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Copper removal from contaminated soil through electrokinetic process with reactive filter media

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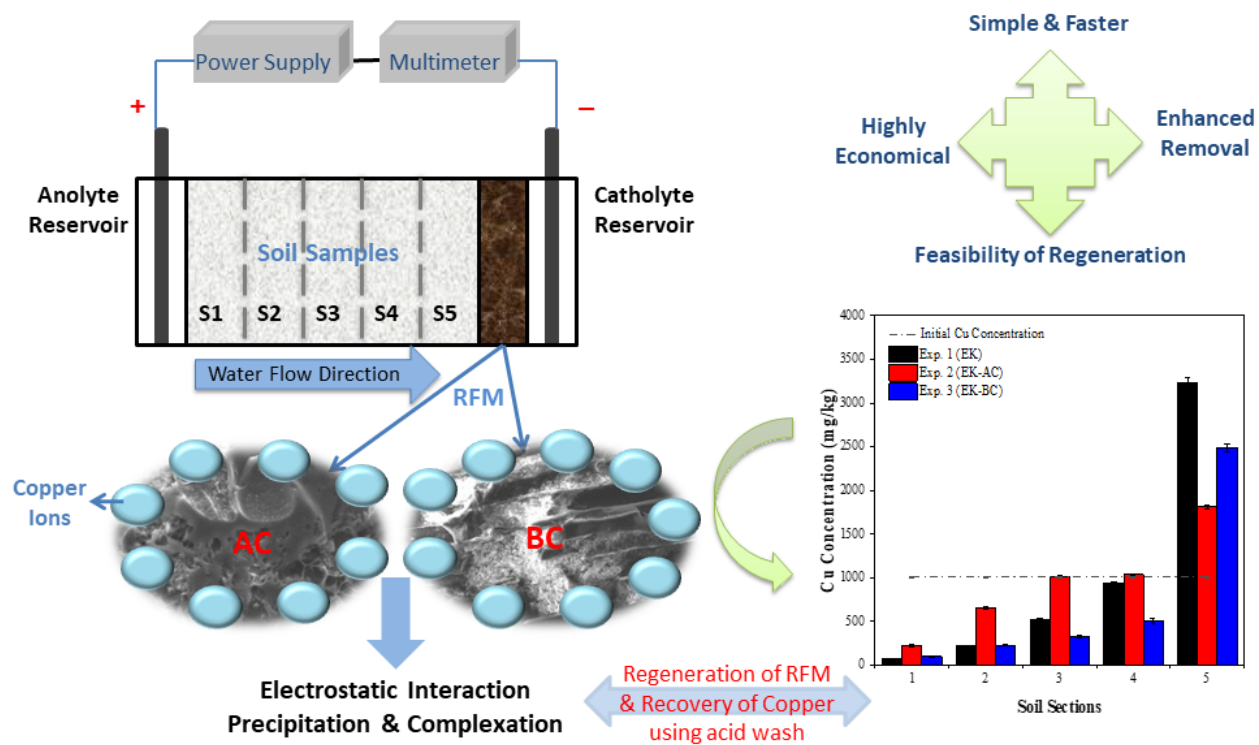
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Journal

1 **Copper removal from contaminated soil through electrokinetic process with**
2 **reactive filter media**

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19 **Abstract**

20 Electrokinetic (EK) has been used in the removal of metal ions from contaminated soil. This
21 study focused on integrating the EK technique with different reactive filter media (RFM) of
22 activated carbon (AC) and biochar (BC) for the first time without adding chemicals to
23 facilitate the removal of copper ions from the contaminated kaolinite soil. Tests based on EK,
24 EK coupled with AC (EK-AC), and EK combined with BC (EK-BC) were performed under
25 an electric potential of 10 volts, and the overall removal efficiency of copper ions decreased
26 as EK-BC > EK-AC > EK. The results show that 27% of copper in the soil was captured by
27 BC, compared with only 10% by AC. Additional EK-BC test performed under a constant
28 current (20 mA) revealed that the acid front swept across the soil, resulting in 70.6-95.0%
29 copper removal from soil sections 4 to 1 close to the anode region with more copper
30 accumulation in section 5. Similar to the EK-BC test under a fixed voltage, 26% of copper in
31 the soil was captured by BC during EK-BC treatment under a constant current although with a
32 higher energy consumption. Moreover, RFM was regenerated by flushing with an acid
33 solution, achieving 99.3% of copper recovery in BC and 78.4% in AC. Although the
34 permeability of AC-RFM was higher than that of BC-RFM, copper contaminant was more
35 easily leached out from the BC-RFM. The findings demonstrated the feasibility of
36 contaminant entrapment in BC-RFM and recovery by acid leaching, with potential for
37 sustainable soil remediation.

38

39 *Keywords:* Electrokinetic; Reactive filter media; Biochar; Activated carbon; Copper; Soil
40 decontamination

41 1. Introduction

42 Soil provides essential resources to both humans and nature (Lima et al., 2017), and soil
43 contamination is a globally significant concern, which may result from a variety of
44 agricultural, industrial and other human activities (Bi et al., 2011; Gomes et al., 2012;
45 Cameselle et al., 2013; Belhaj et al., 2016; Nguyen et al., 2019). Heavy metals are widely
46 detected in soil, and are of great risk to the environment and public health due to their toxicity
47 and persistence (Yuan et al., 2016; Nguyen et al., 2019). Great efforts have been made to
48 overcome the problems associated with soil pollution, by developing different strategies and
49 methods (Song et al., 2017). Electrokinetic (EK) remediation stands out as an alternative
50 technique that overcomes the shortcomings in the other decontamination techniques, such as
51 applicability for the low-cost and on-site treatment of low-permeability soils (Agnew et al.,
52 2011). EK soil remediation has been tested under laboratory and field conditions for the
53 potential applications in soil remediation and treatment (Zhao et al., 2016; Fu et al., 2017;
54 Sivapullaiah et al., 2015; Hassan et al., 2015; Iannelli et al., 2015; Kim et al., 2011).
55 Regarding the results of laboratory tests and field applications, the EK remediation technique
56 has several barriers when applied as a single remediation process (Peng et al., 2011). When
57 the direct current is imposed across the treated soil, an alkaline pH front is developed near the
58 cathode region, resulting in contaminants precipitation and retarding further contaminants
59 transport and removal. On the other hand, contaminants precipitation in the soil near the
60 cathode requires further treatment to prevent contaminants rebound in soil.

