

1 Remediation of lead-contaminated water by virgin coniferous 2 wood biochar adsorbent: batch and column application

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8 9 **Abstract**

10 In this paper, RE-CHAR[®] biochar, produced by a wood biomass pyrolysis process, which
11 is usually applied as a soil fertilizer, was investigated for a novel use, that was as adsorbent for
12 remediating a lead-contaminated solution. Firstly, a deep physical and chemical
13 characterization of RE-CHAR[®] biochar was carried out. Then, the adsorption capacity of lead
14 from 50 mg/L and 100 mg/L solutions was determined under batch and continuous flow
15 conditions. Kinetics of the batch adsorption process were very rapid and complete removal
16 was achieved within 4 h contact time at both Pb concentrations, using a biochar dosage of 5
17 g/L. These data were best fitted by the pseudo second-order model, with the rate constant and
18 the equilibrium capacity equal to $k_s = 0.0091$ g/min and $q_e = 9.9957$ mg/g at 50 mg/L Pb, and
19 $k_s = 0.0128$ g/min and $q_e = 20.1462$ mg/g at 100 mg/L Pb, respectively. The Langmuir
20 isotherm model best fitted the equilibrium data at both Pb concentrations, with the Langmuir
21 constant and maximum adsorption capacity equal to: $b = 11.5804$ L/mg and $q_{\max} = 4.6116$
22 mg/g at 50 mg/L Pb, and $b = 2.8933$ L/mg and $q_{\max} = 9.5895$ mg/g at 100 mg/L Pb.
23 Continuous flow column tests showed that adding biochar to the soil of the adsorbent bed
24 significantly extended the breakthrough and exhaustion times, with respect to the column
25 filled with soil only. The Thomas model best fitted the experimental data of the breakthrough
26 curves, with the constant $k_{TH} = 5.28 \times 10^{-5}$ mL/min·mg and the maximum adsorption capacity
27 $q_0 = 334.57$ mg/g which was comparable to the values reported for commercial adsorbents.

28 Based on these results, it can be assessed that RE-CHAR[®] biochar can be used as an effective
29 adsorbent for lead removal from water solutions even at high concentrations.

30
31 **Key words:** adsorption; batch; biochar; column; lead; remediation.
32

33 **1. Introduction**

34 Charcoals (or biochars) are produced by means of the thermal decomposition of organic
35 residues from different sources, conducted under controlled conditions of the oxidizing agent
36 (Basu 2010; Glaser 2007; Popa and Visa 2017). In particular, biochar can be obtained by the
37 pyrolysis process of biomasses (Hagemann et al. 2018; Kan et al. 2016; J. Li et al. 2016) or
38 vegetable waste from agriculture and forestry (Joseph et al. 2017; Keske et al. 2019;
39 Yargicoglu et al. 2015). Furthermore, it is generated as a residue of the gasification process
40 (Lugato et al. 2013; Rollinson 2016; Yao et al. 2018).

41 Quality and properties of the biochar depend on many factors, such as feedstock type and
42 operating conditions of the production process (Ahmed et al. 2016a; Allaire et al. 2015; Aller
43 2016; Lange et al. 2018; Tang et al. 2013; Tripathi et al. 2016; K. Weber and Quicker 2018).
44 Table 1 shows the impact of parent materials and production process conditions on the
45 elemental composition and surface area of biochar (Chen et al. 2008; Jindo et al. 2014; Kong
46 et al. 2011; Mašek et al. 2012; Nguyen et al. 2009, 2010; Uchimiya et al. 2011).

47

48 **Table 1.** Influence of feedstock and production process conditions on surface area
49 and elemental composition of biochar.

Feedstock type	Reactor	Temperature °C	Residence time h	Heating rate °C/min	C (%)	O (%)	BET Surface area m ² /g	Ref.
Apple tree branch (AB)	Commercial electric furnace	400-800	10	10	70.18 – 84.84	20.56 –5.81	11.90– 545.43	(Jindo et al. 2014)
Oak tree (OB)	Commercial electric furnace	400-800	10	10	70.52 – 82.85	21.47 – 17.29	5.60– 398.15	(Jindo et al. 2014)
	Slow pyrolyzer	350-600	n.d.	n.d.	n.d.	n.d.	450 - 642	(Nguyen et al. 2010)
Rice husk (RH)	Commercial electric furnace	400-800	10	10	44.59 – 40.41	16.32 – 2.69	193.70 – 295.57	(Jindo et al. 2014)
	Gold image furnace	350, 450, 550 and 650	n.d.	5 and 100	66.14 – 89.61	57.2	29.19 – 7.64	(Mašek et al. 2012)
Rice straw (RS)	Commercial electric furnace	400-800	10	10	49.92 – 29.17	12.02 – 3.71	46.60 – 256.96	(Jindo et al. 2014)
Pine wood chips (PC)	Gold image furnace	350, 450, 550 and 650	n.d.	5 and 100	69.64 – 87.89	44.7	26.58 – 8.29	(Mašek et al. 2012)
Pine needle	Pyrolyzer	100-700	6	n.d.	50.87 – 86.51	42.27 – 11.08	0.65 – 490.8	(Chen et al. 2008)
Wheat	Gold	350, 450,	n.d.	5 and	70.88	53.1	21.96	(Mašek

Feedstock type	Reactor	Temperature	Residence time	Heating rate	C	O	BET Surface area	Ref.
		°C	h	°C/min	(%)	(%)	m ² /g	
straw (WS)	image furnace	550 and 650		100	– 94.90		– 0.00	et al. 2012)
Cotton seed hulls	Box furnace	200-800	4	n.d.	51.9 - 90	40.5 - 7	4.7 - 322	(Uchimiya et al. 2011)
Corn stover	Slow pyrolizer	350-600	n.d	n.d	n.d.	n.d.	293 - 527	(Nguyen et al. 2009)
Soybean stalk	Muffle furnace	300, 400, 500, 600 and 700	8	n.d	n.d	n.d.	144.14 – 250.23	(Kong et al. 2011)

50

51 Currently, biochar is mainly used as a soil amendment due to the capacity of improving
52 its properties and quality (Lomaglio et al. 2018; Schmidt et al. 2014). Agegnehu et al. (2017)
53 observed an increase of soil pH from 7.1 to 8.1 as a consequence of the addition of 39 t/ha
54 herbaceous biochar. Glaser et al. (2002) reported that low amounts of biochar added to soils
55 (i.e. 300 g/kg) increased the availability of base cations (ECEC) (i.e. above 4.8 cmol_c/kg) and
56 base saturation (BS) (i.e. above 660%). Mean soil organic carbon content (SOC), after 67
57 days, increased between 5.1 and 14.2 g/kg, with the addition of 1-2% biochar to Norfolk Ap
58 soil (Novak et al. 2009). Burrell et al. (2016) disclosed the change in the value of electrical
59 conductivity (EC) of soils amended with 3% biochar for 3 years, of different soil types: for
60 instance, a decrease of about 37 μS cm⁻¹ was observed in planosol soil, whereas an increase of
61 about 25 μS cm⁻¹ was measured in černožem and cambisol soil. In a review of several studies

