of Practice for Base
521 Metals Smelters and Refineries: Code of Practice, Canadian Environmental Protection
522 Act. Available at http://ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=9233A7E7-
523 1&offset=2. Accessed 15 June 2018
524 Freundlich, H. M. F. (1906). Over the adsorption in solution. *The Journal of Physical*
525 *Chemistry*, *57*, 385–471.
526 Gregg, S. J., & Sing, K. S. W. (1991). *Adsorption, surface area, and porosity*. London, UK:
527 Academic Press.
528 Hamid, S. B. A., Chowdhury, Z. Z., & Zain, S. M. (2014). Base catalytic approach: a
529 promising technique for the activation of biochar for equilibrium sorption studies of
530 copper, Cu(II) ions in single solute system. *Materials*, *7*(4), 2815–2832.
531 doi:10.3390/ma7042815

Health Canada. (1992). Guidelines for Canadian Drinking Water Quality: Guideline Technical Document – Copper. Available at https://www.canada.ca/content/dam/canada/health-canada/migration/healthy-canadians/publications/healthy-living-vie-saine/water-copper-cuivre-eau/alt/water-copper-cuivre-eau-eng.pdf. Accessed 15 June 2018

Kołodyńska, D., Krukowska, J., & Thomas, P. (2017). Comparison of sorption and desorption studies of heavy metal ions from biochar and commercial active carbon. *Chemical Engineering Journal*, *307*, 353–363. doi:10.1016/j.cej.2016.08.088

Lagergren, S. (1898). About the theory of so-called adsorption of soluble substances. *Kungl. Svenska vetenskapsakademiens handlingar*, *24*(4), 1–39.

Lamb, D. T., Naidu, R., Ming, H., & Megharaj, M. (2012). Copper phytotoxicity in native and agronomical plant species. *Ecotoxicology and Environmental Safety*, *85*, 23–29. doi:10.1016/j.ecoenv.2012.08.018

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, *40*(9), 1361–1403. doi:10.1021/ja02242a004

Lazzarini, A., Piovano, A., Pellegrini, R., Leofanti, G., Agostini, G., Rudić, S., et al. (2016). A comprehensive approach to investigate the structural and surface properties of activated carbons and related Pd-based catalysts. *Catalysis Science & Technology*, *6*(13), 4910–4922. doi:10.1039/C6CY00159A

Lee, J. A., Marsden, I. D., & Glover, C. N. (2010). The influence of salinity on copper accumulation and its toxic effects in estuarine animals with differing osmoregulatory strategies. *Aquatic Toxicology*, *99*(1), 65–72. doi:10.1016/j.aquatox.2010.04.006

Lehmann, J., & Joseph, S. (Eds.). (2015). *Biochar for Environmental Management: Science, Technology and Implementation*. Abingdon, UK: Routledge.

556 Lima, I. M., Boateng, A. A., & Klasson, K. T. (2010). Physicochemical and adsorptive
557 properties of fast-pyrolysis bio-chars and their steam activated counterparts. *Journal of*
558 *Chemical Technology & Biotechnology*, *85*, 1515–1521. doi:10.1002/jctb.2461
559 Lima, I. M., Boykin, D. L., Thomas Klasson, K., & Uchimiya, M. (2014). Influence of post-
560 treatment strategies on the properties of activated chars from broiler manure.
561 *Chemosphere*, *95*, 96–104. doi:10.1016/j.chemosphere.2013.08.027
562 Liu, W.-J., Jiang, H., & Yu, H.-Q. (2015). Development of biochar-based functional materials:
563 toward a sustainable platform carbon material. *Chemical Reviews*, *115*(22), 12251–
564 12285. doi:10.1021/acs.chemrev.5b00195
565 Marsh, H., & Rodríguez-Reinoso, F. (2006). *Activated carbon* (1st ed.). Amsterdam, NL:
566 Elsevier.
567 Mohan, D, & Chander, S. (2001). Single component and multi-component adsorption of metal
568 ions by activated carbons. *Colloids and Surfaces A: Physicochemical and Engineering*
569 *Aspects*, *177*(2–3), 183–196. doi:10.1016/S0927-7757(00)00670-1
570 Mohan, Dinesh, & Chander, S. (2006). Removal and recovery of metal ions from acid mine
571 drainage using lignite—a low cost sorbent. *Journal of Hazardous Materials*, *137*(3),
572 1545–1553. doi:10.1016/j.jhazmat.2006.04.053
573 Nordstrom, D. K., Blowes, D. W., & Ptacek, C. J. (2015). Hydrogeochemistry and
574 microbiology of mine drainage: an update. *Environmental Geochemistry of Modern*
575 *Mining*, *57*, 3–16. doi:10.1016/j.apgeochem.2015.02.008
576 Peng, H., Gao, P., Chu, G., Pan, B., Peng, J., & Xing, B. (2017). Enhanced adsorption of
577 Cu(II) and Cd(II) by phosphoric acid-modified biochars. *Environmental Pollution*,
578 *229*, 846–853. doi:10.1016/j.envpol.2017.07.004
579 Radovic, L. R., & Rodriguez-Reinoso, F. (1997). In P. A. Thrower (Ed.), *Chemistry and*
580 *Physics of Carbon* (Vol. 25). New York, USA: Marcel Dekker.