61 Progress has been made to enhance the extraction efficiency of electrokinetic remediation
62 in the last decades (Yeung and Gu, 2011; Lima et al., 2017; Zhao et al., 2016; Lim et al.,
63 2004; Lohner et al., 2008; Yeung, 2011). The current efforts focus on improving the
64 efficiency of the EK process, and facilitating its applicability by adding enhancement agent
65 such as surfactants and chelating agents to enhance the contaminant mobility, or acids/bases
66 solution to control the pH of the electrolyte, and application of a combined system such as

67 EK-bioremediation, EK-phytoremediation and EK-permeable reactive barrier (PRB) (Yeung
68 and Gu, 2011; Lim et al., 2004; Lohner et al., 2008; Li et al., 2020). However, the choice of
69 an appropriate enhancement technique is significantly important in the EK system in terms of
70 treatment duration, cost, and environmental impact. For example, the application of the
71 enhancement agent may affect the soil matrix, then the electrolyte ought to be recouped at the
72 end of the EK treatment (Lim et al., 2016; Yeung, 2011). The application of enhancement
73 agents in the EK remediation system has not always been favoured since some laboratory
74 tests were not successful (Tian et al., 2017). The capability of an EK remediation process
75 utilizing blends of eco-friendly improving agents (e.g. rhamnolipids, saponin, citric acid) was
76 evaluated for the first time by Tian et al. (2017) to simultaneously remove contaminants
77 including Cd, Cr, Cu, Pb, Zn and PAH/PCB from harbor sediments. Their experimental
78 results demonstrated that the mixture of the agents could only remove small quantities of
79 metals (4.4–15.8%) and only a slightly better removal of PAH (29.2%) and PCB (38.2%).
80 Among these enhancement techniques, PRB offers the enrichment or detoxification of the
81 contaminants with a short treatment period and prevents the contamination of the catholyte
82 solution (Zhao et al., 2016). A range of experimental studies have been recently conducted in
83 integrating PRB application with EK in order to improve contaminants removal from soil
84 during the EK remediation (Zhao et al., 2016; Yuan and Chiang, 2007; Ma et al., 2010; Ren et
85 al., 2014; Cang et al., 2009; Yuan et al., 2009). When a PRB is combined with an
86 electrochemical remediation, the transport of contaminants through the barrier is provided by
87 the electroosmotic flow of soil pore fluid, electromigration of charged species, and
88 electrophoresis of charged particulates. The reactive barrier becomes an adsorbent for the
89 contaminants during the electroosmosis and electromigration process. One of the
90 significances of the EK-PRB approach is the reduction of contamination concentration in the
91 catholyte and anolyte solutions (Zhao et al., 2016), therefore eliminating the need for their
92 recycling. The sorption and degradation reactions of many contaminants are pH dependent,

93 hence the pH gradient generated by the EK remediation process may affect the sorption and
94 degradation mechanism in PRB (Yeung and Gu, 2011). When a PRB is applied in the EK
95 remediation system to improve its remediation efficiencies of organic, inorganic, or mixed
96 contaminants, consideration should be given to factors such as the type, cost, and particularly
97 the lifetime of reactive media which would limit its applications. The treatment media in
98 PRBs implemented with EK may include a different kind of adsorbent materials such as zero-
99 valent iron (ZVI), activated carbon (AC), and activated bamboo charcoal (Zhao et al., 2016;
100 Yuan and Chiang, 2007; Ma et al., 2010; Ren et al., 2014; Cang et al., 2009; Yuan et al.,
101 2009). Among all PRBs, ZVI is the most popular reactive material due to its low cost (Cang
102 et al., 2009). However, the lifetime of ZVI is short because of the contamination coating the
103 surface of the ZVI particles, preventing flow through the barrier (Cang et al., 2009).
104 Additionally, iron reactivity can be decreased if it is exposed to silica or natural organic
105 matter (Ren et al., 2014; Cang et al., 2009). In an investigation into the application of ZVI as
106 a PRB in EK remediation of Cr-contaminated soil, Cang et al. (2009) reported that the
107 electrochemical remediation coupled with a ZVI-PRB could achieve 72% removal efficiency
108 of Cr, and the amount of Cr in the anolyte and catholyte was smaller when EK was combined
109 with ZVI.

110 The application of AC as RFM in the EK system was evaluated in the copper contaminated
111 kaolinite soil. AC is widely used as an adsorbent material in both water and soil treatment as
112 it has shown high performance of contaminants removal (Brändli et al., 2008; Ando et al.,
113 2010; Bhatnagar et al., 2013; Ahmed et al., 2015). Due to its high surface area, AC removes
114 metal contaminants from soil through surface adsorption (Üçer et al., 2006). Despite the
115 advantages of AC, there are also concerns such as the high production costs and availabilities
116 of sufficient amounts of suitable forms of AC (Alhashimi and Aktas, 2017; Ahmed et al.,
117 2015). Accordingly, there is intensive research in using alternative carbon material especially
118 biochar (BC) for contaminant removal (Beesley et al., 2010; Ahmed et al., 2015; Alhashimi

119 and Aktas, 2017). Alhashimi and Aktas (2017) reported that BC has lower energy demand
120 and global warming potential impact compared with AC. BC has been successfully applied in
121 recent years to reduce the mobility of heavy metals in soil because of its affinity for heavy
122 metals, low cost, and availability (Beesley et al., 2010; Khalid et al., 2017; Zeng et al., 2015;
123 Alhashimi and Aktas, 2017). BC has some significant features such as higher porosity, high
124 surface area, variable charge, and functional groups, and when added to the soil can change
125 the soil properties (Beesley et al., 2010; Anawar et al., 2015). As a result, these features can
126 enhance soil water-holding capacity, pH, surface sorption capacity, cation exchange capacity
127 (CEC), and base saturation (Beesley et al., 2010; Anawar et al., 2015).

128 In the EK process, the extraction of heavy metal ions precipitated in the soil near the
129 cathode region complicates the remediation process due to the low permeability of most
130 contaminated soils. Studies on the impact of RFM on the performance of the EK process for
131 metal removal from soil are scarce. This study investigated the performance of the EK
132 process for copper removal using AC and BC as RFM. BC has a high affinity for heavy metal
133 adsorption, and there is no study yet comparing the impact of the type of RFM on the
134 efficiency of heavy metal removal in the EK process. The impact of AC and BC as RFM on
135 the removal of heavy metals from soil and the energy requirements for the EK treatment were
136 investigated and compared with the performance of the conventional EK process (without
137 RFM). This study selected copper to be the heavy metal contaminant due to a large number of
138 reports on soil contamination by copper ions (Boiteau et al., 2011; Hadri et al., 2012), which
139 requires remediation. Furthermore, AC and BC RMFs have the potential of buffering alkaline
140 pH near the cathode and hence the advancement of an alkaline front in the soil. RFM is
141 loaded close to the cathode zone to trap copper ions precipitated in the soil near the cathode.
142 The high permeability of AC and BC will facilitate the extraction of copper ions at the end of
143 the EK process while AC and BC RMFs will be recycled and reused. Both AC and BC are
144 cost-effective and permeable, and have good adsorption capacity for heavy metals; hence,

145 they can provide long-term services as they can be regenerated by acid leaching. This study
146 will provide valuable knowledge of the performance of RFM in the EK system while
147 comparing their performance in terms of removal efficiency and regeneration potential.