62 conducted at different scales (laboratory, field, field plots, greenhouse), Blanco-Canqui
63 (2017) reported that, in the upper 15 cm of soils depth, bulk density decreased of at least 10%
64 while porosity increased at the same percentage. Plant growth and health showed different
65 responses in relation to the biochar source and application rate. In the review of crops
66 responses (mainly maize and tomato) by Agegnehu et al. (2017), it was highlighted an
67 increase of plant growth yield of 50% on average. Application of biochar to soil can also
68 reduce nutrient leaching by increasing the soil retention capacity and stimulate the growth rate
69 of microorganisms (Jien et al. 2017; Rasa et al. 2018). For instance, Hagemann et al. (2017)
70 observed 2.0 g NO₃⁻-N/kg after 60 days of aerobic composting plus 6 months of storage.
71 Bashir et al. (2018) measured 224.13 mg/kg of microbial mass carbon (MBC) in a soil
72 amended with 1.5% sugarcane bagasse-derived biochar. Thanks to the high heterogeneous
73 specific surface (Kasozi et al. 2010) and the well-distributed pore network that includes
74 micropores (<2 nm), mesopores (2–50 nm) and macropores (>50 nm), biochar showed also to
75 possess a high ion exchange capacity, such as $10 \leq \text{CEC} \leq 69 \text{ cmol}_c/\text{kg}$ at near neutral pH as
76 reported by Mukherjee et al. (2011).

77 Due to the these properties, biochar was tested as adsorbents for the removal of pollutants
78 from different environmental compartments (Ahmad et al. 2014; Cha et al. 2016; De Gisi et
79 al. 2016; Qian et al. 2015; Rosales et al. 2017; Wei et al. 2018). In water and wastewater, it
80 was capable of adsorbing a wide range of pollutants such as lead, arsenic, copper, cadmium,
81 chromium, mercury, zinc and nickel (Ahmad et al. 2014; De Gisi et al. 2016; Z. Ding et al.
82 2016; M. I. Inyang et al. 2016; Mohan et al. 2007; Oliveira et al. 2017; Qambrani et al. 2017;
83 Reddy et al. 2014; Xiao fei Tan et al. 2016; Xiaofei Tan et al. 2015). Biochar was also applied
84 to the remediation of groundwater contaminated by slow-release secondary sources (Luciano
85 et al. 2010; Tatti et al. 2016, 2019).

86 Adsorption capacity was further enhanced through different activation processes, such as
87 biological, thermal or physical-chemical (Boni et al. 2018a; Z. Ding et al. 2016; R. Li et al.
88 2017; Rajapaksha et al. 2016; B. Wang et al. 2017; H. Wang et al. 2015; Wei et al. 2018).
89 Biochar was dosed to contaminated soils with the aim to reduce pollutant leaching (Bashir et
90 al. 2018; Beesley et al. 2011, 2014; Lomaglio et al. 2018; K. Lu et al. 2017; Park et al. 2011;
91 Puga et al. 2015; Tang et al. 2013; Yin et al. 2016; Zhang et al. 2016). When incorporated to
92 soil, it demonstrated to be capable of binding heavy metals to carbonates and organic matter:
93 as a consequence, the adsorption process was enhanced due to metals building bonds with
94 oxygen, carbon and nitrogen-containing functional groups (Bashir et al. 2018; Cha et al. 2016;
95 Lehmann et al. 2011; Park et al. 2011; Yin et al. 2016). In addition, the high pH, Cation
96 Exchange Capacity (CEC), microporous structure and excess of soluble salts, which are
97 present on the biochar surface, increase the heavy metal immobilization through precipitation
98 and surface adsorption (Beesley et al. 2011; Febrianto et al. 2009; Janus et al. 2015; Sohi et
99 al. 2010; Uchimiya et al. 2010, 2011; Vithanage et al. 2017; B. Wang et al. 2017; M. Wang et
100 al. 2017).

101 As compared to commercial adsorbents, use of biochar represents a more economically
102 and environmentally sustainable alternative because it offers a new opportunity of reuse to
103 vegetable products and green wastes from agriculture and forestry. Therefore, its employment
104 fully fits the goals of the circular economy which require to limit waste materials by their
105 recovery and reuse. Furthermore, using biochar in place of commercial adsorbents allows to
106 avoid the environmental impact of the industrial activities required for their production.

107 Lead is one of the most studied toxic substances. It negatively affects almost all
108 vertebrate systems and also human health through drinking water ingestion (Abadin et al.
109 2007; Flora et al. 2012; Wani et al. 2015). Due to the associated risks (Cobbina et al. 2013;
110 Hanna-Attisha et al. 2016), Italian legislation requires Pb concentration to be below 0.01

111 mg/L in groundwater, 0.2 mg/L and 0.3 mg/L in the effluents discharged into surface waters
112 and sewage systems, respectively (Italian decree n. 152/06).

113 Several technologies have been developed to remove lead and other heavy metals from
114 the environment thus preventing it from spreading. For instance, different types of adsorbents
115 have been applied to contaminated soils and water to reduce/immobilize, metal content such
116 as talc, chalcopryrite and barite (Rashed 2001), soil-washing agents (Neilson et al. 2003),
117 activated red mud (Naga Babu et al. 2017), sophorolipids (Qi et al. 2018), nanoadsorbent from
118 different sources (Chiavola et al. 2016; Safatian et al. 2019).

119 In this study, a virgin coniferous wood biochar produced in Italy was tested as adsorbent
120 for removing lead from aqueous solutions. To this purpose, a number of experimental trials
121 was carried out in laboratory to evaluate the adsorption capacity under both batch and
122 continuous flow conditions.

123 The novelty of the present paper is represented by the new application of virgin
124 coniferous wood biochar as adsorbent media for lead-contaminated solution in batch and
125 column plants. This paper demonstrates the feasibility of a different use for this waste
126 product, thus allowing to comply with the basic principles of the circular economy.

127

128 **2. Materials and methods**

129 **2.1. Production of biochar**

130 RE-CHAR[®], supplied by RECORD IMMOBILIARE S.r.l. (Lunano, Italy), is produced
131 from a wood biomass (virgin coniferous wood, mainly pine) through a pyrolyzation process
132 conducted under the following operating conditions: 600 °C average gasification temperature,
133 750 °C effluent gas temperature and 300 °C inlet air temperature. The pyrolysis plant aims at
134 energy production, and generates biochar as a solid residue product. Currently, this biochar is

135 used as a soil improver for which it has received the Italian certification (0019841/17, decree
136 75/2010 “*reorganization and revision of the rules on soil improvers*”).