581 Ríos, C. A., Williams, C. D., & Roberts, C. L. (2008). Removal of heavy metals from acid
582 mine drainage (AMD) using coal fly ash, natural clinker and synthetic zeolites.
583 *Journal of Hazardous Materials*, *156*(1–3), 23–35. doi:10.1016/j.jhazmat.2007.11.123
584 Sekhula, M. M., Okonkwo, J. O., Zvinowanda, C. M., Agyei, N. N., & Chaudhary, A. J.
585 (2012). Fixed bed column adsorption of Cu (II) onto maize tassel-PVA beads. *Journal*
586 *of Chemical Engineering & Process Technology*, *03*(02). doi:10.4172/2157-
587 7048.1000131
588 Shim, T., Yoo, J., Ryu, C., Park, Y.-K., & Jung, J. (2015). Effect of steam activation of
589 biochar produced from a giant *Miscanthus* on copper sorption and toxicity.
590 *Bioresource Technology*, *197*, 85–90. doi:10.1016/j.biortech.2015.08.055
591 Sing, K. S. W. (1985). Reporting physisorption data for gas/solid systems with special
592 reference to the determination of surface area and porosity (Recommendations 1984).
593 *Pure and Applied Chemistry*, *57*(4), 603–619. doi:10.1351/pac198557040603
594 Tan, X., Liu, S., Liu, Y., Gu, Y., Zeng, G., Hu, X., et al. (2017). Biochar as potential
595 sustainable precursors for activated carbon production: multiple applications in
596 environmental protection and energy storage. *Bioresource Technology*, *227*, 359–372.
597 doi:10.1016/j.biortech.2016.12.083
598 Tarazona, P. (1995). Solid-fluid transition and interfaces with density functional approaches.
599 *Proceedings of the 14th European Conference on Surface Science*, *331*, 989–994.
600 doi:10.1016/0039-6028(95)00170-0
601 Visual MINTEQ version 3.1. (2018). *https://vminteq.lwr.kth.se/*.
602 Wilson, K., Yang, H., Seo, C. W., & Marshall, W. E. (2006). Select metal adsorption by
603 activated carbon made from peanut shells. *Bioresource Technology*, *97*(18), 2266–
604 2270. doi:10.1016/j.biortech.2005.10.043

Wu, F.-C., Tseng, R.-L., & Juang, R.-S. (2009). Characteristics of Elovich equation used for the analysis of adsorption kinetics in dye-chitosan systems. *Chemical Engineering Journal*, *150*(2–3), 366–373. doi:10.1016/j.cej.2009.01.014

Xie, R., Jin, Y., Chen, Y., & Jiang, W. (2017). The importance of surface functional groups in the adsorption of copper onto walnut shell derived activated carbon. *Water Science and Technology*, *76*(11), 3022–3034. doi:10.2166/wst.2017.471

Table captions

Table 1. Textural and physicochemical properties of biochars and activated biochars

Table 2. Kinetic parameters obtained from the adsorption of Cu onto biochars and activated biochars

Table 3. Parameters of Cu adsorption isotherms onto biochars and activated biochars

Table 4. Comparative sorption capacity of activated biochars and commercial activated carbon for Cu^{2+} in water

Table 5. Composition (mg L^{-1}, except for pH and Eh) of initial and final (after adsorption with KOHBBS) AMD