148

149 **2. Materials and methods**

150 *2.1. Materials and soil preparation*

151 Commercial kaolinite in the form of a fine white powder obtained from the N-Essential Co.
152 Ltd (Australia) was used as a model soil in this study, and its characteristics are summarised
153 in **Table 1**. Briefly, 1000 g of the kaolinite soil was used in each EK test. Prior to testing, 2.52
154 g of copper sulphate (CuSO_4 , Aldrich, UK) was weighed and dissolved in 1 L of distilled
155 water. The Cu solution was stirred on a magnetic stirrer for 20 min, then added to the soil and
156 mixed thoroughly with a stainless spatula. The contaminated soil was stored for 72 h to allow
157 for copper adsorption by the soil to occur and reach equilibrium (Altaee et al., 2008). The
158 saturated soil was packed into the electrokinetic cell in layers and compacted uniformly using
159 a hand compactor. The initial electric conductivity (EC) and pH of kaolinite soil were
160 measured using a multi-metre (model HACH HQ40d), by making a soil suspension with a
161 ratio of 1:5 (w/v) dry soil to distilled water and stirring on magnetic stirrer for at least 5 min.
162 Soil sample was dried in an oven at 105 °C overnight. Copper concentration (**Table 1**) was
163 measured by a Vanta handheld X-ray Fluorescence (XRF) analyzer (M series), from Olympus
164 Corporation. AC and BC RFM were used in two separate electrokinetic remediation processes
165 under the same experimental conditions to investigate the feasibility of copper removal from
166 the kaolinite soil. In each experiment, a measured amount of RFM was placed in the soil
167 compartment close to the cathode to trap the copper ions and buffer the advancement of
168 alkaline front in soil. The chemical and physical properties of RFM used in this study are
169 presented in **Table 2**. Briefly, 25 g of granular activated carbon (GAC), purchased from
170 James Cummings and Sons Pty Ltd, Australia, was evaluated as an adsorbent for the copper

171 removed by the electrokinetic process. At the end of the EK experiment, precipitated copper
172 ions were leached out of AC RFM by flushing with an acid pH solution before reuse to reduce
173 the treatment cost.

174 BC was obtained from Karr Group Co, USA (**Table 2**). BC (25 g) was packed in the EK
175 cell near the cathode to capture copper ions. Similar to the soil pH measurement procedure,
176 the pH of AC and BC was determined to be slightly alkaline at 8.2 and 8.95 respectively,
177 which is suitable for the precipitation of copper ions (**Table 2**). The permeability of the RFMs
178 was measured by the constant head flow permeability test, which was recommended for the
179 coarse-grained soils with regard to AC and BC particle sizes (Table 2). A scanning electron
180 microscope (SEM) with energy dispersive spectrometer (EDS) (model Zeiss Evo-SEM) was
181 used to determine the morphological and chemical composition of the RFMs. Fourier
182 transform infrared spectroscopy (FTIR) (Miracle-10: Shimadzu) was used to determine
183 surface functional groups. The spectra of RMFs were obtained by measuring the absorbance
184 from 400 to 4000 cm^{-1} using a combined 40 scans. The zeta potential values of the AC and
185 the BC were measured using a Nano-ZS Zeta-seizer (Model ZEN3600) from Malvern
186 Panalytical, before and after the EK treatment.

187

188 *2.2. EK reactor setup*

189 A schematic diagram of the EK experimental apparatus and the EK cell used in this study is
190 shown in **Fig. 1**. The electrokinetic experiments were conducted in a 23 cm \times 8 cm \times 11 cm
191 reactor, made of plexiglass material to facilitate visual observation. This reactor consisted of
192 three compartments: two electrode compartments placed at each end of the sample
193 compartment and the contaminated soil compartment. On both sides, two graphite rod
194 electrodes (15 cm \times 1 cm) were connected to a DC bench power supply (EA-PS 3016-10B,
195 EA Electro-Automatik) to apply the electric current, which was recorded hourly using a
196 current meter (Keithley 175 Autoranging multimeter). The graphite electrodes were purchased

197 from Graphite Australia Pty Ltd. Two cellulose filter papers (pore size 5-13 μm , LLG
198 Labware), supported by a perforated plexiglass plate, were placed between the soil and the
199 electrode compartments to prevent soil particles penetrating into the electrolyte cells. RFM
200 was loaded into the soil compartment near the cathode, and a filter paper was also placed
201 between RFM and the soil to separate them at the end of experiment. Distilled water was used
202 as the anolyte and catholyte solution, respectively. Distilled water was periodically added to
203 the anolyte compartment to replenish water losses due to the electroosmotic flow and water
204 electrolysis.

205

206 *2.3. Test design*

207 Four sets of EK experiments were conducted to investigate copper removal from the
208 contaminated kaolinite soil (**Table 3**). In all tests, a constant voltage (10 V) was applied
209 across the electrodes, except in Exp. 4, which was performed under a constant current of 20
210 mA. The experiments were stopped after seven days when the electric current across the soil
211 specimen diminished, and the electroosmotic flow was decreased.

212 Exp. 1 was the conventional EK experiment on spiked kaolinite with 1000 mg kg^{-1} copper
213 concentration. Exp. 2 and Exp. 3 were carried out to investigate the effect of RFM, AC and
214 BC, respectively, on the electrokinetic removal of copper from the kaolinite soil. Exp. 4 was
215 implemented to investigate the performance of EK-RFM under constant electrical current of
216 20 mA.

217 At the end of experiments, aqueous solutions from the anode and cathode compartments
218 and the electrode assemblies were collected. Then, the soil specimen was divided into five
219 equal sections, and each section was preserved in plastic bags. Each soil section was then
220 homogenized, and samples were taken for pH, EC, and copper concentration measurements.

221

222 **3. Results and discussion**

223 *3.1. Electrical current*

224 During the electrokinetic treatment, electrical current through soil cell is strongly correlated
225 with the content of free ions; hence, electrical current is an essential factor affecting the
226 efficiency of contaminants transmission through soil (Zhou et al., 2017; Zhu et al., 2016). The
227 change of electric current over time in Exp. 1 to Exp. 3 is shown in **Fig. 2a**. Generally, in the
228 EK system, the electric current initially increased to a maximum value within a short time due
229 to the solubilisation and movement of ions in the soil towards the cathode compartment
230 (Ammami et al., 2015). Then, the electric current gradually reduced as a result of metal ions
231 precipitation close to the cathode zone or in the high soil pH (Ammami et al., 2015;
232 Bahemmat et al., 2016; Zhu et al., 2016). With increasing electric current, the higher copper
233 removal was achieved by the EK test. The electrical current was low at the beginning of the
234 EK experiments since it takes time for anolyte and catholyte to enter the contaminated soil
235 and for contaminant ions to dissolve and desorb from the soil (Zhou et al., 2017). The
236 electrical current in the EK and EK-BC experiments was higher than that in the EK-AC test.
237 In the EK experiment, the electric current reached the peak (15 mA) after 24 h but started
238 decreasing dramatically thereafter due to the depletion in the migration of copper ions in soil-
239 pore fluid and the precipitation of $\text{Cu}(\text{OH})_2$ at the cathode region. The electrical current
240 reached 7.21 mA after 168 h at the end of the EK treatment. The electric current in the EK-
241 BC reached a maximum amount of 14.9 mA after 48 h then dropped to 6.79 mA at the end of
242 the EK process. However, in this experiment, the electric current remained higher for a longer
243 period compared to that of the EK test. The reason may be attributed to the adsorption of
244 hydroxide ions generated at the cathode reaction by BC, which promoted the transport of the
245 acid front in the soil. This caused solubilisation and movement of copper ions in the soil and
246 resulted in an increase in the electric current in the EK-BC test. The average electric current
247 was similar between the EK-BC (11.33 mA) and EK (11.30 mA) processes. The electric
248 current in the EK-AC test was relatively low, with the average and maximum electric current

249 of 5.522 mA and 7.9 mA, respectively, which would adversely affect the removal of copper
250 ions in the soil.

