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2 Efficiency of eight modified materials for

3 As(V) removal from synthetic and real mine

4 effluents

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26 **Abstract**

27 Arsenic (As) contamination is a major problem especially for active gold mine operations. In
28 the present study, **eight** low-cost materials including biochar (B), Fe-loaded biochar (BF),
29 activated biochar (BC), Fe-loaded activated biochar (BCF and BFC), thermally modified
30 dolomite (MD), wood ash (WA), and modified wood ash (MWA) were comparatively used for
31 the efficiency in As(V) removal from synthetic and real mine effluents, through batch and
32 column testing. Batch adsorption tests were conducted in beakers with a ratio adsorbent material
33 and As(V) synthetic and real solutions of 0.1g: 10 mL at concentrations of 850 and 300 µg/L
34 As, respectively. Column adsorption tests were performed in 3 reactors with As(V)
35 concentration of up to 900 µg/L in contaminated neutral drainage (CND) collected from a local
36 gold mine. Results from batch testing with synthetic effluents showed the best performance for
37 As(V) removal in the following order: MD > WA > BCF > BF > BFC > MWA > BC > B.
38 Consistent findings were obtained in batch and column testing with the real mine effluent.
39 Although iron grafted biochars are good adsorbents, their performance for As(V) removal was
40 limited probably because of the very low As concentration in this study. In the same time, MD
41 was found to be the most efficient material for As(V) removal but the final pH must be
42 monitored and eventually adjusted. As(V) was completely removed by MD in batch testing
43 (99.9%) and column testing (99.6%) after more than 112 days to bellow the authorized monthly
44 mean allowed by Canadian discharge criteria. Thus, MD seems to be the most efficient material
45 among the tested ones for the removal of As(V) in batch and column testing from synthetic and
46 mine effluents.

47

48 **Keywords:** Low-cost sorbents, adsorption, arsenic, batch and column tests, mine effluent

49 1. Introduction

50 Arsenic (As) is a “traditional contaminant” in the environment due to its high toxicity,
51 carcinogenicity (group 1 carcinogens) and wide occurrence (Hu et al., 2015). Typically, As is
52 found in water as arsenate As(V) (AsO_4^{3-}) and arsenite As(III) (AsO_3^{3-}), both species being
53 present in non-ferrous ores such as copper, lead, zinc, gold and uranium (Lorenzen et al., 1995).
54 In regions with active mining activities, As can be found in either acid mine drainage (AMD)
55 or contaminated neutral drainage (CND). In CND, the common inorganic arsenic species are
56 arsenate (H_2AsO_4) and arsenite (H_3AsO_3) (Hu et al., 2015). Other anthropogenic sources of As
57 are discharges from various industries, including fertilizers, insecticides and herbicides
58 production, glass manufacturing, and petroleum refinery (Ansone et al., 2013). The dissolution
59 of As-containing minerals and ores, as well as industrial discharges may ultimately entail
60 drinking water contamination. To protect the population and the environment, Canada
61 legislation enforces As discharge criteria of 10 and 500 $\mu\text{g/L}$ (Health Canada, 2006), in drinking
62 water and wastewater, respectively. In Québec’s province of Canada, the monthly mean
63 concentration allowed for As from mine effluents is 200 $\mu\text{g/L}$ (MDDELCC, 2012).

64 Several methods are available for As removal from contaminated water, including
65 coagulation, filtration, oxidation, precipitation, reverse-osmosis and ion-exchange resin
66 (Kowalski, 2014). Most of these methods are costly, difficult to be employed at large scale and
67 produce large amounts of unstable sludge. Adsorption is one common method generally used
68 due to the availability of low-cost precursors for the production of adsorbents, easiness of
69 operation in batch and column reactors, no sludge disposal and simple material’s regeneration
70 (Mohan and Pittman, 2007). Various adsorbents have been tested for As removal from water
71 including dolomite, biochar, fly ash and activated carbon (Calugaru et al., 2018). Activated
72 carbons were found, despite their high advantages (specific surface area, abundant surface

73 functional groups and well-developed porosity) not suitable for anionic contaminants because
74 of their negative-charged surface (Hu et al., 2015).