Figure captions

Fig. 1. SEM images of activated biochars prepared from WB and BS wood residues in presence of CO_2 (a and b); steam (c and d); and KOH (e and f)

Fig. 2. Adsorbed amounts of Cu^{2+} at initial concentration of 100 mg L^{-1} (q_t) as function of time for both biochars: ( ) BWB, ( ) BBS; and activated biochars: ( ) CO2BWB, ( ) CO2BBS, (○) H2OBWB, (●) H2OBBS, (□) KOHBWB, and (■) KOHBBS

Fig. 3. a) Adsorbed isotherms of Cu^{2+}, and b) Cu^{2+} adsorption (%) as function of different initial concentrations of Cu^{2+} (C_0 = 5, 10, 20, 50, 100, and 200 mg L^{-1}) for both biochars: ( ) BWB, ( ) BBS; and activated biochars: ( ) CO2BWB, ( ) CO2BBS, ( ) H2OBWB, ( ) H2OBBS, ( ) KOHBWB, and ( ) KOHBBS ■

Fig. 4. Adsorbed Cu^{2+} from real effluent (mg L^{-1}) as function of the contact time for both biochars: (◇) BWB, (◆) BBS; and activated biochars: (△) CO2BWB, (▲) CO2BBS, (○) H2OBWB, (●) H2OBBS, (□) KOHBWB, and (■) KOHBBS

Fig. 5. Desorption efficiency of Cu^{2+} ions after a) chemical regeneration using three different eluents: HNO_3 0.1 M, H_2SO_4 0.5 M, and HCl 1 M, and b) after six cycles adsorption-desorption

680 **Table 1.** Textural and physicochemical properties of biochars and activated biochars

	BWB	***BBS***	***CO2BWB***	***CO2BBS***	***H2OBWB***	***H2OBBS***	***KOHBWB***	***KOHBBS***
Textural properties								
S_{BET} (m^2 g^{-1})	177*	208*	881**	735**	590**	412**	1700**	1662**
V_t (cm^3 g^{-1})			0.53	0.39	0.34	0.18	0.75	0.72
$V_{\mu, N2}$ (cm^3 g^{-1})			0.33	0.28	0.23	0.17	0.75	0.72
$V_{\mu, CO2}$ (cm^3 g^{-1})	0.11	0.14	0.28	0.20	0.22	0.20	0.36	0.45
V_m (cm^3 g^{-1})			0.20	0.11	0.11	0.01	0.00	0.00
Physicochemical properties								
pH	5.0	6.7	10.2	10.3	9.9	9.3	8.2	9.3
C (%)	75.4	75.4	89.9	88.9	89.1	83.8	77.5	80.1
H (%)	3.5	3.8	0.9	0.6	0.6	0.8	1.7	1.0
N (%)	0.9	0.9	0.4	1.2	0.2	0.8	2.0	2.7
S (%)	0.5	0.5	0.0	0.1	0.0	0.0	0.1	0.0
O° (%)	19.7	19.4	8.8	9.2	10.1	14.6	18.7	16.2

681 S_{BET} obtained from *CO_2 and **N_2 adsorption analysis; °O content was obtained by difference (O% = 100 – CHNS%)

682

683

684

685

686

687

688

689

690

691

692

693

694 **Table 2.** Kinetic parameters obtained from the adsorption of Cu onto biochars and activated

695 biochars

		Pseudo-first order			***Pseudo-second order***			***Elovich's equation***		
	$q_{exp.}$ (mg g^{-1})	q_e (mg g^{-1})	k_1 (h^{-1})	R^2	q_e (mg g^{-1})	k_2 (mg (g h)$^{-1}$)	R^2	a (mg (g h)$^{-1}$)	$1/b$ (mg g^{-1})	R^2
BWB	10.04	9.09	0.04	0.79	4.78	0.0041	0.65	2.79	2.43	0.82
BBS	9.98	10.81	0.05	0.99	14.14	0.0093	0.72	2.22	2.06	0.97
CO2BWB	48.91	33.99	0.081	0.92	35.71	0.0049	0.51	$2.17 . 10^1$	11.51	0.92
CO2BBS	25.25	23.96	0.072	0.83	11.4	0.0018	0.33	$1.13 . 10^4$	2.04	0.96
H2OBWB	24.90	8.86	0.058	0.61	10.16	0.0029	0.27	$2.07 . 10^1$	4.55	0.95
H2OBBS	19.18	7.95	0.061	0.56	3.80	0.024	0.12	7.83	4.90	0.67
KOBBW	25.15	9.08	0.069	0.66	7.40	0.0132	0.06	$1.08 . 10^3$	2.70	0.73
KOHBBS	36.71	7.61	0.053	0.70	9.51	0.0023	0.02	$9.79 . 10^2$	4.07	0.95