251 3.2. Soil pH

252 Soil pH has a significant impact on the environmental behaviour of heavy metals in soil. Low
253 pH environment can improve the dissolution of heavy metals and removal from the
254 contaminated soil (Yuan et al., 2016). Chemical reactions during the EK process would cause
255 a substantial change in soil pH and result in contaminant dissolution or precipitation
256 (Cameselle et al., 2013). The distribution of pH across the soil from anode to cathode
257 (sections 1 to 5) after the remediation experiments is shown in **Fig. 2b**. It is clear that the
258 electrokinetic process changed the soil pH. In general, the soil pH after EK treatment was low
259 in sections close to the anode side due to hydronium ions transport across the soil, but
260 gradually increased in the soil sections close the cathode as a result of hydroxide ions (OH^-)
261 migration in the soil from the cathode to the anode (Yuan et al., 2016; Fu et al., 2017). The
262 reduction in pH favoured the removal of the contaminants, because of the production of
263 H^+ ions from water electrolysis at the surface of the anode ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) (Zhao et
264 al., 2016; Masi et al., 2017). An increase in the soil pH in the sections near the cathode was
265 due to the advancement of OH^- generated through water electrolysis at the cathode ($2\text{H}_2\text{O} +$
266 $2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$) and affected the pH distribution across the soil. As observed in **Fig. 2b**, the
267 pH profile from section 1 to section 5 in the EK-BC test was lower than that of the EK and
268 EK-AC experiments, especially in the soil sections close to the cathode region (sections 3 to
269 5), which would favour copper removal by EK-BC. It was probably caused by the interaction
270 between BC and hydroxide ions in the soil near the cathode. EK-AC test generally showed
271 higher soil pH in the sections 1 to 4 (except section 5), compared to those of the EK and EK-
272 BC experiments. Higher pH across the soil sections confirmed that the application of AC in
273 the EK system did not assist in the removal of copper ion from the soil sections close to the
274 anode side. However, the soil pH in section 5 was lower in the EK-AC than that in the EK,

275 resulting in less copper precipitation in the soil close to the cathode (**Fig. 3**). It seems that
276 both RFM could trap contaminants by lowering the soil pH close to the cathode. However,
277 AC RFM unfavourably served during the EK process for copper removal in most soil sections
278 compared to the results in the EK and EK-BC (**Fig. 4a**). In **Fig. 2b**, it is clearly illustrated that
279 the soil pH with the value above the initial pH of the soil (pH 5.44) would cause contaminant
280 precipitation in the soil during the EK treatment, as observed in section 5 in all EK tests with
281 or without RFM. EK treatment also affected the pH of RFMs, especially BC which
282 dramatically increased from 8.95 to 11.07 while pH of AC changed from 8.2 to 9.34.

283

284 *3.3. Electrical conductivity of soil*

285 The soil EC of different sections after seven days of EK treatment presented a decreasing
286 trend from the anode to the cathode (**Fig. 2c**). In general, the results of soil EC were
287 consistent with those of soil pH, demonstrating that the content of free ions in the soil near the
288 anode region was higher than that close to the cathode. The reason would be that the acid
289 condition facilitated the dissolution of ions in the soil, as demonstrated in **Fig. 2c**. The soil
290 conductivity of the EK-AC was the lowest because of copper precipitation in the soil at early
291 stage of the EK process and hence reduced the soil EC. Additionally, acid and alkaline fronts
292 met closer to the anode in the EK process when AC was applied as an RFM. EK-BC showed
293 more electrical conductivity because of more copper solubilisation due to the migration of
294 acid front closer to the anode and hence solubilizing more copper ions. The soil EC in the EK-
295 BC test was higher than that of the EK and the EK-AC systems, because of the lower soil pH
296 in the EK-BC, which caused higher dissolution of copper ions in the soil.

297

298 *3.4. Removal of copper from soil*

299 **Fig. 3a** shows the distribution of residual copper in soil after remediation. Copper distribution
300 in the soil follows the profile of soil pH, which is very acidic close to the anode side and

301 continuously increased towards the cathode where it is slightly alkaline (**Fig. 2b**). For the EK
 302 and EK-BC, copper concentrations were found to be lower than the initial concentration of
 303 copper in the soil, particularly in the sections close to the anode (sections 1 to 4) (**Fig. 3a**).
 304 Most of copper ions were accumulated in section 5, close to the cathode region through
 305 precipitation as $\text{Cu}(\text{OH})_2$ due to the high soil pH.

306 The residual concentrations of Cu in the soil sections, especially in sections 3 to 5 for the
 307 EK with BC RFM (Exp. 3) were significantly lower than those of the EK and EK-AC tests.
 308 Cu transport rate toward the cathode was enhanced in the EK-BC compared to the EK and the
 309 EK-AC. This is probably due to the lower soil pH (**Fig. 2**) in the EK-BC, which enhanced the
 310 efficiency of EK process and copper removal. In the case of the EK-BC experiment, the
 311 concentration of Cu decreased rapidly from the initial concentration (1000 mg kg^{-1}) to about
 312 100 mg kg^{-1} in section 1, gradually increased to about 500 mg kg^{-1} in section 4, and reached
 313 2490 mg kg^{-1} in section 5. For the EK-AC test, copper concentrations were lower than the
 314 initial concentration in the sections 1 and 2, ranged between 230 mg kg^{-1} and 650 mg kg^{-1} ,
 315 and showed no significant changes in section 3 to section 4 compared with the initial Cu
 316 concentration. The results indicate that copper concentration in the soil was not affected when
 317 the soil pH was around the initial pH of the soil (**Fig. 2b**). Compared to the EK experiment,
 318 the integration of AC RFM in the EK system decreased Cu concentration mainly in section 5,
 319 which adversely affected Cu transport rate in the other soil sections toward the cathode. In the
 320 EK only process, the content of copper close to the anode was low ranging from about 100
 321 mg kg^{-1} to 220 mg kg^{-1} in sections 1 to 2, which is similar to that in the EK-BC. Then it
 322 reached approximately 950 mg kg^{-1} in section 4 and drastically increased to around 3250 mg
 323 kg^{-1} in section 5 while getting close to the cathode, because of the high pH in the region. The
 324 removal efficiency can be calculated by Eq. (1):

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_f}{C_0} \times 100 \quad (1)$$

325 where C_o (mg kg^{-1}) is the initial copper concentration in soil, and C_f (mg kg^{-1}) is the final
326 copper concentration in soil after EK remediation. As shown in **Fig. 3b**, in sections 1 to 4, the
327 copper removal ranges from 92% to 47% in the EK-BC system while it changes from 92% to
328 6.5% for the EK experiment. Hence, the application of BC in the EK system has not only
329 affected the Cu removal in section 5, but considerably in sections 3 and 4. For the EK-AC
330 test, Cu removal percentage was 78% in section 1, and then decreased to almost zero in
331 sections 3 and 4. High pH in section 5 resulted in the negative removal of Cu there for the EK
332 experiments. However, the negative removal in that section for the EK-AC test was less due
333 to low Cu transport rate through the soil. Hence, less free Cu ions were transported across the
334 soil from the anode to the cathode during the EK-AC treatment. **Table 4** shows the mass
335 balance and overall Cu removal in the EK experiments. The overall copper removal in the
336 EK-AC and the EK-BC was 10% and 27% respectively, higher than that in the EK test. The
337 application of BC represented the highest removal in the EK system without adding
338 chemicals. The soil pH was expected to be responsible for the different removal efficiencies
339 of copper in the EK treatments. According to the mass balance, the best performance was
340 obtained when BC was loaded in the EK cell near the cathode compartment (Exp. 3).