75 The method used to improve the performance of conventional adsorbents for the removal
76 of As is their impregnation with a cation, e.g., Fe, or the use of low-cost materials, e.g., fly ash,
77 dolomite, biochar, containing an important amount of inorganics that could have the ability of
78 interacting with anionic contaminants. The mechanism of Fe grafting or inorganics (e.g., Fe,
79 Ca, Na, Mg) presented on the composition of carbon-derived materials includes: physical
80 adsorption, reduction-oxidation, ion exchange, and complexation (Calugaru et al., 2018). In the
81 case of Fe grafting, the role of the material is to fix Fe on accessible sites for subsequent sorption
82 of contaminants and to provide a large surface area for interacting with them (Gu et al., 2005;
83 Muñiz et al., 2009).

84 Several studies have shown the potential of low-cost, both raw and modified materials for
85 the removal of As(III) and As(V) from synthetic effluents. For example, Salameh et al. (2015)
86 increased the adsorption capacity of raw dolomite from 0.65 to 2.16 mg/g of As(V) from
87 synthetic effluent ($C_0 = 0.05\text{--}2$ mg/L) by charring. It was to note that dolomite charred at 800°C
88 contains mainly CaCO_3 and MgO . Moreover, Sasaki et al. (2014) used thermally treated (24h
89 at 105°C) waste cement and concrete sludge, composed mainly of CaCO_3 , Ca(OH)_2 , and SiO_2 ,
90 which removed up to 92 and 100 % of As(V) (1.5 and 1.9 mg/g As(V) sorption capacity,
91 respectively), when the initial synthetic solution contained 10 mg/L of As(V). Wood ash also
92 contains significant amounts of CaCO_3 and CaO , which were reported effective for As removal
93 (Calugaru et al., 2018; Genty et al., 2012; Girón et al., 2013), therefore wood ash was
94 investigated in the present study.

95 Municipal biochar, rice husk and their modified form using $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ impregnation
96 removed up to 55 % ($C_0 = 90$ $\mu\text{g/L}$), 25% ($C_0 = 90$ $\mu\text{g/L}$) and > 95 % ($C_0 = 800$ $\mu\text{g/L}$) of As(V),
97 respectively (Agrafioti et al., 2014). Sorption capacity at neutral pH was about 1 mg/g As(V)

98 for empty fruit bunch biochar and for rice husk biochar, whereas iron loading increased it to
99 1.5–2.0 mg/g (Samsuri et al., 2013). Activated carbon and its impregnated product with Fe(III)-
100 oxide adsorbed 0.09 and 4.5 mg/g of As(V) ($C_0 = 1$ mg/L), respectively (Reed et al., 2000).
101 Other Fe-loaded activated carbons presented high adsorption capacity (51.3 mg/g) for the
102 removal of As(V) from an As-rich synthetic effluent ($C_0 = 20$ –22 mg/L) (Chen et al., 2007).
103 Similarly, the maximum adsorption capacity of As(V) using pine biochar supported by zero-
104 valent Fe improved from 0.2 mg/g to 124.5 mg/g ($C_0 =$ up to 400 mg/L) (Wang et al., 2017).
105 Ansone et al. (2013) developed new sorbents by impregnation with iron oxyhydroxides of peat,
106 shingles, straw, sands, cane and moss. The most performant proved to be the iron-modified peat,
107 which sorbed 98 % of As(V) when initial concentration was 100 mg/L. As for the iron-modified
108 shingles, moss and straw, their As(V) removal percentage was of 95, 97 and 99, respectively,
109 when initial concentration was 45 mg/L. Iron-modified cane and sand sorbed 97 and 94% of
110 As(V) when its initial concentration was of 40 and 10 mg/L respectively. Biomass of
111 *Staphylococcus xylosus* was loaded with Fe from FeCl₃ and the new material showed 4.23 mg/g
112 sorption capacity when initial As(V) concentration was 10 mg/L. However, at neutral pH, the
113 As(V) removal was of only 30% (Aryal et al., 2010). Zeolitic imidazolate framework-8 (ZIF-8)
114 showed 90 mg/g As(V) removal capacity from synthetic solution initially containing 20 mg/L
115 As(V) at pH = 8 (Liu et al., 2018). Moreover, AMD sludge alginate beads were synthesized and
116 employed to remove As(V) from synthetic effluents. At pH 7, 90% of the As(V) was removed
117 from the synthetic solution of initial concentration of 10 mg/L, which means that residual As(V)
118 was still 1 mg/L (Lee et al., 2015). Thus, biochar and iron seems promising for As(V) removal
119 in contaminated waters.