696

697

698

699

700

701

702

703

704

705

706

707

708

709

710

711

712 **Table 3.** Parameters of Cu adsorption isotherms onto biochars and activated biochars

	Freundlich			***Langmuir***				
	k_f	n	R^2	q_{exp} (mg g^{-1})	q_{max} (mg g^{-1})	b (L mg^{-1})	R_L	R^2
BWB	1.16	0.52	0.82	85	120	0.001	0.45–0.99	0.15
BBS	1.45	0.60	0.88	77	105	0.001	0.45–0.99	0.21
CO2BWB	17.66	0.26	0.90	127	127	0.016	0.06–0.93	0.92
CO2BBS	5.82	0.34	0.89	98	102	0.005	0.16–0.98	0.73
H2OBWB	11.11	0.26	0.80	122	132	0.005	0.15–0.97	0.77
H2OBBS	5.45	0.30	0.77	101	100	0.003	0.22–0.98	0.51
KOBBWB	10.80	0.26	0.86	105	109	0.006	0.14–0.97	0.73
KOHBBS	17.51	0.23	0.94	137	132	0.009	0.10–0.96	0.81

713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733

734 **Table 4.** Comparative sorption capacity of activated biochars and commercial activated carbon

735 for Cu^{2+} in water

Activated biochar precursor	*gAC:mL*	*pH*	*Activation/ S_{BET} (m^2 g^{-1})*	*q_{max} (mg g^{-1})*	*Kinetic/ Isotherm model*	*C_0 (mg L^{-1})*	*References*
Soybean straw	1:100	4.8	Steam (up to 793)	96% removal	−	64	(Lima et al. 2010)
Date pits	0.1:100	−	Steam (1467)	203	Langmuir	600	(Bouchelta et al. 2012)
Waste peels of mangosteen fruits	0.4:100	5.5	CO_2/KOH (367)	19	Pseudo-second order; Langmuir and Freundlich	50−100	(Hamid et al. 2014)
Broiler litter Broiler cake	1:100	4.8	Steam (up to 425)	104 49	−	2690	(Lima et al. 2014)
Miscanthus plant	0.2:100	6	Steam (322)	14	Two-compartment model; Langmuir	0.2−150	(Shim et al. 2015)
Colocasia esculenta roots	0.06:100	5	Steam (102)	2.3	Pseudo-second order; Langmuir	30	(Banerjee et al. 2016)
Hickory chips	−	5	NaOH (873)	54	−	2−250	(Ding et al. 2016)
Pine sawdust	0.025:100	4.5	H_3PO_4 (900)	2	Freundlich	1−10	(Peng et al. 2017)
White birch	0.1:100	4.5	CO_2 (880)	127	Elovich, Freundlich	5−1000	**Present study**
Black spruce	0.1:100	4.5	KOH (1662)	137	Elovich, Freundlich	5−1000	**Present study**
NORIT C GRAN	1:100	4.8	H_3PO_4 (624)	56	-	1270	(Wilson et al. 2006)

736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751

752 **Table 5.** Composition (mg L^{-1}, except for pH and Eh) of initial and final (after adsorption with

753 KOHBBS) AMD

Parameter	***Initial AMD***	***Final AMD***	***Removal (%)***
pH	2.70	2.60	-
Eh (mV)	584	548	-
Dissolved oxygen	10.0	7.90	-
Al	141	145	0
Ca	466	468	0
Cd	< 0.05	< 0.05	0
Co	9.38	0.502	95
Cr	0.067	0.093	0
Cu	1.753	0.0055	99
Fe	468	405	13
K	4.41	24.9	0
Mg	131	138	0
Mn	10.9	9.72	11
Na	57	52.5	8
Ni	0.367	0.605	0
Pb	0.143	0.0813	43
Zn	4.92	4.62	6
NO_2^-	16	16.3	0
NO_3^-	750	726	3
SO_4^{2-}	2390	2411	-
PO_4^{3-}	16.1	12.1	25

754

755