341

342 3.5. Characterisation of RFMs

343 The surface characteristics of RFMs, which were examined by SEM coupled with EDS (**Fig.**
344 **4**), clearly confirmed the presence of copper on BC and AC after the EK treatment. The
345 percentage of copper in BC was higher than that in AC RFM. EDS results showed that the Cu
346 content was 0.38% in BC and only 0.10% in AC, indicating that the removal of copper in the
347 EK treatment with BC RFM was higher than that in using AC RFM. Also, the zeta potential
348 measurements of the RFMs before and after EK experiments illustrated that the zeta potential
349 of BC was more negative than AC before EK treatment (**Fig. 5**), suggesting more negative
350 charges being available in BC than in AC. Therefore, BC can potentially adsorb larger

351 amounts of the positively charged heavy metal cations than AC. FTIR spectra are widely used
352 to provide valuable information on the functional properties of BC and AC (Lu et al., 2013;
353 Ahmed et al., 2017). Both BC and AC before and after EK treatment presented approximately
354 the same spectra. However, the stronger bands have been observed in BC, before and after EK
355 treatment compared to those in AC-EK operation, which demonstrates the great potential of
356 EK-BC for copper removal. The FTIR spectra from BC and AC after EK treatment (**Fig. 6**)
357 showed a peak in the region 3600-3700, which is related to OH stretching. A strong band at
358 approximately 1002.5 cm^{-1} is presented in EK-BC spectra attributed to copper absorption.

359

360 *3.6. Performance of EK-RFM under constant current*

361 Since the EK treatment with BC RFM exhibited a higher copper removal efficiency in the
362 contaminated kaolinite soil, further EK-BC experiments were carried out under constant
363 current of 20 mA to explore for treatment improvement. Copper concentrations in sections 1
364 to 4 significantly reduced, ranging from 50 mg kg^{-1} to 294 mg kg^{-1} and the majority of copper
365 was precipitated in section 5. Moreover, 26% of Cu was captured by BC. Approximately
366 70.6%-95.0% of copper removal was successfully achieved from sections 4 to 1 at an electric
367 current of 20 mA. The reason is due to a high electric current, which promoted water
368 electrolysis reaction at the anode and generated more hydronium ions that migrated across the
369 soil and facilitated the removal of copper ions from the soil. **Fig. 7** shows that soil pH was
370 acidic, except in section 5, which was higher than initial soil pH (5.44). This alkaline pH
371 retarded copper ions dissolution and resulted in significant precipitation of copper in section 5
372 close to the cathode compartment. It is concluded that maintaining a constant electric current
373 in the EK-BC operation could significantly enhance copper removal in the first four soil
374 sections close to the anode but did not decrease copper accumulation in section 5.

375 In relation, the energy consumption E_u (Wh m^{-3}), which is a major factor affecting the
376 total cost of the EK remediation (Yuan et al., 2017; Masi et al., 2017), was calculated by Eq.
377 (2) (Kim et al., 2012):

$$E_u = \frac{1}{V_s} \int V I dt \quad (2)$$

378 where V_s represents the volume of soil (m^3), V is the applied voltage (V), I the electric
379 current (A) and t the treatment time (h).

380 The energy consumption per unit volume of soil in the EK experiments (**Fig. 8**) shows
381 that the EK-AC approach was the least demanding and the EK-BC (constant current) was the
382 most demanding. Low energy consumption observed in case of EK-AC would be due to less
383 ion migration through the soil sections 1 to 4 which was compatible with the results shown in
384 **Fig. 2**. The EK and EK-BC experiments carried out under a constant voltage required almost
385 the same value of power consumption, at 10.78 and 10.81 kWh m^{-3} respectively. Of all tests,
386 the EK-BC under a constant electrical current consumed the highest amount of energy (43.5
387 kWh m^{-3}). At a constant electric current, high concentrations of dissolved ions would be
388 transferred through the system, particularly through the soil sections 1 to 4, which in turn
389 increased the rate of electrolysis reactions at the electrodes by sustaining the electric current
390 and thus producing the increased energy expenditure in this experiment. Such a high energy
391 consumption may limit its practical application compared with fixed voltage tests, since there
392 was not a significant difference between them in terms of overall Cu removal efficiency.
393 However, using solar cell-based power supply for EK remediation treatments will reduce
394 energy consumption when compared with traditional power supply (Jeon et al., 2015; Zhou et
395 al., 2017).

396

397 *3.7. Regeneration of RFM*

398 In order to be practicable, the regeneration of RFM is essential. A plastic column packed with
399 used RFM was flushed using a concentrated acid (HNO_3) solution with a pH of 1.5. The acid

400 solution was circulated by a peristaltic pump for 5 h at 5 mL min⁻¹ flow rate to facilitate the
401 recovery process. At the end of the leaching process, RFM was flushed with deionized water
402 to neutralize the pH to normal conditions before reuse. After leaching, samples of RFM were
403 tested for the copper concentration by XRF analyser. Moreover, the permeability of the RFMs
404 was measured by performing a constant head permeability test, and the result (**Table 2**)
405 demonstrated a high permeability of AC. However, XRF results suggested a higher copper
406 recovery by BC at 99.3% than by AC at 78.4%. The findings therefore favour BC for the
407 regeneration process and to be reused as RFM for future EK experiments.

408

409 **4. Conclusions**

410 This study investigated the remediation of Cu contaminated soil with integrated EK-RFM
411 treatment. The removal efficiency of Cu increased with the application of RFM which trapped
412 copper. The overall removal efficiency of the EK process decreased as EK-BC > EK-AC >
413 EK. BC adsorption of copper facilitated Cu removal in all soil sections while the application
414 of AC as RFM improved Cu removal only in soil section 5 near the cathode. Integration of
415 AC with EK technique increased soil pH in most of soil sections, except section 5, as well as
416 reducing the electric current through the soil. This reduced the rate of copper removal in the
417 majority of soil sections in the EK-AC system. However, AC RFM adsorbed a considerable
418 amount of Cu in soil section 5 due to interactions between AC and hydroxide ions near the
419 cathode. SEM-EDS results confirmed the presence of copper on BC and AC after EK
420 treatment, whereas the percentage of copper in BC was higher than that in AC. In addition,
421 the more negative charges available in BC than in AC could offer a higher copper removal
422 from contaminated kaolinite soil in the EK-BC treatment. BC could be easily recovered by
423 acid leaching after EK treatment; however, it has lower permeability compared to AC. The
424 application of a fixed electric current in the EK-BC process significantly enhanced the
425 removal rate of copper in soil, especially in the sections 1 to 4, by lowering the soil pH.