120 However, many of the available studies for As removal using raw and modified materials
121 were conducted only with synthetic effluent whereas only very few studies have proposed the
122 use of low-cost materials for the polishing treatment of As(V) from neutral mine effluents, at

123 concentrations lower than 1 mg/L but higher than the threshold fixed by law. For instance,
124 zerovalent iron (waste) fillings were employed for the passive field treatment of As in
125 circumneutral (pH between 5.80 and 8.83) mine drainage in a former Sb mine in Slovakia. The
126 system, containing 150 kg of iron fillings treated 360 L of mine drainage/h during 2.3 years,
127 while average As concentration decreased from 452 to 50.6 µg/L. However, Fe concentration
128 varied from 10.8 to 36.5 mg/L in the influent (mine drainage) and from 11.0 to 60.0 mg/L in the
129 treated effluent (Sekula et al., 2018). In Québec's province of Canada, a second step should be
130 added to this As treatment system, in order to decrease also monthly average Fe concentration
131 below 3 mg/L.

132 In this context, the objective of this study is to assess the comparative efficiency of several
133 materials (wood ash, dolomite and biochar and their modified products) for As(V) removal from
134 synthetic effluents and real CND, in batch and column reactors.

135

136 **2. Materials and methods**

137 2.1 Synthesis of adsorbents

138 *2.1.1 Raw and modified biochar*

139 Three types of materials were produced: 1) Biochar; 2) Activated biochar in presence of
140 CO₂; and 3) Iron impregnation on 1) and 2). Firstly, residues of white birch (WB) from Abitibi-
141 Témiscamingue, Québec, were milled (< 6 mm) and converted into biochar (B) through a fast
142 pyrolysis CarbonFX technology. The biochar was then activated (BC) in a homemade prototype
143 pilot furnace at 900 °C in presence of CO₂. More details on furnaces and conditions applied
144 were presented elsewhere (Braghiroli et al., 2018). The B and BC were then impregnated with
145 Fe by mixing with FeCl₃ solutions containing 2.5% Fe³⁺, at pH 12, which was adjusted with
146 NaOH 10 N (Sigma Aldrich). The mixture was soaked for 4 h and then dried at 70°C for 12 h.
147 The dried material was afterwards washed with distilled water to reach pH 7, and dried again at

148 110 °C for 24 h. Finally, three materials were obtained: 1) Biochar impregnated with Fe (BF),
149 2) Biochar impregnated with Fe and further activated (BFC), and 3) Biochar activated and
150 impregnated with Fe (BCF).

151 *2.1.2 Modified dolomite*

152 Dolomite mineral ($\text{CaCO}_3 \cdot \text{MgCO}_3$) was provided by Temiska Silice (Saint-Bruno-de-
153 Guigues, QC, Canada) and thermally modified (MD) to produce a mixture of CaCO_3 (calcite)
154 and MgO (periclase). MD was prepared by thermally activation of dolomite in an oven at 750°C
155 for 1 h. More details on the preparation and initial/final characterization of MD are available
156 elsewhere (Calugaru et al., 2016).

157 *2.1.3 Raw and modified wood ash*

158 Wood ash (WA) was provided by Boralex (Sanneterre, QC, Canada). Modified wood ash
159 (MWA) was prepared by heating WA in an oven at 375 °C for the purpose of mineralizing its
160 organic content and increasing of its mineral composition. The calcinated material was mixed
161 with solid NaOH, and heated in an oven at 600 °C for 2 h. Then, the new material was
162 hydrothermally treated at 95 °C until the evaporation of the liquid phase. The MWA prepared
163 was then washed and dried at 140 °C for 24 h. More details on the preparation and
164 characterization of MWA were provided elsewhere (Calugaru et al., 2017).

165 2.2 Physical and chemical characterization of biochar and activated biochar

166 Raw and modified materials were characterized for the following physicochemical
167 parameters: pH, pH_{PZC} , elemental composition (C, H, N, S, and O) and Fe concentration,
168 specific surface area, and pore volume. The pH was determined according to a standard test
169 method (ASTM D3838 - 05(2017)) using a SevenMulti, Mettler Toledo (Greifensee,
170 Switzerland) equipped with Inlab Routine Pro electrode. The pH_{PZC} (i.e., a pH value at which
171 the sorbent surface has zero electrical charge density) was determined using the salt / solid
172 addition method (Belviso et al., 2014; Bakatula et al., 2018). Elemental composition was

173 determined in a CHNS elemental analyzer, Perkin Elmer 2400 CHNS/O Analyzer (Waltham,
174 MA, USA), by combustion of the samples in a stream of pure O₂. Fe concentration was analyzed
175 by X-ray fluorescence (XRF) (Axios mAX, PANalytical). Pore texture parameters were
176 obtained by N₂ adsorption at -196 °C, and CO₂ at 0 °C, using a Micromeritics ASAP 2460
177 automatic apparatus (Norcross, GA, USA). Ultramicroporosity was analyzed by CO₂ adsorption
178 (V_{μ, CO_2} (cm³/g)), whereas micro- and mesoporosity were analyzed by N₂ adsorption. The N₂
179 adsorption isotherms obtained were used to evaluate: i) surface area, S_{BET} (m²/g), calculated by
180 the Brunauer-Emmett-Teller (BET); ii) micropore volume, V_{μ, N_2} (cm³/g), determined by the
181 Dubinin–Radushkevich (DR) equation (Dubinin, 1989); iii) total pore volume, V_t (cm³/g),
182 calculated from the amount of nitrogen adsorbed at the relative pressure of 0.97 (Gregg and
183 Sing, 1991).

184 2.3 Batch testing

185 Batch testing was conducted in plastic tubes containing 0.4 g of each adsorbent material
186 together with 40 mL of 1 mg/L As(V) synthetic CND using HAsNa₂O₄ · 7H₂O (Sigma Aldrich),
187 at pH 7. The same procedure was repeated with real CND (< 1 mg/L) sampled from a local gold
188 mine. The adsorbent and As solution were left mixing for 1, 4, 8, 10, 18, 24, and 48 h on a multi-
189 position stirring plate, at 500 rpm, and at room temperature (20 °C). Then, the adsorbents and
190 supernatants were separated by filtration. The pH, redox potential (Eh), and conductivity
191 (μS/cm) of the supernatant were measured after each contact time. The Eh was measured using
192 LDO Hatch meter (London, ON, Canada) with a double junction Ag/AgCl reference electrode.
193 The concentrations of As(V) were determined by ICP-AES (Inductively Coupled Plasma -
194 Atomic Emission Spectrometry; Varian, Vista-AX CCO, Palto Alto, California, USA).

195 Sorption capacity at any time q_t (mg/g) and the As(V) adsorption (%) were calculated
196 following Eqs. 1 and 2, respectively:

$$197 \quad q_t = [C_0 - C_t] \cdot \frac{V}{m} \quad (1)$$

198
$$\text{Adsorption (\%)} = [C_0 - C_e] \cdot \frac{100}{C_0} \quad (2)$$

199 where C_0 , C_t , V , and m represent, respectively, the concentrations of As(V) in effluent (mg/L)
200 initially and at t moment, total volume of solution (L), and amount of the material used (g).

201 2.4 Column testing

202 Column testing was conducted only for the most performants among the studied adsorbents
203 (MD, BF, BCF and BFC) in batch testing. The plastic column height and the mass of sorbents
204 were around 200 mm and between 52 and 75 g (for biochar-derived materials), and 80 mm and
205 120 g (for MD), respectively. The volume of liquid in column was different according to the
206 hydraulic residence time (HRT) as materials properties were different (porosity and density).
207 This requested different column lengths and masses of materials to get 2 h of HRT, according
208 to Eq. 3:

209
$$\text{HRT} = \frac{n \cdot V}{Q} \quad (3)$$

210 where n is the porosity, V_T is the total volume of the column and Q is the effluent flow rate.

211 Three different layers composed the columns: a permeable membrane (to prevent losses of
212 fine sorbent material), a layer of glass beads (15 mm diameter) and a layer of adsorbent material.
213 The influent was fed in a vertical upward flow to the columns, using a peristaltic pump. The
214 average flow was of 0.5 mL/min for the MD column and of 1.5 mL/min for the BF, BCF and
215 BFC columns. The sampling of treated effluent was carried out on a weekly basis. On the
216 collected samples, pH, Eh, the conductivity and the concentrations of As(V) were measured as
217 previously described (section 2.3). The CND was provided by a local site mine and according
218 to Eh-pH diagram from Takeno (2005), the pH and Eh of the CND were found in the region of
219 As(V) species.

220

221 3. Results and discussion

222 3.1 Characterization of materials

223 Elemental composition and porous structure of the materials: biochar, dolomite and wood
224 ash are presented in Table 1. Biochar-derived materials presented high content of organic
225 compounds (carbon, hydrogen, and oxygen) whereas modified dolomite and wood ash-derived
226 materials had high content of Ca in a form of calcite, Mg, Si, Fe, and Na.

227 After thermal treatment, i.e., fast pyrolysis followed by activation, activated biochars
228 showed higher carbon content (89.9 %) compared to B (75.4 %). As expected, after Fe
229 impregnation, materials had increased Fe content: 3, 7.5, and 12.6 % for BF, BCF, and BFC,
230 respectively, according to XRF analysis. Only the main inorganics presented in WA and MWA
231 are shown in Table 1. Other chemical elements including Ba, Cr, Cu, Sr, Ti and Zn were also
232 presented in WA and MWA composition and varied between 0.1 and 0.9 %.

233 Among the studied materials, BC showed the most developed porous structure, whereas
234 MD had the lowest surface area followed by MWA, WA and BF. After Fe impregnation, a steep
235 decrease in surface areas was noticed, as materials were loaded with Fe blocking most of their
236 porous structure. This is consistent with previous studies (Samsuri et al., 2013; Wang et al.,
237 2017).

238 All pHs are above pH_{PZC} so sorbent surface is negatively charged and potentially attracting
239 cations, except in the case of B in which its pH was lower than its pH_{PZC} ($5 < 6.6$). With Fe
240 addition, pH was still higher than pH_{PZC} , but oxyanions fixation (e.g. As), at somehow, was
241 improved (Reed et al., 2000). High chemical affinity and complex bound between Fe and
242 oxyanionic As species are also extensively reported (Gu et al., 2005; Chen et al., 2007; Hu et
243 al., 2015; Wang et al., 2017). This might explain the behaviour of Fe grafted materials
244 synthesized in the present study that displayed a pH higher than 10. Other similar studies found
245 that As sorption was improved by increasing the pH ($pH > 8$; $pH_{PZC} = 7.2$) due to As speciation
246 in solution (Zhang et al., 2015).

247 3.2 Batch testing with synthetic and mine effluent

248 Comparative evolution of As(V) concentration from synthetic effluent in batch studies (Fig.
249 1 a) showed high removal with some materials (e.g., MD) but only slight variation with others
250 (e.g., B, BC and MWA). After 48 h of testing, As(V) concentration varied from 850 to 780 µg/L
251 for B and MWA, respectively. In the same time, BC decreased As concentration from 850 to
252 590 µg/L during the first hours; then, increased it back to 790 µg/L probably due to its negative
253 charged-surface, in electrostatic repulsion with the anionic contaminant. Some expected
254 variation of As(V) concentration was noticed but was probably due to the heterogeneity of
255 materials, especially for BFC and BCF. The MD showed the highest adsorption capacity for the
256 treatment of As(V) from synthetic effluent due to the presence of CaCO₃ and MgO from
257 dolomite [CaMg(CO₃)₂] charring process.

258 As a general trend, biochar-derived materials enhanced the pH (from around 7 to 10) and
259 decreased the Eh (from around 220 to 120 mV). For MD, there was higher increase of pH (from
260 around 7 to 11) while the Eh was maintained around the initial value (90 mV). In both cases, at
261 somehow, there is no connection between these parameters and the efficiency of As(V)
262 treatment. Also, As(V) precipitation was not evidenced in the present study. However, it was
263 reported in the literature the precipitation of arsenic oxide and arsenic carbonate with the use of
264 modified dolomite for the sorption of As(V) (Salameh et al., 2015).

265 In the present study, only four materials adsorbed the most of As(V) and found below 200
266 µg/L, the threshold (T) according to Québec's guideline of As in mine effluents, in the following
267 order: MD, WA, BCF and BF.

268 In batch testing carried out for As(V) removal from CND at approximately 300 µg/L (Fig.
269 1 b), all materials showed satisfactory performance in reducing the concentration to below the
270 discharge criteria in the following order: MD > WA > BF > BCF > BFC ~ MWA > B > BC.
271 Adsorption kinetics of As(V) on raw and modified materials with synthetic and real mine

272 effluents are presented in Fig. 1 c) and d), respectively. The MD proved to be the best in As(V)
273 removal by sorption from synthetic effluent ($q_t = 820 \mu\text{g/g}$), whereas BCF presented the highest
274 adsorption capacity (Fig. 1 d)) from real mine effluent ($q_t = 270 \mu\text{g/g}$).

275 The pH of biochar-derived materials after adsorption testing with synthetic and CND
276 effluents (Fig. 1 e) and Fig. 1 f), respectively) varied from 6 to 10, and from 7 to 9, respectively
277 with respect to the contact time. However, MWA, MD and WA raised the pH of the effluent to
278 around 12, 10–11, and 9–10, respectively, in both types of effluents to above discharge criteria
279 (6 to 9.5).

280 3.3 Column testing with mine effluent

281 The column testing was carried out with MD and Fe-loaded biochars based on their better
282 comparative performance and pH range allowed by Québec's requirements for CND discharge.
283 Other contaminants (e.g., Mn, Cr, Co, Pb, Ni, Mn), in addition to As(V), were also present in
284 the CND but at acceptable concentrations according to Québec's law.

285 The MD showed the best efficiency for As(V) removal with very low As concentrations
286 ($0.5\text{--}1.9 \mu\text{g/L}$) in treated water for over 112 days of testing (Fig. 2). In the same time, BCF
287 remained below $200 \mu\text{g/L}$ for 63 days, but after 70 days As(V) concentration exceeded the
288 criteria at the same As(V) concentration as CND. The BF and BFC displayed saturation at about
289 20 days and were less effective for the treatment of As(V) in columns. These materials showed
290 some toggling during batch testing. For this reason, the hydraulic residence time should be
291 higher than 2 h and, consequently, the flow rate lower than 1.5 mL/min to favor the substrate –
292 As(V) interactions and therefore the As(V) treatment.

293 Even though they showed the least performance for As(V) removal, Fe-loaded biochars
294 maintained almost the same pH of the effluent, whereas MD raised the pH to between 8.75 and
295 10.12. After 84 days, the pH was raised to higher than 9.5 until 112 days. Thus, MD was found

296 to be the most appropriate material for the treatment of As(V) but pH must be monitored and
297 eventually adjusted following batch or column treatment.

298 3.4 Comparative performance of tested materials

299 Considering the As removal efficiency, from synthetic and real effluents in batch testing,
300 and the number of days when As concentration was below 200 µg/L in the column testing, MD
301 seems the most performant among all materials tested within this study (Table 1). BCF is
302 another promising material, mainly for the treatment of the real mine effluent (bearing a lower
303 As concentration). In the same time, BF and BFC showed an average performance for As
304 removal through column tests in presence of the CND.

305 A direct comparison between the materials evaluated in the present study and other sorbents
306 effective for the As treatment available in the literature is difficult as experimental conditions
307 are different. However, at least MD and BCF showed satisfactory performance in As(V)
308 removal from synthetic and real CND in batch and column reactors. The As removal by MD
309 and BCF were 99.7% from average initial concentrations of 196 and 290 µ/L, respectively. The
310 number of days when As concentration was below 200 µg/L in the column treated effluent was
311 112 and 63 for MD and BCF respectively. Briefly, MD and BCF were promising for As(V)
312 removal from neutral mine effluents, at final concentrations lower than 1 mg/L As but higher
313 than the discharge criteria.

314

315 4. Conclusion

316 The efficiency of several low-cost, raw and modified materials was compared for the treatment
317 of As(V) from synthetic and real CND effluents, in batch and column testing. Among the Fe-
318 loaded biochars, the activated biochar impregnated with Fe (BCF) was the most efficient
319 material, whereas modified dolomite (MD) showed the best efficiency. Both materials reduced
320 As(V) concentration to below discharge criteria according to the actual Québec's law.
321 Therefore, they proved promising for reducing overall toxicity of real mine effluents. Moreover,

322 both materials could be appropriate for passive treatment of mine waters. Further, the
323 availability of the raw material (to reduce transport costs) and, the activation cost, whenever
324 both raw materials are easily accessible, would eventually guide the employer. However, the
325 use of MD requires pH control and final adjustment.

326

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433 **Figure captions:**

434 **Fig. 1:** a) and b) As(V) concentration; c) and d) adsorption capacity (q_t); and e), and f) the pH
435 as function of time using a synthetic ($C_0 \sim 850 \mu\text{g/L}$) and real mine CND ($C_0 \sim 300$
436 $\mu\text{g/L}$) effluents, respectively, on raw and modified materials.

437 **Fig. 2:** Evolution of a) As(V) concentration and b) pH as function of time during the treatment
438 of a real CND on raw and modified biochar, dolomite and wood ash

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458 **Table captions**

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

460 **Table 2.** Comparative performance of tested materials

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

	<i>B</i>	<i>BC</i>	<i>BF</i>	<i>BFC</i>	<i>BCF</i>	<i>MD</i>	<i>WA</i>	<i>MWA</i>
<i>Textural properties</i>								
S _{BET} (m ² /g)	177**	881*	57**	311*	549*	4.2*	44*	23*
V _t (cm ³ /g)	-	0.53	-	0.20	0.29	-	-	-
V _μ (cm ³ /g)	0.11	0.33	0.06	0.12	0.22	-	-	-
V _m (cm ³ /g)	-	0.20	-	0.08	0.27	-	-	-
<i>Physicochemical properties</i>								
pH	5.0	10.2	7.7	10.5	10.2	11.6	13.8	12.6
pH _{PZC}	6.6	9.5	6.4	8.7	9.9	11.1	11.4	12.7
C (%)	75.4	89.9	61.1	72.2	75.9	-	-	-
H (%)	3.5	0.9	3.6	1.3	1.5	-	-	-
N (%)	0.9	0.4	0.2	0.2	0.2	-	-	-
S (%)	0.5	0.0	0.4	0.0	0.2	-	-	-
O° (%)	19.7	8.8	31.7	18.8	9.6	-	-	-
Ca (%)	-	-	-	-	-	19.9	14.2	36.4
Si (%)	-	-	-	-	-	1.5	12.8	22.7
Fe (%)	-	-	3.0	7.5	12.6	0.7	5.3	16.9
Al (%)	-	-	-	-	-	0.2	2.6	4.7
K (%)	-	-	-	-	-	0.2	2.1	1.6
Mn (%)	-	-	-	-	-	0.1	1.1	2.8
Na (%)	-	-	-	-	-	-	0.7	10.5
Mg (%)	-	-	-	-	-	3.9	0.7	1.0

485 S_{BET} obtained from **CO₂ and *N₂ adsorption analysis; °O content was obtained by difference

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494 **Table 2.** Comparative performance of tested materials

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<i>Adsorbent material</i>	<i>gAC:mL</i>	<i>As removal (%) (C₀, µg/L)</i>		<i>Number of days < 200 µg/L</i>
		<i>Batch (Synthetic effluent)</i>	<i>Batch (Real effluent)</i>	
B	1:100	1.9 (854)	63.2 (156)	-
BC	1:100	9.8 (886)	43.5 (156)	-
BF	1:100	75.2 (854)	97.2 (255)	28
BCF	1:100	80.1 (842)	95.4 (290)	63
<i>BFC</i>	1:100	32.5 (798)	89.3 (260)	21
<i>MD</i>	1:100	99.9 (836)	99.7 (196)	112
WA	1:100	86.9 (758)	96.3 (127)	-
MWA	1:100	8.9 (858)	68.1 (89)	-