137 The wood biomass used as a feedstock is produced by the forest management activities
138 and is composed by wood chips having a particle size distribution predefined by a mechanical
139 treatment. Feedstock complies with the A1/A2 quality classes of the UNI EN ISO 17225-4:
140 2014 standard.

141 Due to processing issues, broad-leaved wood chips from coppice are also used along with
142 wood chips, in a mixture of oak, orniello and hornbeam. As far as the production process is
143 concerned, the biomass is transported from the storage tank to the drying phase through
144 mechanical systems using rakes and augers; here, the water content is reduced to about 10%
145 through the insufflation of 8000 m³/h hot air by means of the Air Handling Unit (AHU).
146 Then, the biomass suitable for gasification is selected through sieving, and automatically
147 loaded to the plant where it undergoes a thermochemical conversion in an oxygen deficient
148 environment.

149 **2.2. Analytical methods**

150 Prior to be used, RE-CHAR[®] was chemically and physically characterized according to
151 standard procedures reported in previous published papers (Qambrani et al. 2017).
152 Particularly, bulk density, specific weight, field capacity, porosity, moisture content, ash
153 content and pH were determined following the analytical procedures outlined by Allaire et al.
154 (2015) and Pituello et al. (2015). The value of pH point of zero charge was measured by
155 applying the method reported in Noh and Schwarz (1990). Elemental analysis of the surface
156 (EDX), percentage of the major components and average dimension of pores were determined
157 by using a HR FESEM Zeiss Auriga (SEM; Rome, Italy) at 3000× magnification and 10 kV
158 acceleration voltage.

159 Lead concentration in the aqueous phases was determined using a Perkin Elmer atomic
160 absorption spectrophotometer with flame atomization (F-AAS; Perkin-Elmer model 3030B),
161 whose detection limit was 0.1 mg/L. The calibration curve was determined using standard
162 solutions at 2 mg/L and 4 mg/L Pb (APAT and IRSA/CNR 2003). Samples were properly
163 diluted using the relative method (APAT and IRSA/CNR 2003) to fall within the instrument's
164 calibration curve.

165 **2.3. Chemical solutions**

166 A stock solution (at 30 g/L Pb²⁺) was prepared by dissolving lead(II) nitrate salt (supplied
167 by Carlo Erba, Milan, Italy; solubility in water = 52 g/100 mL, at 20 ± 0.1 °C) into Milli-Q
168 water (18.5 MΩ·cm).

169 Proper dilutions of the stock solution in deionized water (0.055 μS/cm) allowed to obtain
170 the lead contaminated solutions at the required concentrations (i.e. 50 mg/L and 100 mg/L)
171 for the experimental tests. Stock and lead-contaminated solutions were stored at 4°C until
172 their use.

173 **2.4. Batch tests**

174 Batch experiments were carried out, using the jar-tester apparatus, to determine kinetics
175 and equilibrium data of the adsorption process of lead onto the RE-CHAR[®] biochar. The
176 experiments were conducted at 50 and 100 mg/L of lead as initial concentrations. These
177 values, being very high and far above the limits posed by the Italian legislation, were selected
178 with the aim to test the adsorption capacity of the biochar under severe contamination
179 conditions (Kołodziejńska et al. 2017).

180 In the batch tests, 5 g/L of biochar were added to the Pb-contaminated solution and
181 maintained for 6 h under mixing conditions at 120 rpm constant stirring speed. Liquid
182 samples were collected at different times: 5, 15, 30, 45 and 60 min within the first hour, and
183 afterwards at 1 h intervals until the end of the tests. The samples were filtered by a vacuum

184 filtration system using a 0.2 µm glass microfibre filters (Munktell, Ahlstrom) and then the
185 liquid phase was analyzed.

186 Through the above batch tests, it was possible to determine the equilibrium time of the
187 adsorption process. The experimental data were fitted using the following kinetic models:
188 zero, first, second, saturation, pseudo-first and pseudo-second-order (Sirini 2002). The best
189 fitting model between the experimental and the modelled data was determined based on the
190 value of the regression coefficient, R^2 , using the linearized form of the model equations.

191 Another series of batch tests was conducted with the aim of obtaining the equilibrium
192 data. In this case, the following adsorbent dosages of RE-CHAR[®] were added to the solutions
193 at 50 and 100 mg/L Pb concentrations: 0.5, 1, 2, 4, 5, 6, 8 and 10 g/L. The content was
194 maintained under mixing conditions for a duration equal to the equilibrium time previously
195 determined.

196 At the end of these tests, liquid samples were collected, filtered by a vacuum filtration
197 system using a 0.2 µm glass microfibre filters (Munktell, Ahlstrom) and analyzed for the
198 residual Pb concentration in solution.

199 The equilibrium data were fitted by the Langmuir (Langmuir 1918), Freundlich
200 (Freundlich 1907) and Brunauer–Emmett–Teller (BET) (1938) isotherm models. The best
201 fitting model of the experimental data was determined based on the value of R^2 , using the
202 linearized form of the model equations.

203 Lead percentage removal (R%), lead adsorbed per unit weight of adsorbent at time t (q_t)
204 and at equilibrium time (q_e) were calculated using the following equations (1, 2, and 3,
205 respectively), obtained through the mass balance of lead between the liquid and solid phases:

206

$$R\% = \frac{(C_0 - C_t)}{C_0} 100\% \quad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

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208 where V is the volume of the aqueous solution, m is the mass of RE-CHAR[®], C_0 (equal to 50
209 and 100 mg/L Pb), C_t and C_e indicate lead concentration in the liquid phase at time $t = 0$, t and
210 at equilibrium, respectively.

211 All the batch experiments were conducted in duplicate and the results obtained were
212 averaged.

213 **2.5. Column tests**

214 The adsorption capacity of biochar in a column plant was investigated using a lab-scale
215 apparatus. These tests were performed following the procedures outlined in a previous paper
216 by the same authors (Boni et al. 2018a). For instance, glass columns, having 18 cm height and
217 1 cm diameter, were filled by alternating layers of sand, soil and biochar. Particularly, a
218 previously sterilized quartz sand was placed on the bottom; 1 g of agricultural soil (made by
219 29% clay, 28% silt, 43% sand and 2% organic matter, by weight) was posed above, followed
220 by a layer of RE-CHAR[®] disposed on the top.

221 The mass of biochar used in the column test, equal to 0.5 g, was selected according to the
222 procedure previously determined by the same authors (Boni et al. 2018b).

223 Biochar and sand particle having a size smaller than 2 mm were previously discarded, in
224 order to limit by-pass phenomena along the column walls (Perry and Green 2008). One more
225 column, filled as the previous one but without the the layer of RE-CHAR[®], was operated
226 under the same conditions as a control.

227 The lead contaminated solution, at a concentration $C_0 = 100$ mg/L Pb, was continuously
228 fed to the top of the columns through peristaltic pumps, at 60 mL/h flow rate. This high

229 concentration of lead was chosen to test the RE-CHAR[®] adsorption capacity under severe
230 conditions, and to obtain a rapid development of the breakthrough curve.

231 By recording Pb concentrations in the eluates versus column operating time allowed to
232 determine the breakthrough curves. Then, the breakthrough and saturation times were
233 calculated, assuming to correspond to the time when Pb concentrations in the eluate, C,
234 corresponds to $C/C_0 = 5\%$ and $C/C_0 = 95\%$, respectively (Chern and Chien 2002; Hai et al.
235 2018).

236 The experimental data of the column tests were fitted using the Yoon–Nelson (1984), Thomas
237 (1944) and Bohart–Adams (1920) models (Ahmed et al. 2016b; Bhaumik et al. 2013) to
238 determine the adsorption capacity.

239

240 3. Results and discussion

241 3.1. Biochar characterization

242 Values of the main chemical-physical properties of RE-CHAR[®] were determined through
243 the characterization phase conducted as described in section 2.3. The results obtained are
244 shown in Table 2.

245

246 **Table 2.** Main physical and chemical properties of RE-CHAR[®] (% on dry weight).

Physical and Chemical Properties	Symbol	Unit	Values
Bulk density	γ_s	g/cm^3	1.931
Specific weight	γ_d	g/cm^3	0.167
Field capacity	ω_c	g in 100 g	700
Porosity	n	%	91.35
Carbon	C	%	92.56

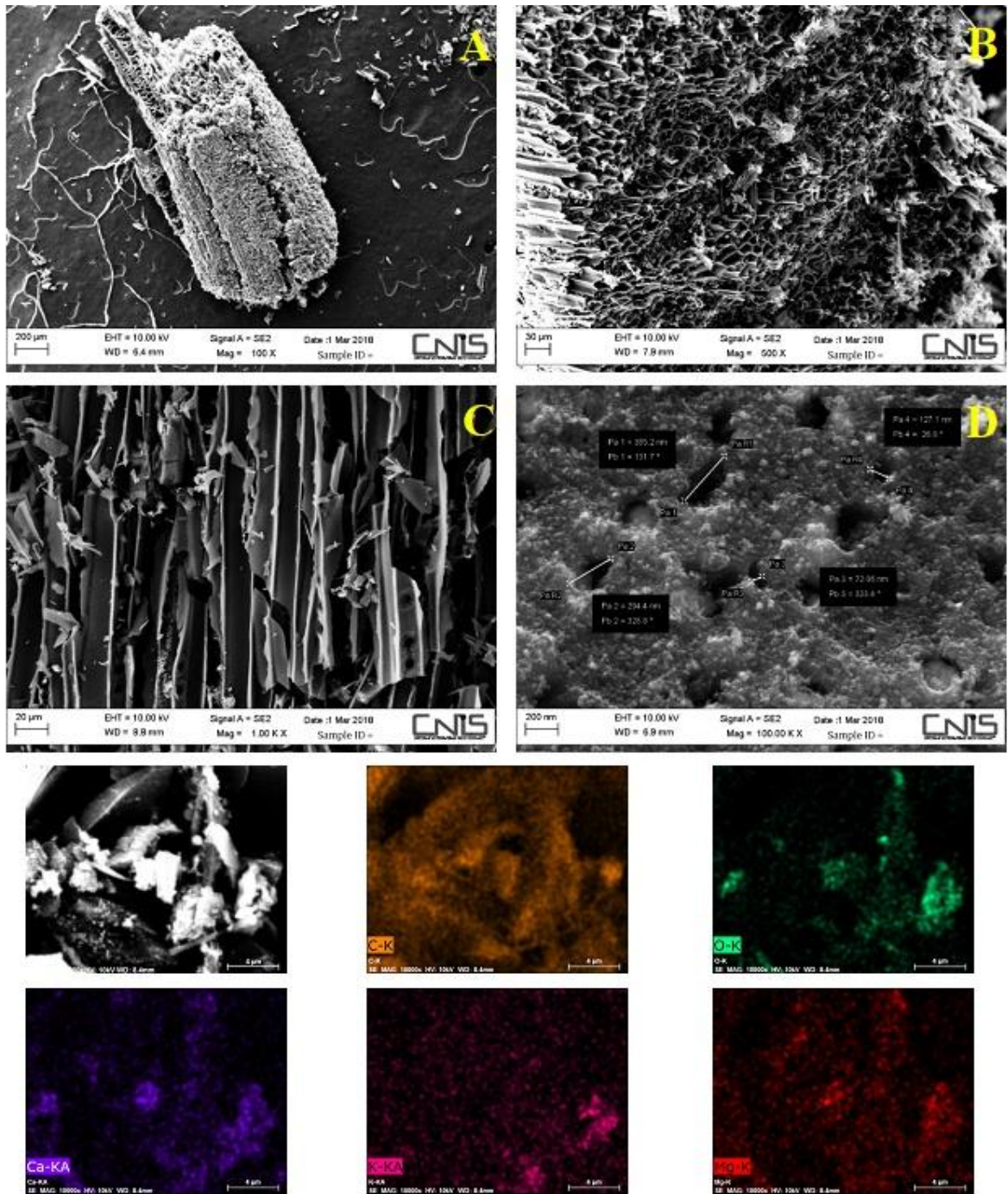
Oxygen	O	%	5.87
Calcium	Ca	%	0.81
Potassium	K	%	0.53
Magnesium	Mg	%	0.18
Moisture content	ω	%	2.94
Ash content	cc	%	56.87
Potential of Hydrogen	pH	-	12.40
Point of zero charge	pH _{PZC}	-	12.98

247

248 Characterization provided values in accordance to those reported by the specialized
 249 literature. For instance, carbon and oxygen contents were found equal to 92.6% and 5.9%,
 250 respectively, whereas Qambrani et al. (2017) measured C = 93.7% and O = 5.8% in a biochar
 251 produced from turkey litter pine needle pyrolyzed at 700 °C. The ash content was found to be
 252 56.9% in the present case, likely a direct effect of the high pyrolysis temperature (600 °C). In a
 253 recent study by other authors, the ash content of biochar produced from swine manure was
 254 observed to be about 53%, being the pyrolysis temperature equal to 700 °C (Klasson 2017).

255 The Scanning Electron Microscope (SEM) images of RE-CHAR[®] surface are shown in
 256 Figure 1, at various magnifications: (A) 79 X; (B) 2.50 KX; (C) 2.00 KX; and (D) 100.00 KX.

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Figure 1. Scanning Electron Microscope (SEM) images of the surface and image and color coded Energy Dispersive X-ray (EDX) analysis dot maps of RE-CHAR® at different magnifications: (A) 100 X; (B) 500 X; (C) 1.00 KX; and (D) 100.00 KX.

Figure 1 (A) highlights one chip of biochar, (B) is the transversal cut cross-section, (C) the longitudinal vertically cut cross-section and (D) variously sized pores.

265 From the graphic extrapolations in Figure 1, the average dimension of pores in relation to
266 the magnification used was obtained during image acquisition, i.e. 210 ± 4.0 nm at 100.00
267 KX.

268 Figure 1 shows also the elemental maps of carbon, oxygen, calcium, potassium and
269 magnesium within the biochar samples, whose percentage contents are reported in Table 2.
270 Particularly, amber color is used to indicate carbon, aquamarine for oxygen, dark violet for
271 calcium, magenta for potassium and red for magnesium.

272 **3.2. Batch tests**

273 Figure 2 shows lead percentage removal versus time measured in the batch tests
274 conducted at initial concentrations of 50 mg/L and 100 mg/L Pb. It can be observed that
275 removal rate was initially very fast, reaching values of 70% at 50 mg/L and 85% at 100 mg/L
276 after only 30 min. Thereafter, in the case of $C_0 = 100$ mg/L, it proceeded at a much lower rate,
277 reaching $R\% = 100\%$ after 4 h contact time. For $C_0 = 50$ mg/L, the removal remained constant
278 at about 70% until the end of the first hour ($t = 1$ h) and then increased rapidly assuming a
279 profile similar to that observed at $C_0 = 100$ mg/L; a complete removal ($R\% = 100\%$) was
280 reached at the same time, i.e. $t = 4$ h. Negligible variations were observed afterwards.

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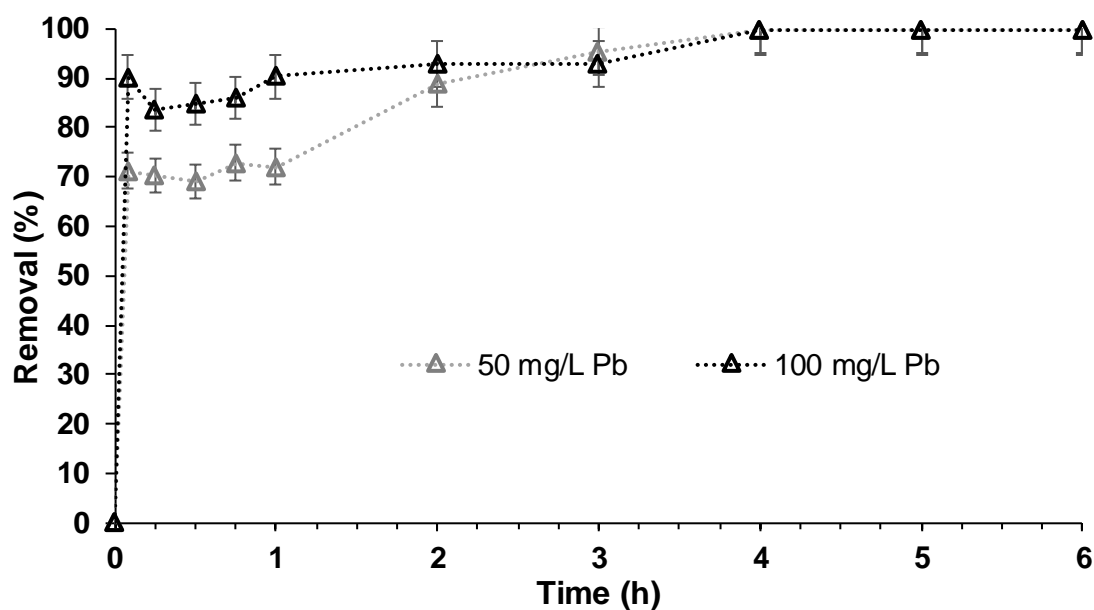


Figure 2. Lead percentage removal versus contact time. Adsorption temperature, mixing rate and biochar dosage: 20 ± 0.5 °C, 120 rpm, 5 g/L.

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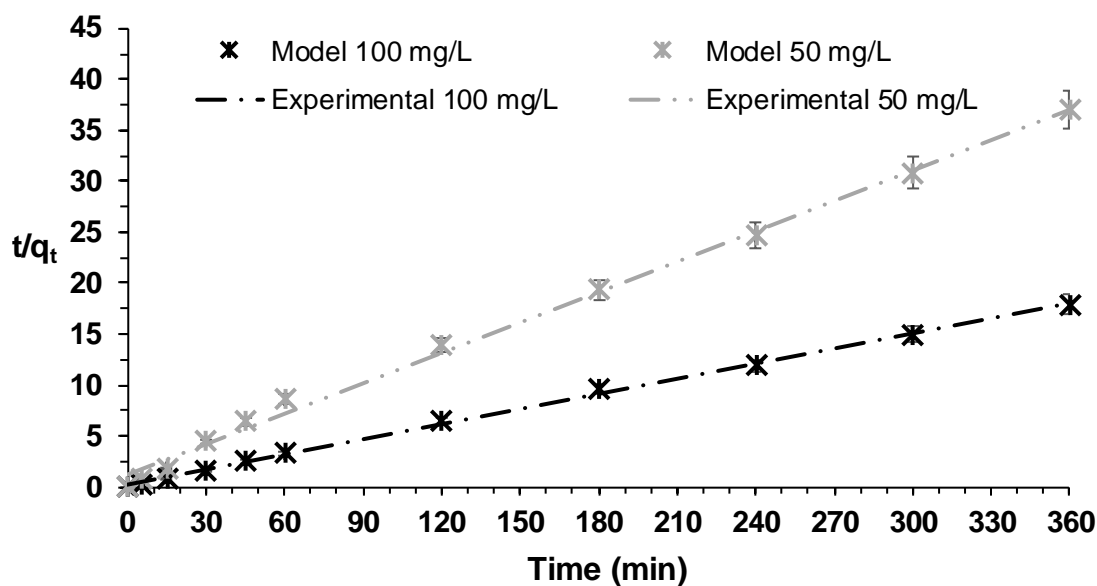
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These results are consistent with the scientific literature: for instance, in Kołodyńska et al. (2012), a similar time-profile was reported for Pb adsorption at the same initial concentration onto biochar produced from pyrolysis of pig and cow manure at 400 °C and 600 °C, although at a slower rate (equilibria was reached after 5 h contact time). Lead sorption, with initial concentrations ranging from 5 to 200 ppm, onto biochar from pyrolysis of raw sugarcane bagasse also reached equilibrium after about 5 h (M. Inyang et al. 2011). The same equilibrium time (5 h) was found in a previous paper by the same authors (Boni et al. 2018b), where the tested biochar was produced by pyrolysis of poplar, oak, robinia, platanus, willow, apple and pear wood. Another study indicated equilibrium times after about 2 hour for the adsorption of 50 mg/L Pb onto a biochar made from a mixture of wood chips, green waste, rice hull, corn cob, nut shells and husks, and cotton gin trash and pomace (Karunanayake et al. 2018). In the same paper (Karunanayake et al. 2018), adsorption on biochar of pinewood and of magnetic switch-grass, at the same Pb concentration, required from 8 to 20 h to reach equilibrium.

300 Therefore, considering the results obtained in the present study and those reported by the
301 literature, it is evident that feedstock and operating conditions of the production process of
302 RE-CHAR[®] influence the rate of removal.

303 The linearized form of the equation of the different kinetic models was used to find out
304 the best fitting of the experimental data. The pseudo second-order model provided the best
305 agreement for both Pb concentrations (higher R^2 value) with respect to the other applied
306 models. Figure 3 shows the experimental and the modelled data in terms of t/q_t versus t . The
307 pseudo second-order equation assumes that the rate of occupation of adsorption sites is
308 proportional to the square of the number of unoccupied activated sites on the surface of the
309 adsorbent (Ho and McKay 1999).

310



311

312 **Figure 3.** Kinetic experimental data and modelled by the linearized pseudo-second-
313 order equation. Adsorption temperature, mixing rate and biochar dosage: 20 ± 0.5
314 $^{\circ}\text{C}$, 120 rpm, 5 g/L.

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316 Through the slope and intercept of the regression line, it was possible to determine the
317 values of the pseudo second-order rate constant, k_s , and of the amount of Pb adsorbed at

318 equilibrium per unit weight of RE-CHAR[®], q_e , both reported in Table 3. The same table also
 319 shows $q_{e,exp}$ which represents the value of q experimentally calculated at $t = 300$ min, which
 320 was assumed to be the equilibrium time based on the batch tests results. It can be noted that
 321 experimental and modelled data of the adsorption capacity do not differ appreciably in both
 322 cases of 50 mg/L and 100 mg/L Pb.

323

324 **Table 3.** Pseudo second-order kinetic model parameters.

C_0	$q_{e,exp}$	q_e	k_s	R^2
(mg/L)	(mg/g)	(mg/g)	(g/min)	-
50	9.7340	9.9957	0.0091	0.9959
100	20.0800	20.1462	0.0128	0.9988

325

326 Comparing the values obtained for the specific adsorption capacity, it can be noted an
 327 almost linear increase of q_e with concentration: for instance, rising Pb in solution from 50
 328 mg/L to 100 mg/L led to a double q_e value.

329 Other studies found that the pseudo second order model was that one better representing
 330 the biochar adsorption process of lead at the same initial concentration as in the present paper
 331 (Boni et al. 2018b; Deng et al. 2017; H. Lu et al. 2012) or at a double concentration (Ifthikar
 332 et al. 2017).

333 The Langmuir model (Langmuir 1918) provided the best agreement (higher R^2 value) of
 334 the experimental data obtained in the equilibrium tests, with respect to Freundlich (1907) and
 335 BET (1938) isotherms, for the lead contaminated water at 50 mg/L Pb ($R^2 = 0.5918$ and $R^2 =$
 336 0.9809 , respectively) and 100 mg/L Pb ($R^2 = 0.5398$ and $R^2 = 0.9860$, respectively).

337 Langmuir model assumes a monolayer adsorption of solutes onto a surface comprised of
 338 a finite number of identical sites with homogeneous adsorption energy (Sivaraj et al. 2001).

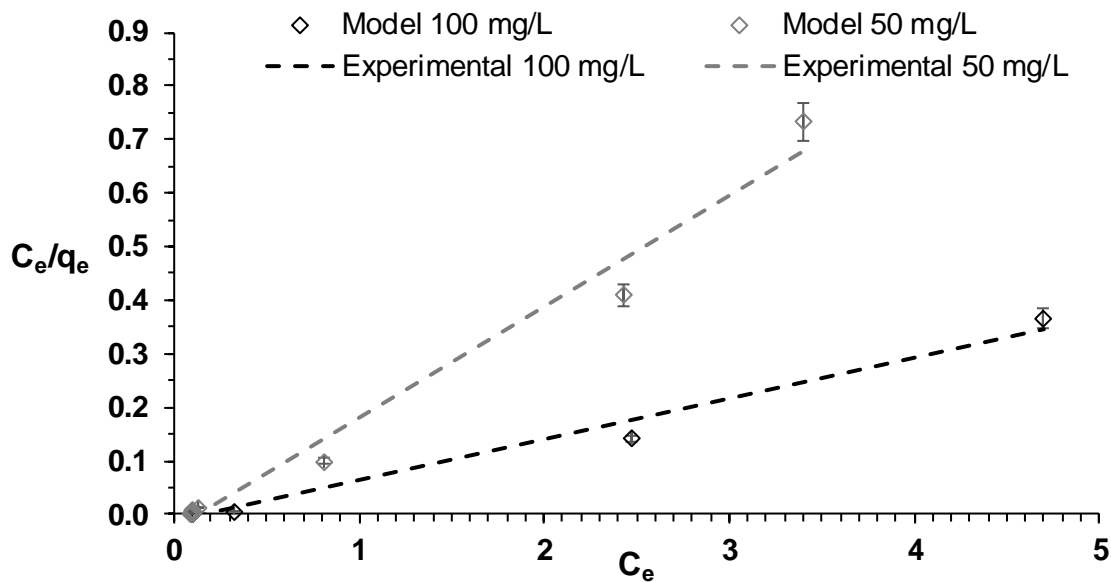
339 This means that once a molecule occupies a binding site, no further adsorption can take place
 340 at that site (Ali et al. 2016). The essential characteristics of Langmuir isotherm can be
 341 expressed in terms of the dimensionless constant separation factor (R_L) for the equilibrium
 342 conditions (Langmuir 1918; T. W. Weber and Chakravorti 1974). This parameter is defined
 343 as:

$$R_L = \frac{1}{(1 + bC_0)} \quad (4)$$

345
 346 where C_0 is the Pb initial concentration (mg/L) and b is the Langmuir constant (L/mg).
 347 According to Hall et al. (1966), using mathematical calculations, it has been shown that the
 348 parameter R_L indicates the isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear
 349 ($R_L = 1$) or unfavourable ($R_L > 1$).

350 Plotting C_e/q_e versus C_e follows approximately a straight line, as highlighted in Figure 4.

351



352

353 **Figure 4.** Equilibrium experimental and modelled data by the linearized Langmuir
354 equation. Adsorption temperature, mixing rate and equilibrium time: 20 ± 0.5 °C,
355 120 rpm, 5 h.

356
357 From the slope and intercept of the regression line, it was possible to calculate the values of
358 the maximum adsorption capacity, q_{\max} , and the constant b , which are reported in Table
359 4. Specifically, q_{\max} represents the amount of solute adsorbed per unit mass of adsorbent which
360 is required for the monolayer coverage of the surface (mg/g), also called monolayer capacity;
361 b is the Langmuir constant related to the affinity between the sorbent and sorbate (L/mg).

362

363 **Table 4.** Adsorption Langmuir isotherm parameters.

C_0 (mg/L)	q_{\max} (mg/g)	b (L/mg)	R^2 -	R_L -
50	4.6116	11.5804	0.9967	0.0017
100	9.5895	2.8933	0.9863	0.0032

364

365 Values of R_L were found to be slightly above zero for both lead concentrations (i.e. $R_L =$
366 0.0017 and $R_L = 0.0032$ for 50 mg/L Pb and 100 mg/L Pb, respectively), thus indicating that
367 the adsorption process of Pb was always slightly favourable.

368 In terms of implementation at full-scale, adsorbents with the highest value of the
369 maximum adsorption capacity, q_{\max} , are the most desirable. The values found in the present
370 study for RE-CHAR[®] fall within the ranges referred by the literature for different biochars
371 used for Pb removal from water solutions (Harris 2009; M. Inyang et al. 2011; M. I. Inyang et
372 al. 2016; Y.-H. Li et al. 2003; Liu and Zhang 2009; Mahdi et al. 2018; Mohan et al. 2007,
373 2014; Uchimiya et al. 2010). For instance, Liu and Zhang (2009), by applying biochar

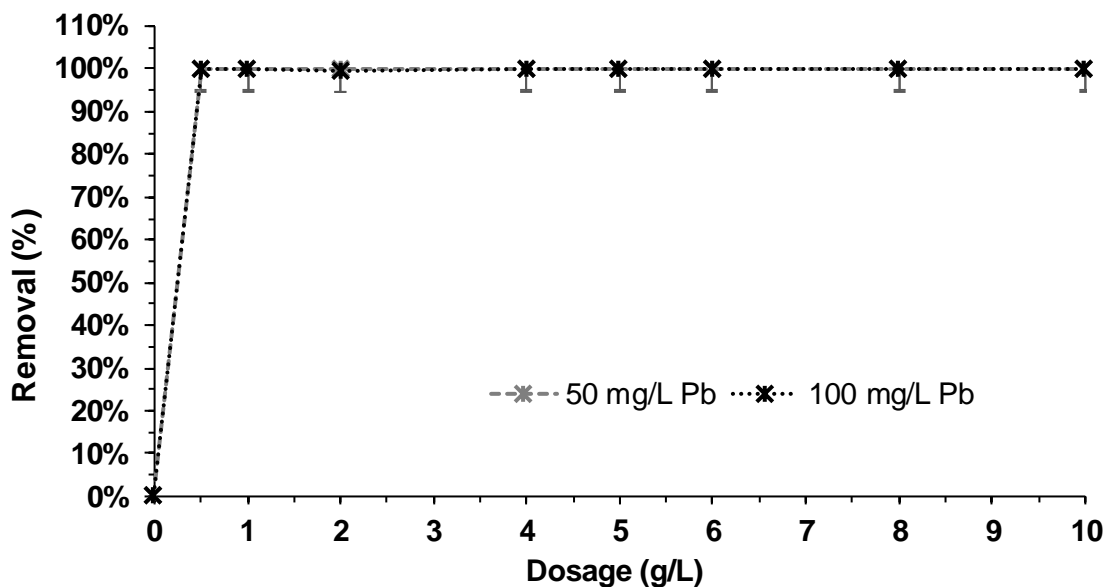
374 prepared from hydrothermal liquefaction of pinewood (P300) to a Pb solution of about 50
375 mg/L, found for the maximum lead sorption capacity a very similar value to that obtained in
376 the present study (i.e. 4.25 mg/g, and 4.61 mg/g, respectively).

377 Using biochar produced at 500° C from sugarcane bagasse and Pb concentration of about
378 80 mg/L, the adsorption capacity resulted to be. 9.13 mg/g, which does not differ appreciably
379 from 9.58 mg/g observed in the present study at 100 mg/L (W. Ding et al. 2014).

380 The slight differences are likely due to the change in the type and operating conditions of
381 the production process, which are known to affect the porosity and microstructure of the
382 adsorbents (W. Ding et al. 2014; Liu and Zhang 2009); these in turn influence the amount of
383 pollutant that can be adsorbed per unit weight of media.

384 The ability of RE-CHAR[®] to remove lead as a function of the adsorbent mass is shown in
385 Figure 5.

386



387

388 **Figure 5.** Percentage of lead removal versus different RE-CHAR[®] dosages at 50
389 mg/L and 100 mg/L Pb. Adsorption temperature, mixing rate and equilibrium time:

390

20 ± 0.5 °C, 120 rpm, 5 h.

391

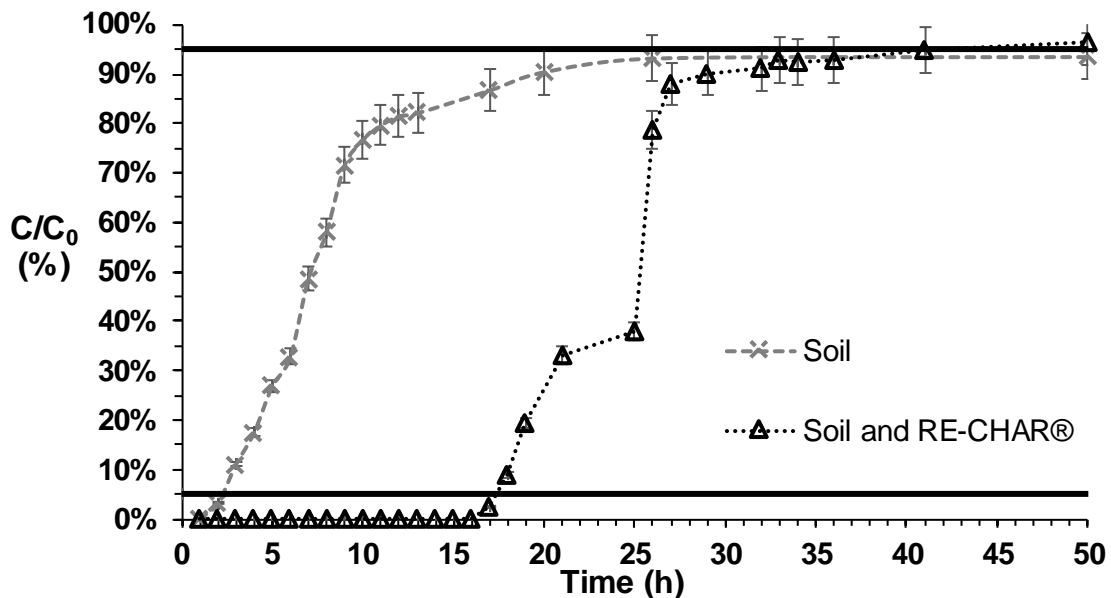
392 It is highlighted that a dosage of 0.5 g/L RE-CHAR[®] was the minimum required to
393 achieve the highest removal percentage, i.e. R% = 100%, at both concentrations of 50 mg/L
394 and 100 mg/L Pb.

395 From this figure it can be deemed that, for Pb contaminated solutions at 50 mg/L and 100
396 mg/L, using a dosage of 1 g/L of RE-CHAR[®] adsorbent makes it possible to comply with the
397 limit set by the Italian legislation for discharge into surface waters and sewage systems
398 (respectively 0.2 mg/L and 0.3 mg/L).

399
400 **3.3. Column tests**

401 Figure 6 shows the breakthrough curves obtained through the column tests. The curves
402 represent the percentage ratio of Pb concentration in the eluate and in the feeding solution, i.e.
403 C/C_0 , versus time of operation of the column plant filled with soil only and soil and RE-
404 CHAR[®]. Figure 6 also shows two horizontal lines drawn at $C/C_0 = 5\%$ and $C/C_0 = 95\%$,
405 assumed to represent the breakthrough and exhaustion conditions, respectively.

406



407

408 **Figure 6.** Breakthrough curves for adsorption of Pb onto soil and soil and RE-
409 CHAR[®] in the column plants. Adsorption temperature, flow rate and initial Pb
410 concentration: 20 ± 0.5 °C, 60 mL/h, 100 mg/L.

411
412 The breakthrough curves obtained for soil and soil and biochar columns showed
413 approximately the same shape: a rapid increase of C/C_0 after breakthrough ($C/C_0 = 5\%$),
414 followed by a trend at a much slower rate towards the exhaustion ($C/C_0 = 95\%$). However, it
415 is worth noting that breakthrough times were reached much faster in the column containing
416 soil only with respect to the column filled with soil and biochar: i.e. few hours and 15 h,
417 respectively. Similarly, exhaustion times appeared after about 25 h and 40 h, respectively.

418 The breakthrough curves of Pb adsorption onto soil and soil and RE-CHAR[®], reported in
419 Figure 6, highlight that the addition of biochar significantly enhanced the adsorption capacity
420 and the operation time of the column plant with respect to the column containing only soil.
421 This implies a higher amount of metal uptaken by the adsorbent and a less frequency of
422 adsorbent bed replacement/regeneration after exhaustion, which lead to reduced operating
423 costs of the treatment plant.

424 Within the specialized literature only one reference could be found on the application of
425 biochar as adsorbent media in a column plant for lead removal from water, which is the work
426 by the same authors (Boni et al. 2018b). Therefore, the findings of the present study can play
427 a key role in view of the implementation of this adsorption process at full-scale which usually
428 applies a column system.

429 By integrating the breakthrough curves between $t = 0$ and $t = 50$ h (which was fixed as
430 the end of the column tests), it was possible to determine the experimental value of the
431 adsorption capacity: this resulted to be equal to $q_{\text{exp}} = 230.96$ mg/g for the column filled with
432 soil and RE-CHAR[®] and $q_{\text{exp}} = 67.07$ mg/g for the column containing soil only. Taking into

433 account that the amount of soil was the same in both columns, the adsorption capacity of RE-
434 CHAR[®] only it was calculated to be 163.89 mg/g.

435 Among the three mathematical models tested, the Thomas equation provided a better
436 description of the experimental breakthrough curves ($R^2 = 0.853$), compared to Yoon–Nelson
437 ($R^2 = 0.850$) and Bohart–Adams ($R^2 = 0.788$). Boni et al. (2018b) also found that Thomas
438 model provided the best fitting of the breakthrough curve experimental data, using biochar
439 from poplar, oak, robinia, platanus, willow, apple and pear wood, for the treatment of a lead
440 contaminated solution. The Thomas rate constant (k_{TH}) and the adsorption capacity (q_0) were
441 obtained from the intercept and the slope of the linearized form of the model equation. By
442 plotting $\ln(C_0/C-1)$ versus t , the following values were found: $k_{TH} = 5.28 \times 10^{-5}$ mL/min·mg
443 and $q_0 = 334.57$ mg/g.

444 The adsorption capacity predicted by the model was higher than that experimentally
445 determined, i.e. $q_{exp} = 230.96$ mg/g; the difference indicates that the adsorbent media had not
446 reached complete saturation at the end of the tests, i.e. at $t = 50$ h, and therefore it still
447 possessed adsorption sites which could be potentially occupied by the adsorbate. As expected,
448 the higher driving force of the adsorption process acting in the continuous flow column plant
449 determined a higher uptake capacity than that measured under batch conditions.

450 In the paper above cited (Boni et al. 2018b), the adsorption capacity predicted by the
451 Thomas model was found to be of the same order of magnitude. thus confirming the data
452 herewith obtained; however, the previous study measured a value of $q_0 = 270.57$ mg/g which
453 is slightly lower, likely due to the different type of feed source for the biochar.

454 The value of q_0 predicted by the model was very similar to the data reported in the
455 specialized literature for the lead maximum adsorption capacity by adsorbents other than
456 biochar used in column plants (Boni et al. 2018b; Harris 2009; M. Inyang et al. 2011; M. I.

457 Inyang et al. 2016; Y.-H. Li et al. 2003; Liu and Zhang 2009; Mahdi et al. 2018; Mohan et al.
458 2007; Uchimiya et al. 2010).

459

460 **4. Conclusions**

461 The present paper demonstrated that RE-CHAR[®] biochar, which is currently used as a
462 soil improver, can be also considered an efficient adsorbent media for the remediation of
463 highly lead-contaminated solutions.

464 For instance, in batch applications, a low dosage and a short contact time are needed to
465 treat the contaminated solution to the point that it is possible to release it into surface waters
466 and sewage systems complying with the limits set by the Italian legislation

467 In the continuous flow applications, operation times of the column plants can be
468 significantly extended by adding biochar to the soil within the adsorbent bed.

469 Therefore, application of RE-CHAR[®] biochar in place of commercial adsorbents is
470 technically and economically feasible.

471 For the optimal exploitation of the RE-CHAR[®] biochar capacity, further tests are
472 required under real operating conditions and with more complex contaminated solutions.

473

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476 biochar.

477

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