426 However, its high energy consumption may be a constraint in its wide application. It is
427 concluded that BC is a better RFM than AC in terms of EK performance, Cu removal and
428 regeneration. As the EK-RFM process has many advantages including short treatment
429 duration, easy installation, efficient contaminant removal, no chemical addition, and
430 feasibility of regeneration, it is a good technique for future sustainable soil remediation.

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433

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Table 1

Chemical and physical properties of kaolinite clay soil.

| Soil characteristics | Value |
|---|-----------------------|
| Particles size analysis (%) | |
| Clay (%) | 67.5 |
| Silt (%) | 30.5 |
| Sand (%) | 2 |
| Permeability (m s^{-1}) | 5.7×10^{-10} |
| Organic matter (%) | Negligible |
| Initial soil pH | 5.44 ± 0.04 |
| Initial electrical conductivity (mS cm^{-1}) | 0.50 ± 0.011 |
| Initial copper concentration (mg kg^{-1}) | 1000 ± 20 |

Table 2

Chemical and physical properties of RFMs.

| Parameter | Activated carbon | Biochar |
|---|-----------------------|-----------------------|
| Particle size analysis (%) | | |
| > 2 mm | 0 | 2.59 |
| 1-2 mm | 71.63 | 14.51 |
| <1 mm | 28.37 | 82.89 |
| Permeability (m s^{-1}) | 1.11×10^{-3} | 0.17×10^{-3} |
| Organic matter (%) | 89.2 | 98.36 |
| Surface area ($\text{m}^2 \text{g}^{-1}$) | 845.036 | 114.05 |
| pH | 8.2 ± 0.15 | 8.95 ± 0.05 |
| Electrical conductivity (mS cm^{-1}) | 2.4 | 0.11 |

Table 3

Summary of the experimental conditions applied.

| Experiment | Type | RFM | Applied constant voltage (V) | Applied constant current (mA) | Cu (mg kg^{-1}) | Treatment duration (d) |
|------------|-------|---------------------|------------------------------------|-------------------------------------|-------------------------------|---------------------------|
| Exp. 1 | EK | - | 10 | | 1000 | 7 |
| Exp. 2 | EK-AC | Activated carbon | 10 | | 1000 | 7 |
| Exp. 3 | EK-BC | Biochar | 10 | | 1000 | 7 |
| Exp. 4 | EK-BC | Biochar | | 20 | 1000 | 7 |

Table 4

Mass balance and removal efficiency of copper in the EK experiments.

| Experiment | Initial Cu in soil (g) | Residual Cu in treated soil (g) | Cu mass in RFM (g) | Cu mass in electrolyte solution (g) | Cu mass in soil pore water (g) | Mass balance (%) | Cu removal (%) |
|------------|---------------------------|---------------------------------------|--------------------------|---|--------------------------------------|---------------------|----------------------|
| Exp. 1 | 1.01 | 1 | - | 0 | 0.008 | 99.80 | 1 |
| Exp. 2 | 1.02 | 0.92 | 0.053 | 0 | 0.007 | 96.08 | 10 |
| Exp. 3 | 0.98 | 0.71 | 0.21 | 0 | 0.005 | 94.39 | 27 |

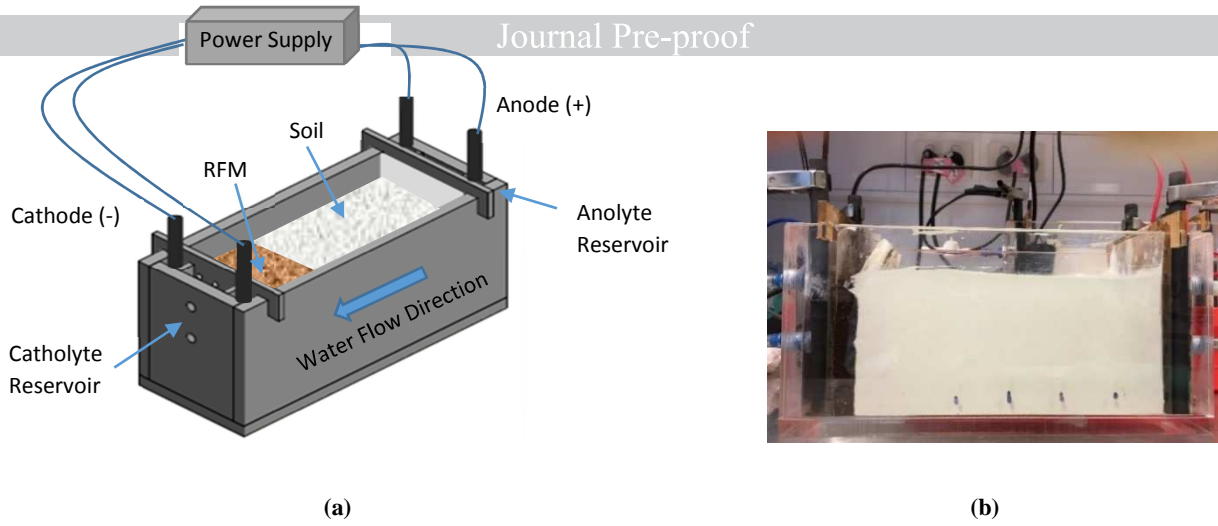


Fig. 1. (a) Schematic diagram of the EK apparatus; (b) front view of the EK apparatus.

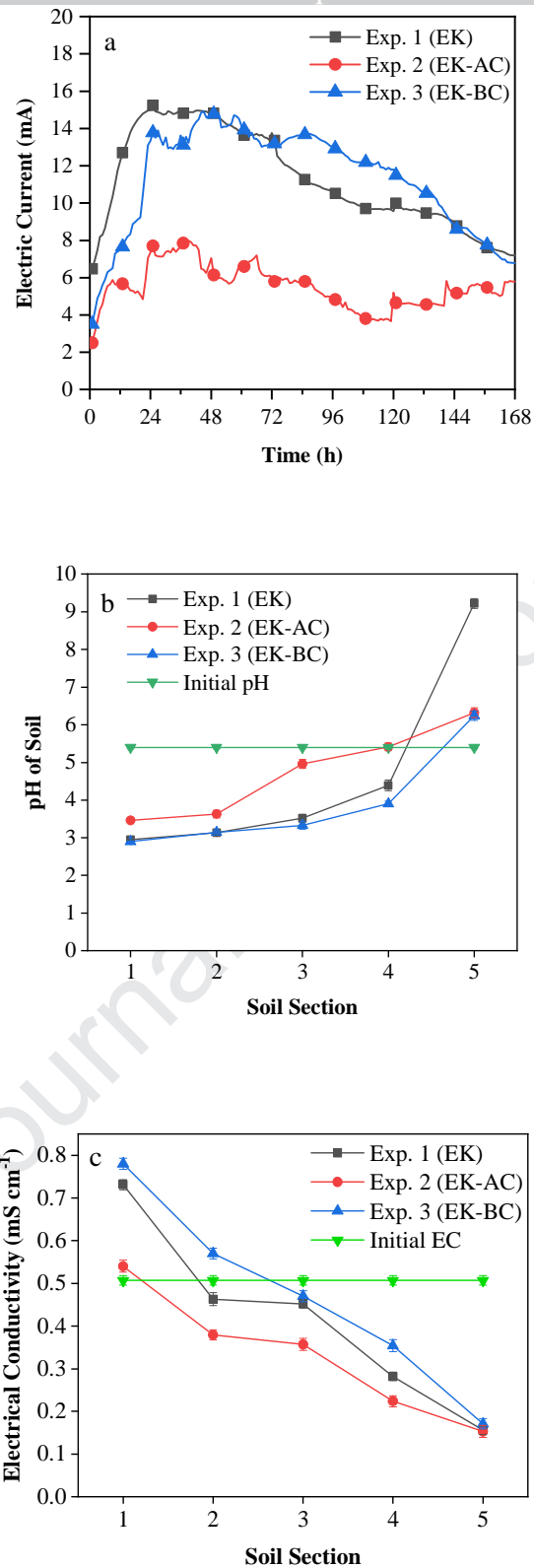


Fig. 2. (a) Change of electric current during the EK treatments (with a constant applied voltage); (b) pH of different soil sections (normalized distance from anode to cathode) after the EK operations; (c) EC of different soil sections (normalized distance from anode to cathode) after the EK operations.

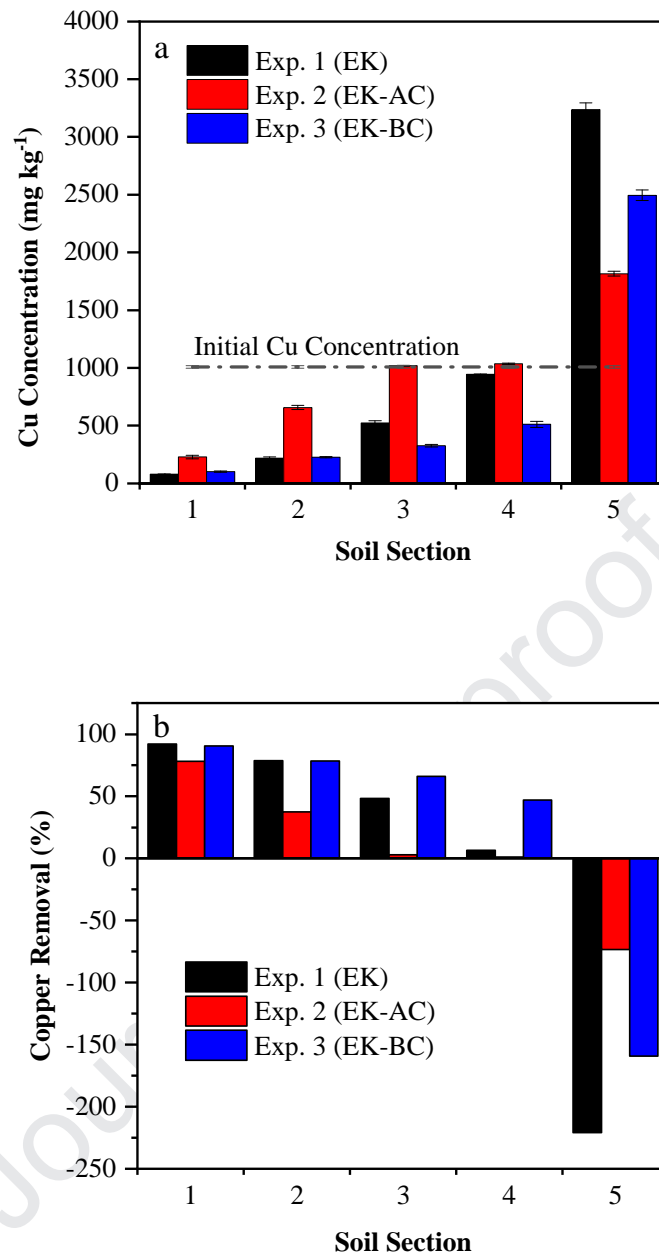


Fig. 3. (a) Copper concentration through the soil sections (from anode to cathode) after EK operation; (b) Efficiency of copper removal through the soil sections.

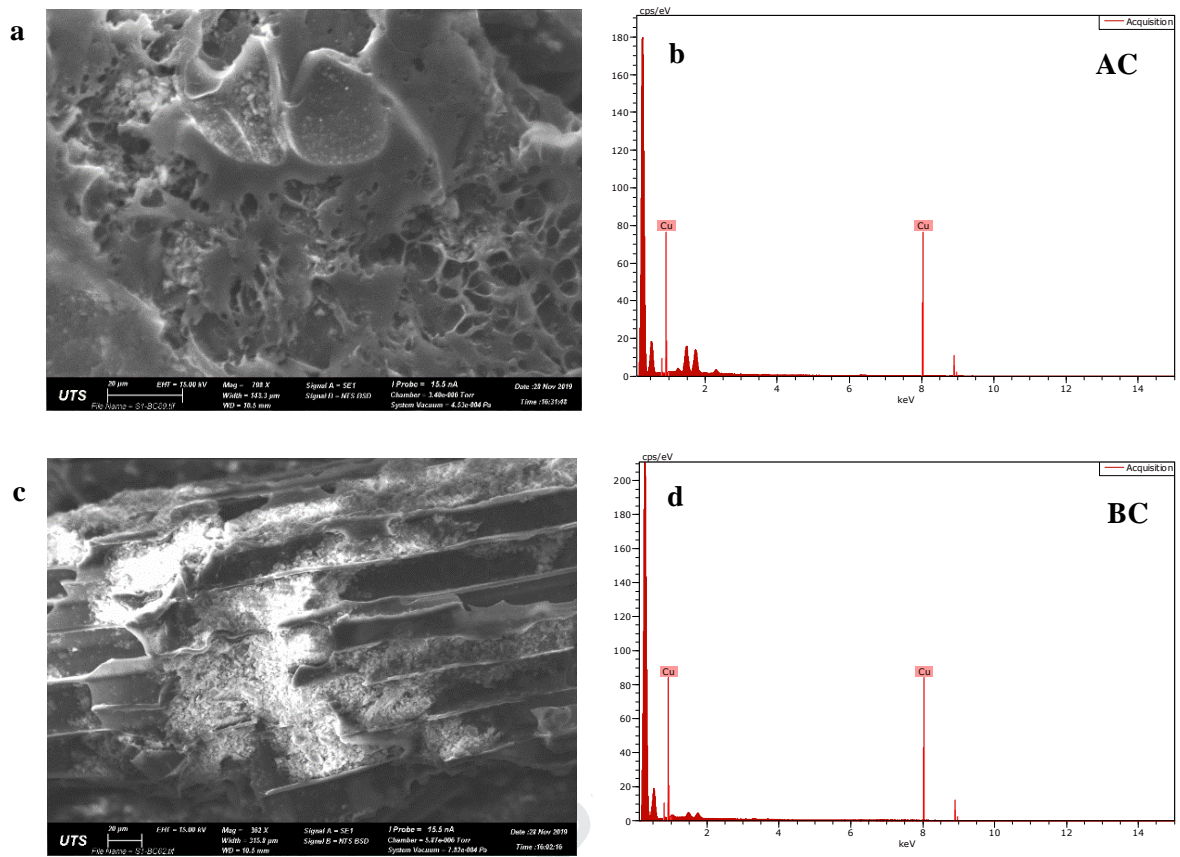


Fig. 4. SEM images and EDS of (a, b) activated carbon and (c, d) biochar after EK treatment.

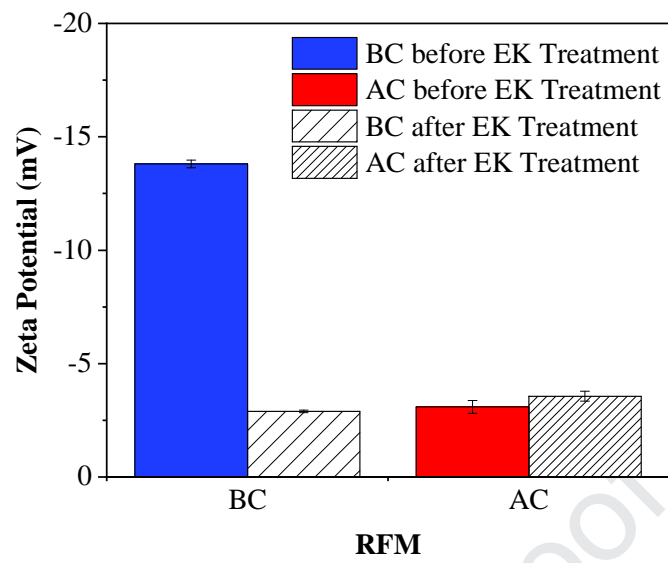


Fig. 5. Zeta potential of BC and AC before and after EK experiments.

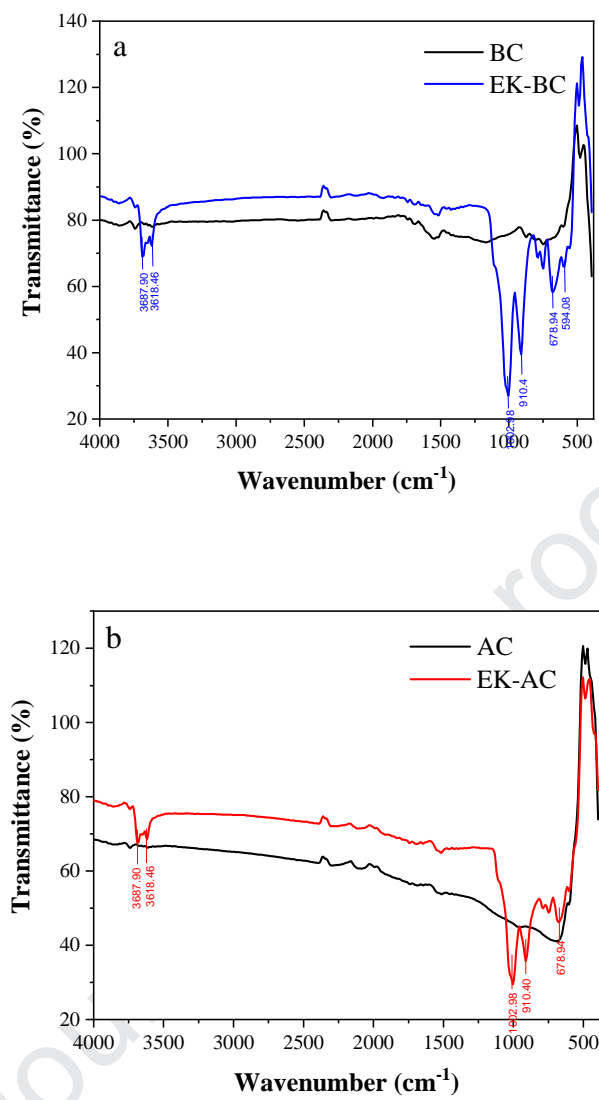


Fig. 6. FTIR spectra of (a) BC before and after EK treatment (EK-BC); (b) AC before and after EK treatment (EK-AC).

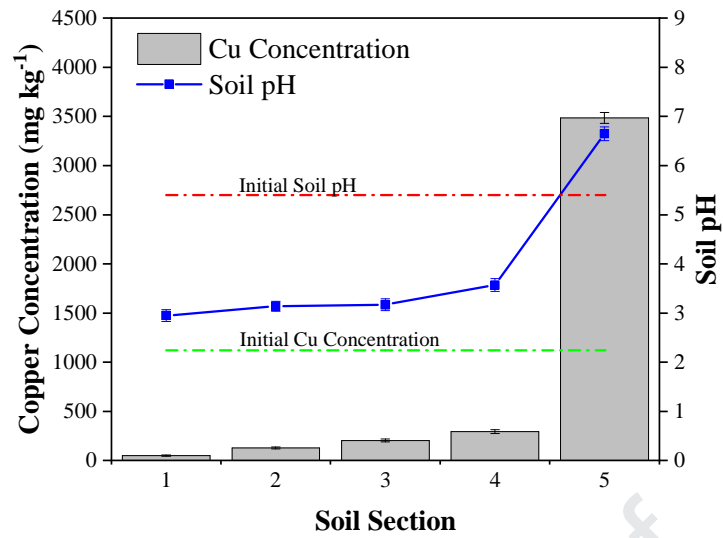


Fig. 7. Residual copper concentration and pH of the soil through the soil sections from anode to cathode after EK-BC treatment under constant current operation.

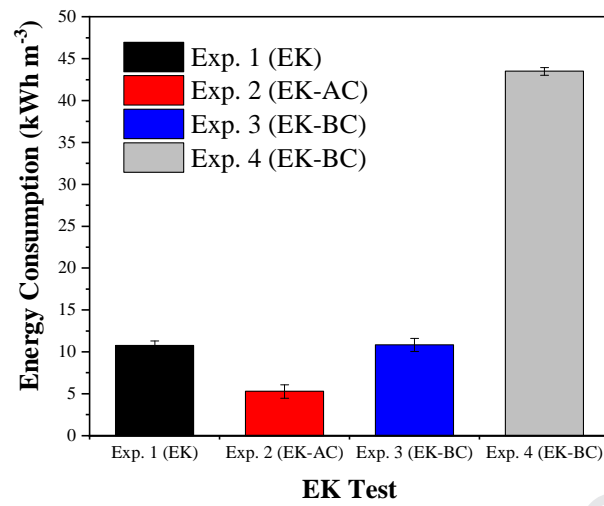


Fig. 8. Energy consumption per unit volume soil for different EK treatment.

Highlights

- Reactive filter media improved electrokinetic removal of Cu in contaminated soil
- Both AC and BC were suitable reactive filter media
- Overall removal efficiency decreased as $EK-BC > EK-AC > EK$
- A constant electric current in EK-BC improved Cu removal
- Reactive filter media was regenerated and reused

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: