

1 **Mechanistic insights into simultaneous removal of copper, cadmium and arsenic from**  
2 **water by iron oxide-functionalized magnetic imogolite nanocomposites**

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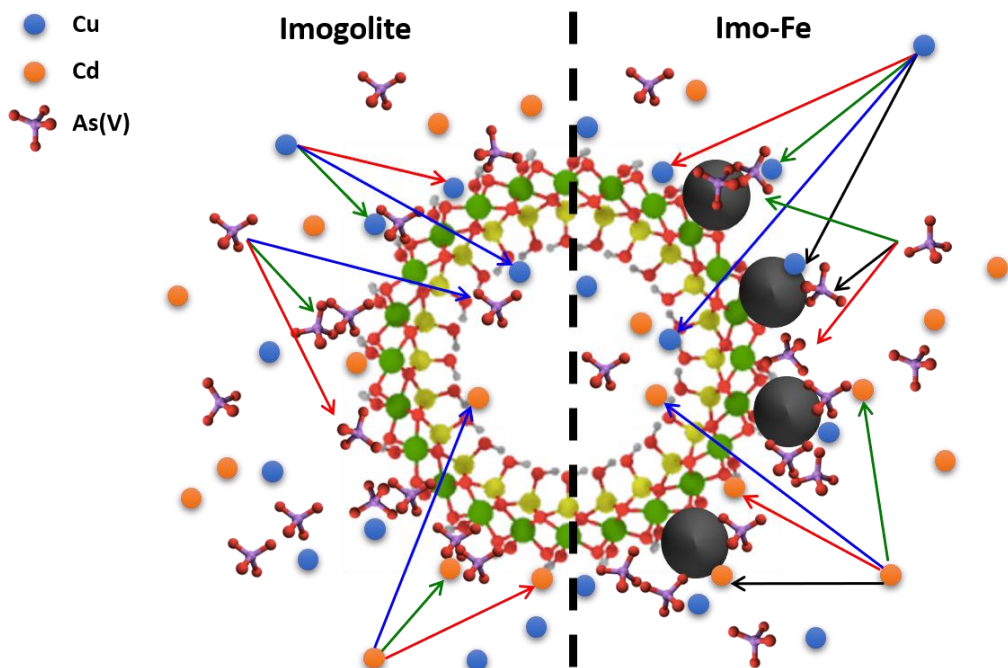
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25 **Graphical abstract**



**Removal process**

- Arsenic adsorbs faster than copper and cadmium.
- Al-OH sites have a preference for copper than for cadmium.
- Differences in ionic radius favor intraparticle diffusion of copper in imogolite.

- Adsorption was greater than 50% for all adsorbates, compared to imogolite.
- The presence of magnetite favors fast adsorption of all adsorbates.
- Intraparticle diffusion of adsorbates is not favored by the presence of magnetite.

- Magnetite functionalization favours the removal of different adsorbates.
- There are fewer specific adsorption sites for cadmium in imogolite and composites.
- The presence of arsenic reduces the electrostatic repulsion of external surfaces in imogolite, and the complexes favor the removal of copper and cadmium.
- The existence of oxyanions in contaminated aqueous solution could favour the removal of divalent heavy metals.

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27

28 **Highlights**

29 • Imo-Fe<sub>50</sub> & Imo-Fe<sub>25</sub> composites showed high efficiency for Cu-Cd-As removal.

30 • Size of magnetite was lower in Imo-Fe<sub>25</sub> than Imo-Fe<sub>50</sub>.

31 • Magnetic behavior of nanocomposites was confirmed.

32 • Arsenate was removed faster than Cu & Cd by both nanocomposites.

33 • Arsenate favoured the removal of Cu & Cd by both nanocomposites.

34

35 **Abstract**

36 Imogolite and magnetic imogolite-Fe oxide nanocomposites (Imo-Fe<sub>50</sub> and Imo-Fe<sub>25</sub>, at 50  
37 and 25% Fe loading (w/w), respectively) were synthesized and tested for the removal of  
38 aqueous copper (Cu), cadmium (Cd), and arsenic (As) pollutants. The materials were  
39 characterized by transmission electron microscopy, and specific surface area and isoelectric  
40 point measurements. The Fe-containing samples were additionally characterized by  
41 Mössbauer spectroscopy and vibrating-sample magnetometry. Significant differences were  
42 found in the morphological, electrophoretic, and magnetic characteristics between imogolite  
43 and the nanocomposites. The *in-situ* Fe-oxide precipitation process modified the active  
44 surface sites of the imogolite. The Fe-oxide, mainly magnetite, favored the contaminants'  
45 adsorption over the pristine imogolite. The adsorption kinetics of these pollutants were  
46 adequately described by the pseudo-second order and intraparticle diffusion models. The  
47 kinetic models showed that surface adsorption was more important than intraparticle  
48 diffusion in the removal of the pollutants by all the adsorbents. The Langmuir-Freundlich  
49 model described the experimental adsorption data, and both nanocomposites showed greater  
50 adsorption capacity than the imogolite. The adsorption of Cu and Cd was sensitive to cationic  
51 competition, showing a decrease of the adsorption capacity when the two cations coexisted,  
52 while their adsorption increased in the presence of arsenate.

53

54 **Keywords:** Adsorption; Imogolite; Nanocomposite; Trace Elements; Water Treatment.

55

## 56 **1. Introduction**

57 The impact and harmful effects to human health generated by the presence of pollutants in  
58 the environment is a highly relevant issue within the context of treatment and management of  
59 water resources. The increasing difficulty to satisfy basic water requirements, and the  
60 anthropogenic origin of numerous pollutants, make it necessary to ensure the supply of  
61 quality water to the world's growing population [1–3]. It is estimated that more than 150  
62 million people in the world are exposed to high concentrations of potentially toxic trace  
63 elements (TEs) like cadmium (Cd), copper (Cu), and arsenic (As) [4–10], because these  
64 pollutants are present in both the ground- and surface water sources. Industrial wastewater  
65 discharge, mining and agricultural activities are important anthropogenic sources which  
66 contribute to increasing amount of TEs in the environment [11–13]. In addition to the direct  
67 addition from industrial wastewater, mining activities add TEs to the environment through  
68 the residues generated by ore extractions (low grade ores) and purification (tailings)  
69 processes, whereas agricultural activities add through the constant application of fertilizers,  
70 biosolids, and soil amendments, severely modifying the biogeochemical cycles of the  
71 elements within the ecosystem [10,14–18]. Untreated effluents from industrial wastewater,  
72 mining and agricultural activities contain high concentrations of TEs, which have a direct  
73 negative effect mainly on the aquatic life [11–13]. Copper (Cu), Cd, and As stand out among  
74 this group of pollutants because of their widespread occurrence in polluted waters and high  
75 degrees of toxicities [2,10,11,13-15]. Their effects on human health are various, for example,  
76 Cu and Cd are responsible for pathological symptoms such as cirrhosis, generalized  
77 hemolysis, hepatic necrosis, generalized weakness, pulmonary edema, fertility problems, and  
78 different types of cancer [19,20]. Cd is specifically responsible for bone damage, commonly  
79 associated with the Itai-Itai disease, described for the first time in Japan in 1940 [20,21].  
80 Arsenic (As) causes even more damage than Cu and Cd due to its genotoxic and cytotoxic

81 characters and ability to induce epidemiological toxicity, causing arsenicosis, diabetes  
82 mellitus, peripheral vascular diseases, and various types of cancer, among other disorders [2].  
83 The World Health Organization (WHO) indicates that the concentrations of these elements in  
84 water for human consumption should not exceed  $1.5 \text{ mg}\cdot\text{L}^{-1}$  for Cu, and  $0.01 \text{ mg}\cdot\text{L}^{-1}$  for Cd  
85 and As [22].

86 Considering the extensive problem caused by the presence of TEs in aqueous matrices, a  
87 considerable number of investigations have focused on the search, design, and application of  
88 different types of removal techniques (e.g., adsorption, absorption, precipitation, and co-  
89 precipitation), using physical and/or chemical processes [23]. In this context, the use of  
90 different nanostructured substrates, such as Fe nanoparticles (e.g., nano-scale zero valent iron  
91 (nZVI)),  $\text{TiO}_2$ , graphene, clay minerals, among others, has been a subject of intense research  
92 [24–26].

93 Imogolite, a nanotubular aluminosilicate, is found in the inorganic phase of soils of volcanic  
94 origin, and it has shown a high ability for the removal of pollutants due to its wide versatility,  
95 high adsorption capacity, and easy functionalization [27–32]. Imogolite’s stoichiometry is  
96  $(\text{OH})_3\text{Al}_2\text{O}_3\text{SiOH}$ , with 100 nm length, and average outer and inner diameters of 2.0 and 0.9  
97 nm, respectively [33,34]. This aluminosilicate has a marked superficial differentiation, where  
98 aluminol groups ( $\equiv\text{Al-OH}$  ( $\text{pK}_{\text{a}1}=9.9$  and  $\text{pK}_{\text{a}2}=11.9$ )) predominate on the outer surface, while  
99 silanol groups ( $\equiv\text{Si-OH}$  ( $\text{pK}_{\text{a}1}=-2.77$  and  $\text{pK}_{\text{a}2}=6.77$ )) constitute the inner surface [18,35]. The  
100 differential pKa values owing to the unique aluminol and silanol structures, as mentioned  
101 above, allow imogolite having positive charges on its outer surface over wide pH values,  
102 while on the inner surface the predominant charge is negative. The behavior of the surface  
103 groups of imogolite would facilitate the simultaneous removal of anions and cations,  
104 respectively, a phenomenon recently described in the literature [18,35,36]. Despite of the  
105 surface properties and flexibility of synthesis, imogolite was scarcely used in

106 decontamination studies, with the adsorption of  $\text{Ni}^{2+}$ , and degradation of azo compounds by  
107 means of Photo-Fenton reactions standing out, using Ge-imogolite and Fe-imogolite,  
108 respectively, whose nanostructures were isomorphic with that of imogolite [31,37]. A recent  
109 study by Arancibia-Miranda et al., showed that the functionality of imogolite with Fe-oxides  
110 favored the removal kinetics of arsenate, besides facilitating an energy-neutral separation of  
111 the adsorbent due to magnetic characteristics [28]. Currently there is no information on the  
112 variation of the ability to remove pollutants in multi-component systems by imogolite where  
113 the chemical properties of pollutants can give rise to synergistic or antagonistic effects in the  
114 contaminant removal performance [38].

115 This work, therefore, studied the removal of Cu, Cd, and As (arsenate) from contaminated  
116 water by magnetite-imogolite nanocomposites (Imo-Fe), a recently developed material. The  
117 specific objectives are: (i) to evaluate the simultaneous removal of Cu, Cd, and As by Imo-Fe  
118 nanocomposites, and (ii) to study the possible removal mechanisms and interactions of Cu,  
119 Cd, and As present in aqueous systems with the nanocomposites.

120

## 121 **2. Materials and methods**

### 122 2.1 Reagents

123 The imogolite sample used in this study was prepared using tetraethyl orthosilicate,  
124 (99.995%, Sigma–Aldrich), NaOH (99.996%, Merck), and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (99.998%,  
125 Merck). The oxidic coatings of Fe was synthesised using  $\text{KNO}_3$  (99.998%, Merck),  
126  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (99.998%, Merck) and  $\text{NH}_4\text{OH}$  (99.997%, Sigma–Aldrich). In adsorption  
127 studies, solutions of  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$  and As ( $\text{As}_2\text{O}_5$  in  $\text{H}_2\text{O}$ ) were prepared from  
128 commercial standards (Titrisol<sup>®</sup>).

129

## 130 2.2 Synthesis of imogolite

131 Tetraethyl orthosilicate (TEOS) was added to a 5 mM aqueous solution of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$   
132 until an Al:Si ratio of 2:1 was reached. Then a 0.1 M NaOH solution was added at a rate of  
133  $1.0 \text{ mL min}^{-1}$  until an Al:Si:OH ratio of 2:1:4 was obtained. The mixture was stirred for 60  
134 min, and then heated at  $95 \text{ }^\circ\text{C}$  for 5 days. Once the aging process was completed, the resultant  
135 mixture was cooled down to ambient temperature. A 0.1 M  $\text{NH}_4\text{OH}$  solution was added  
136 rapidly until a pH of about 8.0 was reached. The solid was concentrated by centrifugation of  
137 the suspension at 9000 rpm for 30 min, and it was washed with double distilled water until  
138 the washings reached an electric conductivity of less than  $0.78 \text{ dS}\cdot\text{m}^{-1}$  [39,40].

139

## 140 2.3 Synthesis of iron oxide and preparation of imogolite-iron nanocomposite

141 To obtain a magnetic Fe-oxide, 0.250 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was dissolved in 20.0 mL of double-  
142 distilled water which was made  $\text{O}_2$ -free by flowing with  $\text{N}_2$ . Then 0.033 g of  $\text{KNO}_3$ , and 0.5  
143 mL of concentrated  $\text{NH}_4\text{OH}$  were added to precipitate the Fe-oxide from the above solution.  
144 The magnetic nanocomposites (hereafter Imo- $\text{Fe}_{50}$  and Imo- $\text{Fe}_{25}$ , at 50 and 25% Fe loading  
145 (w/w), respectively) were prepared according to a procedure described by Arancibia-Miranda  
146 et al. [21].

147

## 148 2.4 Characterization

149 The products were characterized by transmission electron microscopy (TEM), and isoelectric  
150 point (IEP), electrophoretic mobility (EM), and Brunauer–Emmett–Teller (BET) specific  
151 surface area (SSA) measurements. Fe-containing samples were additionally characterized by  
152 Mössbauer spectroscopy, and vibrating-sample magnetometry (VSM) and SQUID  
153 magnetometer.

154



155 The samples were observed with a Zeiss EM 910 transmission electron microscope (Zeiss,  
156 Germany) using 80 kV-acceleration potential. Sample suspension was deposited on a thin  
157 layer of carbon, and the solvent was dried via vacuum evaporation. The carbon film was then  
158 transferred to a perforated Cu support grid for collecting the images.

159 The SSA of imogolite and both nanocomposites was measured by the N<sub>2</sub> method of  
160 Brunauer-Emmett-Teller (BET), and pore size was calculated from the Barrett, Joyner and  
161 Halenda (BJH) analysis of N<sub>2</sub> adsorption/desorption isotherms at 77 K using an automatic  
162 analyser (Quantachrome Nova Station A, Quantachrome, USA, Florida).

163 The <sup>57</sup>Fe Mössbauer analysis was conducted at 298 K with a transmission acceleration  
164 constant setup with a ~30 mCi <sup>57</sup>Co/Rh source, and α-Fe as reference. Data were collected  
165 using a System MS4 spectrometer (Ligth Machenary, USA). Data were stored in a 512-  
166 channel MCS memory unit, with a Doppler velocity ranging around ±10 mm.s<sup>-1</sup>. The  
167 experimental data were fitted to Lorentzian functions (least-square method) using the  
168 NORMOS™ program algorithm.

169 The IEP was determined by measuring the EM (at pH = 5 to 11) under constant stirring of  
170 suspensions on a Zeta Meter 4.0 apparatus (Zeta-Meter, USA, Stauton). About 100 mg of  
171 each sample was suspended in 200 mL of a solution with an ionic strength of 1.0x10<sup>-3</sup> M  
172 (KNO<sub>3</sub>). The IEP was obtained from the EM vs. pH graph as the pH at which EM = 0. The  
173 Helmholtz-Smoluchowski equation was applied for the conversion of EM to zeta potential  
174 (ZP), when this parameter was required [41].

175 The magnetic response was investigated with a vibrating sample magnetometer (VSM)  
176 (homemade) operated at room temperature with a maximum magnetic field of 1.2 Tesla, and  
177 a sensitivity of 10<sup>-4</sup> emu.

178

179 2.5 Batch adsorption experiments

180 The adsorption kinetics were carried out at  $25\pm 2$  °C. Working solutions of the TEs were  
181 prepared by dilution in Milli-Q water of stock solutions of  $1000\text{ mg}\cdot\text{L}^{-1}$  of  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and As  
182 (arsenate), from commercial standards (Titrisol®). In the kinetic studies, 50 mg of samples  
183 were added to 20 mL of the TE solutions (Cd and Cu:  $50\text{ mg}\cdot\text{L}^{-1}$ , and arsenate:  $350\text{ mg}\cdot\text{L}^{-1}$ ;  
184  $\text{pH}=5.0\pm 0.2$ ) using  $1.0\times 10^{-3}\text{ M KNO}_3$  as the background electrolyte. The concentration of  
185 TEs in the suspension was determined at 5, 10, 20, 30, 45, 60, 90, 120, 150, and 180 min  
186 intervals after separation of the solids as described later.

187 In the one-component adsorption isotherm studies, 50 mg of the samples were added to 20  
188 mL of solution containing Cd or Cu ( $0\text{--}100\text{ mg}\cdot\text{L}^{-1}$ ) or arsenate ( $0\text{--}200\text{ mg}\cdot\text{L}^{-1}$ ), at  $\text{pH}$   
189  $=5.0\pm 0.2$ ) using  $1.0\times 10^{-3}\text{ M KNO}_3$  as the background electrolyte with a stirring time of 180  
190 min. The concentration ranges of contaminant elements were chosen to simulate real mining  
191 wastewater concentrations of these elements often encountered in Chile [14,18]. The effect of  
192 competition of different TEs alone was assessed only in the studies of adsorption isotherms,  
193 using a mixture containing, for each TE, the same concentration considered in one-  
194 component systems [11]. The adsorption experiments were carried out at  $25\pm 2$  °C. The  
195 adsorption of the adsorbates in multi-component systems considered the presence of Cu and  
196 Cd at similar concentrations ( $0\text{--}100\text{ mg}\cdot\text{L}^{-1}$ , treatment 1), and the adsorption of those metals  
197 at the same previous concentrations was also evaluated, but in the presence of arsenate ( $0\text{--}100$   
198  $\text{mg}\cdot\text{L}^{-1}$ , treatment 2). The  $\text{pH}$  of each suspension was adjusted to  $5.0\pm 0.2$  by the addition of  
199  $\text{HNO}_3$  or  $\text{KOH}$  ( $1.0\times 10^{-1}\text{ mol}\cdot\text{L}^{-1}$ ).

200 The samples were centrifuged at 10,000 rpm for 30 min followed by filtration of the  
201 supernatant through  $0.22\text{ }\mu\text{m}$  Millex-GX membranes. Elements in the clear supernatant were  
202 then analysed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES,  
203 Perkin Elmer Optima 2000). Eq. 1 gave the amounts of adsorbed ions, as the difference  
204 between their initial and final concentrations in solutions.

205  $q_t = \frac{(C_0 - C_t) \cdot V}{M}$  (Eq. 1)

206 where,  $C_0$  and  $C_t$  are respectively the initial and equilibrium concentrations of TEs ( $\text{mg} \cdot \text{L}^{-1}$ )  
207 at time “ $t$ ”,  $V$  (L) is the volume,  $M$  (g) is the mass of the adsorbent, and  $C_t$  is the amount  
208 adsorbed ( $\text{mg} \cdot \text{g}^{-1}$ ). All the adsorption tests were carried out in triplicate, and average values  
209 were reported.

210

## 211 2.6 Theory

212 The pseudo-first order model (PFO), pseudo-second order model (PSO), and intraparticle  
213 diffusion model, were used to analyse the adsorption kinetics of Cd, Cu, and arsenate on  
214 imogolite, Imo-Fe<sub>25</sub> and Imo-Fe<sub>50</sub> [10,18,42,43].

215 The PFO rate equation is given as Eq. 2 [10,18,42,43]:

216  $\frac{dq}{dt} = k_1 \cdot (q_e - q_t)$  (Eq. 2)

217 where,  $q_e$  and  $q_t$  correspond to the amounts of solute adsorbed at the equilibrium and at time  $t$   
218 (expressed in ( $\text{mg} \cdot \text{g}^{-1}$ )), respectively.  $k_1$  ( $\text{min}^{-1}$ ) is a combination of adsorption ( $k_a$ ) and  
219 desorption ( $k_d$ ) constants [10,18,42,43].

220 The expression of the PSO kinetic model can be written as Eq. 3 [10,18,42,44,45]:

221  $\frac{dq}{dt} = k_2 \cdot (q_e - q_t)^2$  (Eq. 3)

222 where,  $k_2$  is the PSO adsorption rate constant ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ). From this model, the parameter  
223  $h$  ( $\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$ ), which accounts for the initial adsorption rate, and is defined as  $h = k_2 \cdot q_e^2$ ,  
224 can be calculated.

225 The Webber-Morris model, also known as the intraparticle diffusion model or pore-diffusion  
226 model, is a single-resistance model derived from the Fick’s second law of diffusion [46]. The  
227 mathematical expression that defines this model is (Eq. 4):

228  $C_t = k_{\text{int}} t^{1/2} + C$  (Eq. 4)

229 where,  $k_{int}$  ( $\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$ ) is the intraparticle diffusion constant, and  $C$  ( $\text{mg} \cdot \text{g}^{-1}$ ) is a constant  
230 related to the thickness of the surface layer [18,47]. The higher the value of  $C$ , the greater the  
231 boundary layer effect, which is related to intraparticle diffusivity.

232

## 233 2.7. Residual error analysis

234 To evaluate the fit of kinetic and isotherm equations to the experimental data [18,24], the  
235 residual root mean square error (RMSE) can be defined as (Eq. 5):

$$236 \text{ RMSE} = \sqrt{\frac{1}{N-2} \sum_{i=1}^N (q_{e(\text{exp})} - q_{e(\text{cal})})^2} \text{ (Eq. 5)}$$

237 The subscripts “exp” and “calc” show the experimental and calculated values, and  $N$  is the  
238 number of observations in the experimental data; the smaller the RMSE value, the better the  
239 curve fitting.

240

## 241 3. Results and Discussion

### 242 3.1 Sample characterization

243 The presence of magnetite in the nanocomposites was confirmed by Mössbauer spectroscopy  
244 (Supplementary Material; Fig. S1). Differences were found in the percentages of Fe-oxide in  
245 both the nanocomposites, where Imo-Fe<sub>25</sub> showed a slight increase in the hyperfine  
246 parameters of magnetite compared to Imo-Fe<sub>50</sub> (Table S1), mainly in the relative sub-spectral  
247 area (RA). The relative isomeric change of  $\alpha\text{Fe}$  suggested that greater coverage proportions  
248 would favor the oxidation of the Fe-oxide. In the spectra of both nanocomposites, the  
249 presence of a marked doublet was seen, which was attributed to the presence of  
250 superparamagnetic  $\text{Fe}^{3+}$ , indicating that a fraction of the Fe used in the coverage was not part  
251 of the magnetite (Fig. S1), and this was more evident in Imo-Fe<sub>50</sub> than Imo-Fe<sub>25</sub> [20].

252 The nanocomposites obtained were characterized morphologically using TEM (Fig. S2),  
253 estimating their dimensions from measures of multiple particles as 70 to 90 nm, with a mean

254 value of  $82\pm 3$  nm. In the case of imogolite, dispersed nanotubular structures were seen, due  
 255 to the fact that the nanotubes were highly dispersed at the pH ( $\text{pH}=4.00\pm 0.20$ ) at which the  
 256 measurements were made [48]. The average outer diameter of imogolite was  $2.11\pm 0.02$  nm,  
 257 while its length was greater than 500 nm, in agreement with previous observations  
 258 [18,28,49], with a low by-product content. No morphological changes were seen in imogolite  
 259 due to the effect of Fe-oxide coverage, but the synthesis conditions of the Fe-oxide caused a  
 260 high agglomeration in the nanotubes (Fig. S2). The Fe-oxide supported on the Imo-Fe<sub>25</sub>  
 261 nanocomposite showed a diameter distribution between 16 and 46 nm, with a mean value of  
 262  $36\pm 4$  nm. In the case of Imo-Fe<sub>50</sub>, the dimensions of the Fe-oxide nanoparticles were found  
 263 between 20 and 50 nm, with a mean value of  $44\pm 3$  nm [21]. The distribution of Fe-oxide  
 264 immobilized on the surface of the imogolite was sensitive to the degree of coverage, finding  
 265 greater homogeneity of the oxides in the Imo-Fe<sub>25</sub> nanocomposite compared to Imo-Fe<sub>50</sub>.  
 266 This phenomenon was similar to what was described in clay minerals covered with nZVI  
 267 particles [24,50], associated with limited Fe<sup>3+</sup> adsorption sites that imogolite possessed. IEP  
 268 values calculated from the EM measurements [21] were 10.1, 6.4, 8.9, and 7.7, respectively,  
 269 for imogolite, magnetite, Imo-Fe<sub>25</sub>, and Imo-Fe<sub>50</sub> (Fig. 1). According to Eq. 6, the apparent  
 270 surface coverage (ASC) of Fe-oxide on the imogolite surface was worked out by considering  
 271 the zero point charge (ZPC; of magnetite), the molecular weights of imogolite ( $M_S=198.08$   
 272  $\text{g}\cdot\text{mol}^{-1}$ ) and iron oxide ( $M_M=231.54$   $\text{g}\cdot\text{mol}^{-1}$ ), as well as the IEP of both the nanocomposites  
 273 [21].

$$274 \text{ASC} = \frac{(IEP_S - ZPC) \cdot M_S^{-1}}{[(M_M^{-1} - M_S^{-1}) \cdot (ZPC - IEP_S) + M_M^{-1} \cdot (IEP_S - IEP_M)]} \cdot 100 \quad (\text{Eq. 6})$$

275 The Fe-oxide coating was close to 20 (Imo-Fe<sub>25</sub>) and 32 mass% (Imo-Fe<sub>50</sub>), lower than  
 276 stoichiometrically planned (25 and 50 mass%). However, the ASC for Imo-Fe<sub>25</sub> was closer to  
 277 the theoretical value, indicating that the coverage process was more homogeneous when a  
 278 lower Fe percentage was used. This was due to the finite number of sites where Fe could be

279 adsorbed on imogolite, a result consistent with what was seen in the microscopic analysis  
280 (Fig. S2). These results suggested that higher concentrations of Fe might form multilayers,  
281 affecting the proportional variations of IEP and ASC [28,51].

282 The microporous structure of imogolite, Imo-Fe<sub>25</sub>, and Imo-Fe<sub>50</sub> was studied by N<sub>2</sub>  
283 adsorption-desorption, and it was found that the SSA of imogolite (350 m<sup>2</sup>·g<sup>-1</sup>) [52,53]  
284 decreased significantly in both the nanocomposites, and was 15% lower for Imo-Fe<sub>25</sub>, and  
285 35% lower for Imo-Fe<sub>50</sub>, compared to the pristine imogolite (Table S2) [54].

286 Differences in the size and distribution of magnetite as a consequence of Fe concentrations  
287 applied in the coverage process caused changes in the magnetic behaviour of the  
288 nanocomposites too (Fig. S3). A saturation of magnetization was obtained after an applied  
289 magnetic field of 8000 kOe, and it was 92.14 emu·g<sup>-1</sup> for magnetite, but decreased drastically  
290 in the nanocomposites, with values of 6.82 emu·g<sup>-1</sup> for Imo-Fe<sub>25</sub>, and 11.23 emu·g<sup>-1</sup> for Imo-  
291 Fe<sub>50</sub> [24,28,55]. The coercive fields (H<sub>c</sub>) were 53.05 Oe for Imo-Fe<sub>25</sub>, and 57.89 Oe for Imo-  
292 Fe<sub>50</sub>, while this parameter for pure magnetite was 142.81 Oe. The remanence data indicated  
293 that this parameter was significantly greater in magnetite (~11 emu·g<sup>-1</sup>) with respect to the  
294 nanocomposites, and it was about 25 times greater compared to that obtained for Imo-Fe<sub>25</sub>  
295 (0.33 emu·g<sup>-1</sup>) and Imo-Fe<sub>50</sub> (0.56 emu·g<sup>-1</sup>). Despite the evident differences in the magnetic  
296 parameters between magnetite and both the nanocomposites, the values obtained, mainly the  
297 saturation magnetization, allowed classifying them as clearly magnetic materials (Fig. S3).

298 Evolution of the coercive field as a function of temperature for Imo-Fe<sub>25</sub> and Imo-  
299 Fe<sub>50</sub> showed increased values at decreased temperatures. For Imo-Fe<sub>25</sub>, the increase in  
300 coercivity was evident at temperature close to 75 K, while for Imo-Fe<sub>50</sub> this parameter  
301 increased to approximately at 100 K. These results supported that the magnetite nanoparticles  
302 constituting the nanocomposites were smaller in Imo-Fe<sub>25</sub> than Imo-Fe<sub>50</sub>, because at

303 temperatures exceeding 100 K the magnetization of Imo-Fe<sub>25</sub> was more unstable than Imo-  
304 Fe<sub>50</sub> (Fig. S3).

305

## 306 3.2 Kinetic adsorption

### 307 3.2.1 Cadmium and copper

308 The equilibrium time was 60 min of reaction for the adsorption of Cu and Cd on magnetite,  
309 imogolite and both nanocomposites (Fig. 2). The PSO model adequately described the  
310 adsorption kinetics of the TEs. The PSO model gave correlation coefficients ( $r^2 \geq 0.990$ )  
311 greater than those estimated by the PFO models, and the values of  $q_e$  were close to the  
312 experimental ones (Table 1).

313 The values of the initial adsorption constant ( $h$ ), when  $q/t$  approaches zero, showed a  
314 difference between the nanocomposites. This parameter increased considerably for Imo-Fe<sub>25</sub>  
315 and Imo-Fe<sub>50</sub> compared to magnetite and imogolite, due to the formation of new adsorption  
316 sites ( $\equiv\text{Fe-OH}$ ) on the nanocomposites [24,28]. The newly developed adsorption sites favored  
317 the rapid adsorption of TEs by the nanocomposites, as it was observed for the case of Cu and  
318 Cd (Fig. 2).

319 The diffusion of Cu and Cd on both nanocomposites was compared by the intraparticle  
320 diffusion model proposed by Weber and Morris [18,24,47], finding differences in the values  
321 of the parameters given by this model (Table 1). The differences possibly were as a  
322 consequence of the imogolite-Fe oxide surface coverage process (Fig. 3). The multiple curves  
323 seen in Fig. 3 indicated that the adsorption took place by three probable steps [56]. The first  
324 one was a surface adsorption or film diffusion (step I). Adsorption through an intraparticle  
325 diffusion mechanism was evidenced by the second linear zone of the graph (step II), while  
326 the last step corresponded to adsorption on the inner sites of the adsorbent (step III). By  
327 means of this model, it could be inferred that the adsorption of Cu and Cd on imogolite and

328 both nanocomposites took place at the first stage through surface diffusion, where the largest  
329 proportion of these elements was adsorbed, with the highest adsorption values obtained with  
330 Imo-Fe<sub>25</sub> and Imo-Fe<sub>50</sub> [18,24,47].

331

### 332 3.2.2 Arsenate

333 The kinetic adsorption behavior of arsenate in case of all the studied materials was described  
334 adequately by the PSO model (Fig. 3), where parameter *h* was slightly sensitive to the  
335 coverage process, indicating that the presence of Fe-oxide favored the adsorption in short  
336 adsorption times (Table 1). The intraparticle diffusion model for arsenate in case of the  
337 studied adsorbents showed that surface adsorption was the predominant process [18,24,47].  
338 This behavior could be explained by the strong specific interaction of the surface groups of  
339 imogolite and magnetite ( $\equiv\text{Al}_2\text{-OH}$ ,  $\equiv\text{Al-OH}$ , and  $\equiv\text{Fe-OH}$ ) with arsenate, possibly involving  
340 a ligand exchange mechanism, as described in the literature [57].

341 In general, the surface coverage process of imogolite with Fe-oxide gave rise to a synergic  
342 effect on the removal of the adsorbates. There could even be a blockage of the inner surface  
343 of imogolite by Fe<sup>3+</sup> used during the synthesis of magnetite, which mainly affected the  
344 removal of Cu and Cd. The blockage of inner surfaces by Fe<sup>3+</sup> contributed to the variation of  
345 surface charges of the nanocomposites, and the high affinity of Fe-oxides for arsenate ( $\log K$   
346  $((\text{FeO})_2\text{AsO}_4^{3+})=27.1$ ) compared to the affinity that arsenate had with Al ( $\log K$   
347  $(\text{AlO}_4\text{AsH}_2)=9.72$ ) [58,59].

348

### 349 3.3 Adsorption isotherms

350 The removal of Cu, Cd and arsenate by imogolite, magnetite, Imo-Fe<sub>25</sub>, and Imo-Fe<sub>50</sub> was  
351 analysed by the Langmuir-Freundlich (Eq. 7) isotherm model [10,60].

$$352 \quad q = \frac{Q_{sat}(K \cdot C_e)^m}{(K \cdot C_e)^{m+1}} \quad (\text{Eq. 7})$$



353 The Langmuir-Freundlich parameters were obtained by nonlinear least-square regression  
354 analysis, in which  $Q_{\text{sat}}$  is the adsorption capacity of the system ( $\text{mg of adsorbate}\cdot\text{g}^{-1}$   
355 adsorbent),  $K$  correspond to the affinity constant for adsorption ( $\text{L}\cdot\text{mg}^{-1}$ ),  $C_e$  ( $\text{mg}\cdot\text{L}$ ) is the  
356 equilibrium adsorbate concentration, and  $m$  is the index of heterogeneity.

357 The experimental data showed a high level of fitting to the Langmuir-Freundlich model, with  
358  $r^2\geq 0.990$ , indicating that they adequately represented the adsorption behavior of the studied  
359 TE species (Tables 2 and 3).

360

### 361 *3.3.1 Adsorption of copper and cadmium*

362 In general, the adsorption of Cu and Cd on both the nanocomposites was higher than on  
363 imogolite and magnetite, for all the treatments. The maximum adsorption of Cu and Cd on  
364 Imo-Fe<sub>50</sub> (Table 2) suggested that an increased ASC of Fe-oxide favored the adsorption of  
365 both adsorbates, most likely due to the decrease of the electrostatic repulsion, and because of  
366 the presence of new functional groups ( $\equiv\text{Fe-OH}$ ). These behaviors could be confirmed by the  
367 reduction of EM values at working pH ranges with increasing Fe-oxide coverages, from  
368  $\text{EM}=2.78$  (+33.30 mV) for imogolite to  $\text{EM}=2.32$  (+27.79 mV) for Imo-Fe<sub>25</sub>, and  $\text{EM}=1.58$   
369 (+18.93 mV) for Imo-Fe<sub>50</sub> [41]. The relative reduction of surface positive charge resulted in a  
370 reduction of electrostatic repulsion, consequently increasing the adsorption of Cu and Cd  
371 (Fig. 4) [21]. Furthermore, all the materials showed a high capacity for removing Cu than Cd.  
372 This was reflected by the values of  $C_m$ , which were 50% greater for Cu than those determined  
373 for Cd (Table 2). However, the adsorption intensity of Cd, as reflected by the values of  $K$ ,  
374 was greater than Cu for all the studied substrates (Table 2), showing that Cd was adsorbed on  
375 the high energy sites. The shapes of the adsorption curves in one-component systems were  
376 different for each metal; in the case of Cu, they were of the  $L$  type, while for Cd they were of

377 the *S* type, reflecting different interactions that occurred between the surface sites of  
378 imogolite or nanocomposites and the adsorbates [37,60–62].

379 In the case of multi-component systems, the behavior was similar to that of the one-  
380 component systems, both with respect to the type of adsorption curves (type *L* for Cu, and  
381 type *S* for Cd) and adsorption capacities. Higher adsorption capacities of the nanocomposites  
382 for both metals were observed compared to the imogolite, with Cu again showing a greater  
383 adsorption than Cd (Table 2). However, the most noticeable effect of the competition was the  
384 increased value of the *K* constant, which was particularly sensitive for Cu (Table 2),  
385 especially in the case of imogolite, whose value was seven times greater in the competitive  
386 system than that in the one-component system [15]. For Cd, the constant *K* showed an  
387 increase in the case of imogolite, with a value 50% greater in the competitive system than  
388 that in the one-component system. In case of the nanocomposites, no important variations  
389 were seen. The behavior found for imogolite indicated that the adsorption of both the metals  
390 in a competitive system occurred on sites of greater specificity, with a preference for Cu, a  
391 phenomenon similar to that reported by Clark and McBride [62].

392 The presence of arsenate in the solution substantially changed the removal of both the metals  
393 (Fig. 4c and f), showing an increase of the adsorption capacity for Cu and Cd on the studied  
394 materials. The increase was predominant in case of the nanocomposites where the presence of  
395 magnetite influenced this phenomenon (Table 2). This behavior could be explained by the  
396 fact that arsenate was adsorbed more readily than both metals, as determined in the kinetic  
397 studies, generating a kind of functionalization of the adsorbent's surface that changed the  
398 system's surface charge, making it less negative. This likely allowed to overcome the  
399 electrostatic barrier generated between arsenate and the surface of the adsorbents [10,63,64].

400 The types of curves of both metals in the presence of arsenate did not show large variations

401 compared to the Cu/Cd multi-component system, but the affinity constant  $K$  showed an  
402 increase of greater than 10% due to the presence of arsenate.

403

### 404 3.3.2 Adsorption of arsenate

405 The adsorption isotherms of arsenate on imogolite, Imo-Fe<sub>25</sub>, and Imo-Fe<sub>50</sub> are shown in Fig.

406 5. The Langmuir-Freundlich model showed the best fit of the experimental data ( $r^2 \geq 0.955$ )

407 (Table 3). For the two studied systems, single- and multi-components, the curves of the

408 isotherms were of the  $S$  type, showing a good affinity between different substrates and

409 arsenate. The adsorption capacity ( $Q_{\text{sat}}$ ) was greater for the magnetic materials than for

410 pristine imogolite (Table 3), indicating that the adsorption of arsenate was strongly

411 influenced by the type of surface of the substrates. The presence of Cd and Cu affected the

412 adsorption capacity for arsenate of the materials, showing an approximately 20% decrease

413 compared to the one-component system. This behavior could be due to the possible changes

414 in adsorption rates, which would occur when all adsorbates were present in the system,

415 enabling Cd and Cu to occupy surface sites of the adsorbents at times similar to that of

416 arsenate [65,66]. The values of the affinity constants  $K$  obtained from the Langmuir-

417 Freundlich model turned out to be highly sensitive to the coverage process as well as to the

418 presence of the bivalent metals, showing an increased magnitude on Imo-Fe<sub>25</sub> and Imo-Fe<sub>50</sub>

419 compared to imogolite. This effect was slightly greater in the magnetic materials when the

420 three adsorbates coexisted, suggesting that in the competitive system, arsenate (an oxyanion)

421 was adsorbed through a ligand exchange mechanism on the specific surface sites present in

422 imogolite and magnetite. Similar results were reported in case of clay minerals and

423 nanoparticles, where the pH and variation of surface charge favored such adsorption

424 mechanism [10,63,64].

425

426 3.4 Environmental implications and physicochemical properties of magnetite-imogolite  
427 nanocomposites

428 This paper provided new information on the characteristics of imogolite as a support for the  
429 immobilization of magnetite. The size and distribution of magnetite nanoparticles did not  
430 depend exclusively on the presence of the aluminosilicate, rather the concentration of  $\text{Fe}^{3+}$   
431 was a critical factor to consider, where higher amounts of  $\text{Fe}^{3+}$  favored a three-dimensional  
432 growth of Fe-oxides with the formation of multilayers [21]. Our results indicated that the  
433 nanocomposites removed about 100% more TEs than imogolite, where the immobilization of  
434 Fe oxide on imogolite was achieved through a simple step, and with minimum technical  
435 requirement [67]. These observations placed Imo- $\text{Fe}_{25}$  and Imo- $\text{Fe}_{50}$  as alternative and cost-  
436 effective adsorbents for the elimination of TEs from aqueous systems with variable  
437 contaminant contents.

438 The immobilization of Fe oxide on imogolite modified the SSA values in both  
439 nanocomposites, as compared to imogolite, resulting in 15 and 34% decrease of SSA in Imo-  
440  $\text{Fe}_{25}$  and Imo- $\text{Fe}_{50}$ , respectively. Despite these results, both nanocomposites showed higher  
441 Cu and Cd removal capacities, as a consequence of higher availability and affinity of the  
442 newly generated surface sites. Further, the composition of the aqueous solution significantly  
443 affected the removal of the adsorbates, with changes observed in the rate, capacity and  
444 intensity of removal of Cu, Cd, and arsenate (Fig. 5).

445 The data obtained from the adsorption studies, mainly from the isotherms, showed that in  
446 imogolite there were at least four kinds of adsorption sites which held variable selectivity for  
447 metals [68–70]. These sites could be categorized as follows: preferential sites for Cu,  
448 preferential sites for Cd, preferential sites for arsenate, and non-preferential sites for Cu, Cd  
449 or arsenate. In this context, our results showed that in multi-component systems (in which Cu  
450 and Cd coexisted), imogolite had a marked preference for Cu over Cd. The decrease of the

451 adsorption capacity of Cu in the competitive system was 12% compared to the single  
452 component system, while that for Cd exceeded 41% in the same case. These differences  
453 might be associated with the chemical characteristics of each metal ion, where the ionic  
454 radius, polarizability, and electronegativity (EN) would condition their affinity towards  $\equiv\text{Al-OH}$   
455 and  $\equiv\text{Si-OH}$  groups. This has been seen in similar systems where the most adsorbed  
456 metal had the highest EN ( $\text{Cu}_{\text{EN}}=1.90$  vs.  $\text{Cd}_{\text{EN}}=1.62$ ) [71]. In the case of nanocomposites, the  
457 behavior was similar to that found for imogolite, but the Fe-oxide coverage process caused a  
458 slight decrease in the Cd adsorption difference between the single- and multi-component  
459 systems. This was probably caused by electrostatic effects, presence of  $\equiv\text{Fe-OH}$  groups, and  
460 changes in the porosity of the nanocomposites [10,15,57].  
461 The presence of arsenate in the competitive system altered the general adsorption behavior of  
462 Cu and Cd on different substrates, which was evidenced by the increase of the value of  
463 constant K (Table 2). The adsorption of arsenate modified the affinity and selectivity of the  
464 original active sites of imogolite and nanocomposites, which might have reduced the density  
465 of common sites for Cu and Cd, but generated specific sites for each metal. This would also  
466 affect the macroscopic behavior of the adsorption, as observed by the changes of values of  
467 the adsorption constants and types of isotherm curves [47, 58-60].

468

#### 469 **4. Conclusions**

470 The Fe oxide-functionalized magnetic imogolite nanocomposites showed better TE removal  
471 capabilities than the pristine imogolite, and the removal capacity varied according to the  
472 amount of magnetite contained in the nanocomposites. Due to an increasing coverage with Fe  
473 oxide, there was a decrease of IEP, which was associated with a reduction of the positive  
474 surface charge at equilibrium pH for both the nanocomposites, as compared to the pristine  
475 imogolite. The reduction of positive surface charge favored the adsorption of cationic

476 adsorbates ( $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$ ) due to a smaller electrostatic repulsion between the adsorbent and  
477 adsorbates, and through complexing the adsorbates on the surface functional groups.  
478 The adsorption studies showed that the composition of the equilibrating solution strongly  
479 influenced the adsorption of Cu, Cd, and arsenate on imogolite as well as on its magnetic  
480 nanocomposites (Imo-Fe<sub>25</sub> and Imo-Fe<sub>50</sub>). The presence of arsenate favored the removal of  
481 divalent metals such as Cu and Cd. This study showed that Imo-Fe<sub>25</sub> and Imo-Fe<sub>50</sub> were  
482 efficient nanocomposites for the removal of trace elements such as Cu, Cd, and arsenate,  
483 even in systems where there was competition for the adsorption sites. These new adsorbents  
484 are thus a group of promising and efficient materials for TE removal from aqueous solutions,  
485 which could be used in conventional filter systems.

486

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491

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- 697

698 **Figure captions**

699 **Fig. 1.** Electrophoretic mobility vs. pH plots of imogolite, magnetite, Imo-Fe<sub>25</sub> and Imo-Fe<sub>50</sub>.

700 **Fig. 2.** Kinetic adsorption of single components for (a) Cd, (b) Cu, and (c) As in all  
701 substrates. Intraparticle diffusion plots for (d) Cd, (e) Cu, and (f) As adsorption on the  
702 samples. Note that the axes have different scales.

703 **Fig. 3.** Adsorption isotherms in single and multi-components for (a) Cd, (b) Cd/Cu, (c)  
704 Cd/Cu/As, (d) Cu, (e) Cu/Cd, and (f) Cu/Cd/As. The lines show Langmuir-Freundlich's fit.

705 **Fig. 4.** Adsorption isotherms in single and multi-components for (a) As and (b) As/Cu/Cd.  
706 The lines show Langmuir-Freundlich's fit.

707 **Fig. 5.** Schematic diagram of the Cu, Cd and As removal mechanisms by imogolite and Imo-  
708 Fe materials.

709

710 **Table titles**

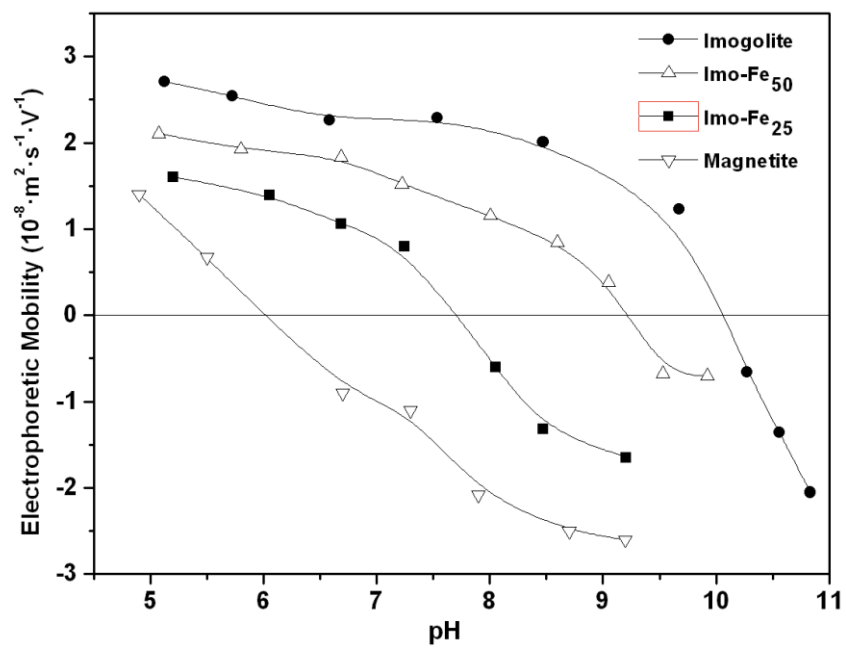
711 **Table 1.** Kinetic parameters predicted from the pseudo-first order, pseudo-second order, and  
712 intraparticle diffusion models.

713 **Table 2.** Related parameters for the adsorption of Cu and Cd on imogolite, magnetite, Imo-  
714 Fe<sub>25</sub> and Imo-Fe<sub>50</sub>.

715 **Table 3.** Related parameters for the adsorption of arsenic on imogolite, magnetite, Imo-Fe<sub>25</sub>  
716 and Imo-Fe<sub>50</sub>.

717

718 **Figures**

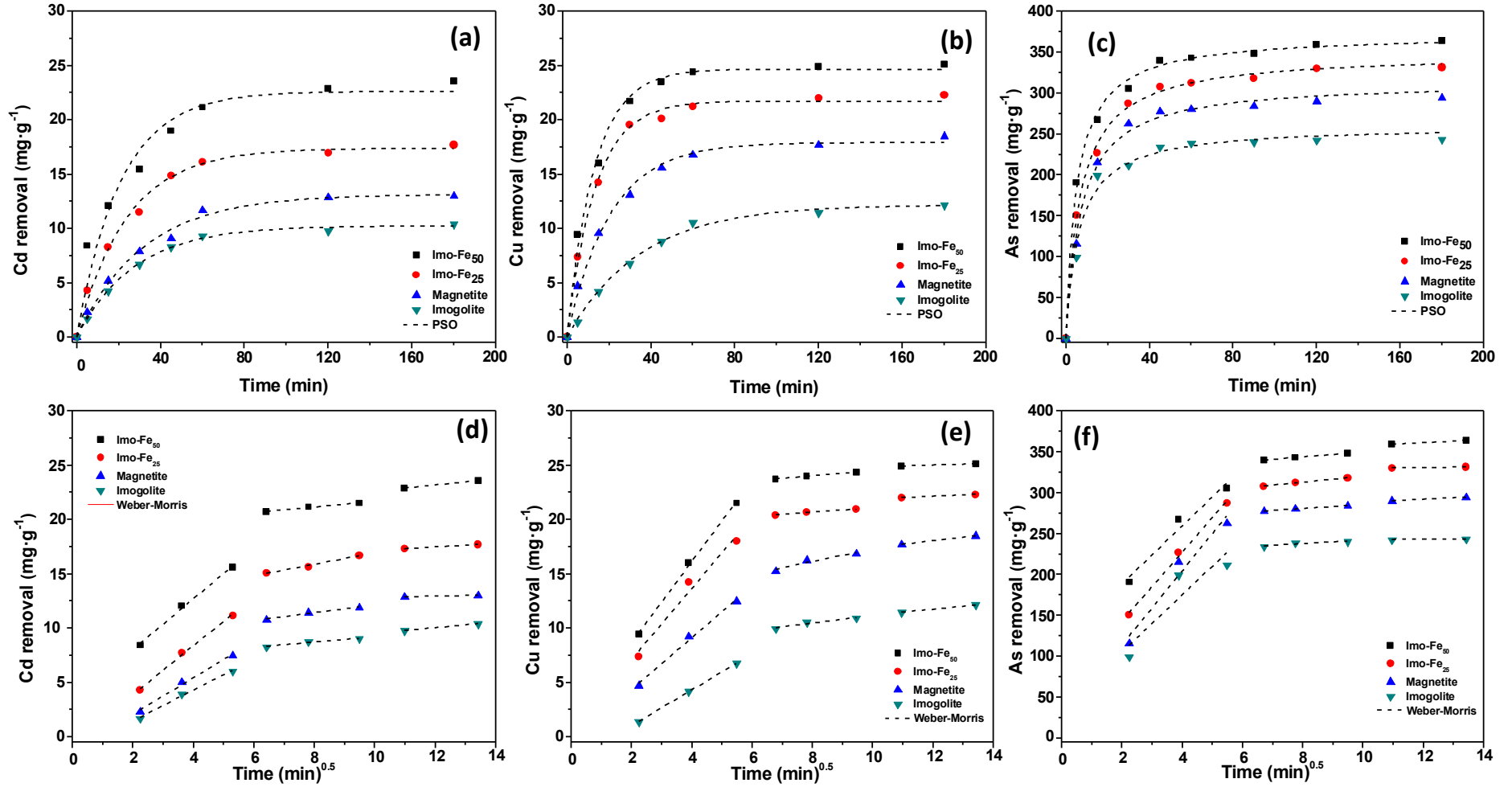


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720 Fig. 1.

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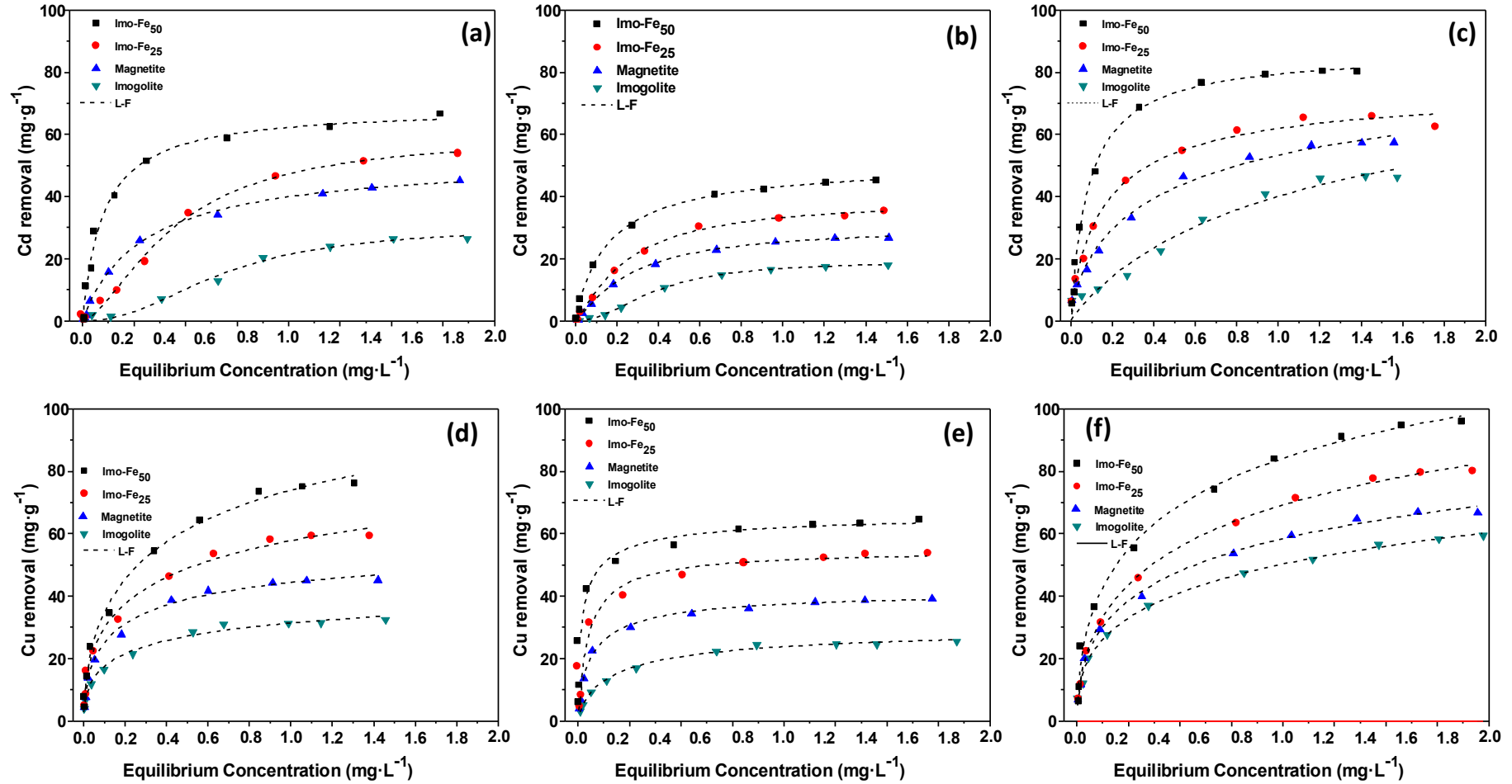




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723 Fig. 2.

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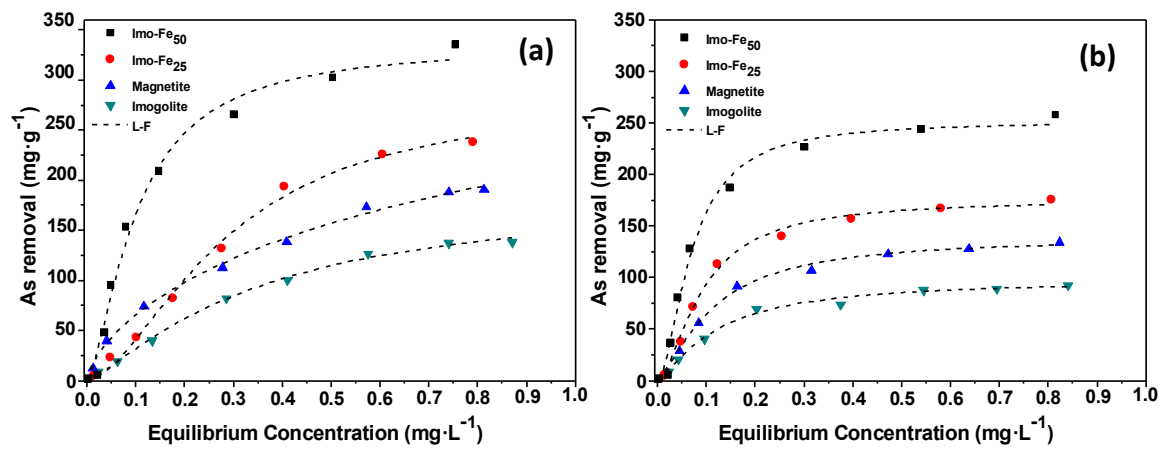


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726 Fig. 3.

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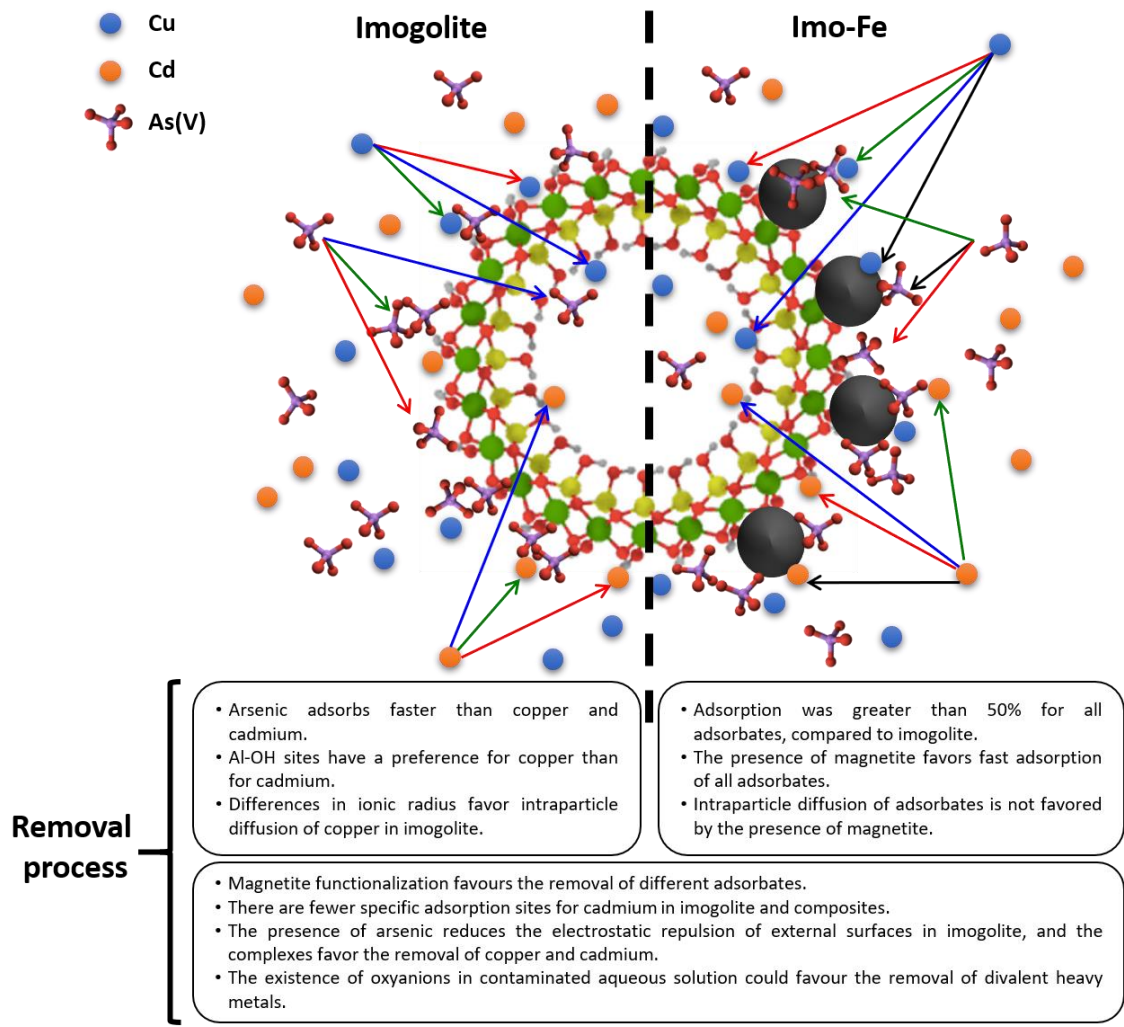
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730 Fig. 4.

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733 Fig. 5.

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737 **Table 1.** Kinetic parameters predicted from the pseudo-first order, pseudo-second order, and intraparticle diffusion models.

Models	Cu	Cd	As	Cu	Cd	As	Cu	Cd	As	Cu	Cd	As
	Imogolite			Magnetite			Imo-Fe <sub>25</sub>			Imo-Fe <sub>50</sub>		
$q_{exp} (mg \cdot g^{-1})$	12.1	10.4	243.3	18.5	13.0	294.5	22.3	17.7	331.3	25.1	23.6	363.9
<i>Pseudo-first order</i>												
$C_{m-cal} (mg \cdot g^{-1})$	14.9 (0.7)*	11.9 (0.6)	260.2 (5.6)	20.5 (2.0)	15.7 (1.0)	314.0 (20.5)	24.3 (0.7)	20.1 (0.8)	348.3 (4.3)	27.3 (0.85)	25.4 (0.7)	371.9 (4.8)
$k_1 (x10^{-3} min^{-1})$	2.8 (0.4)	3.7 (0.6)	109.4 (11.5)	4.8 (0.4)	3.1 (0.5)	95.8 (10.3)	7.1 (0.4)	3.8 (0.4)	97.2 (11.0)	7.5 (0.5)	4.8 (0.4)	112.8 (5.2)
$r^2$	0.983	0.984	0.967	0.995	0.980	0.981	0.985	0.985	0.979	0.985	0.984	0.981
<b>RMSE</b>	0.21	1.3	4.53	0.25	1.65	4.03	0.33	0.81	3.99	0.37	1.2	4.92
<i>Pseudo-second order</i>												
$C_{m-cal} (mg \cdot g^{-1})$	12.7 (0.2)	9.1 (0.2)	237.2 (7.2)	17.9 (0.4)	13.1 (0.7)	285.4 (7.4)	21.7 (0.2)	17.4 (0.9)	317.7 (8.2)	24.7 (0.3)	22.7 (0.7)	342.3 (3.2)
$k_2 (x10^{-4} g \cdot mg^{-1} \cdot min^{-1})$	3.4 (0.1)	2.0 (0.1)	5.9 (0.9)	3.1 (0.5)	2.2 (0.6)	10.1 (0.5)	4.2 (0.7)	2.6 (0.5)	4.1 (0.3)	4.6 (0.8)	2.7 (0.3)	5.1 (0.4)
$h (mg \cdot g^{-1} \cdot min^{-1})$	0.07	0.05	39.99	0.13	0.05	131.30	0.25	0.11	48.53	0.34	0.17	70.53
$r^2$	0.993	0.991	0.994	0.993	0.988	0.994	0.990	0.991	0.997	0.991	0.992	0.996
<b>RMSE</b>	0.19	0.88	3.44	0.14	0.11	0.22	0.12	0.21	3.22	0.34	0.33	4.63
<i>Intraparticle diffusion<sup>#</sup></i>												
$q_{e-2} (mg \cdot g^{-1})$	4.1 (0.3)	3.0 (0.5)	29.6 (1.9)	4.4 (1.1)	5.9 (0.9)	21.4 (2.2)	2.9 (0.1)	5.6 (0.6)	32.1 (2.7)	2.8 (0.3)	5.9 (0.4)	45.0 (2.4)

$k_{int-2} (mg \cdot g^{-1} \cdot min^{1/2})$	0.4 (0.1)	0.2 (0.1)	2.1 (0.3)	0.6 (0.1)	0.4 (0.1)	2.4 (0.6)	0.2 (0.0)	0.5 (0.1)	3.7 (0.2)	0.3 (0.0)	0.3 (0.0)	3.1 (0.1)
$C_2 (mg \cdot g^{-1})$	7.7 (0.7)	6.8 (0.4)	220.7 (9.3)	11.6 (1.3)	8.5 (0.5)	261.5 (0.8)	19.1 (2.1)	11.6 (0.6)	283.3 (1.6)	22.2 (1.92)	19.1 (2.0)	319.3 (1.1)
$r^2$	0.992	0.994	0.995	0.985	0.969	0.993	0.989	0.975	0.996	0.989	0.982	0.993

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739 \* Values in parentheses correspond to standard errors.

740 # RMSE for intraparticle diffusion model was not calculated because the model does not give a relevant  $q_{e-cal}$  value. An approximation could be  
 741 made from the overall curve fitting, but that would be hardly feasible because the curve represents different diffusion processes.

742 **Table 2.** Related parameters for the adsorption of Cu and Cd on imogolite, magnetite, Imo-Fe<sub>25</sub> and Imo-Fe<sub>50</sub>.

	Single-component					Multi-component (Cu+Cd)					Multi-component (Cu+Cd+As)				
	Langmuir-Freundlich					Langmuir-Freundlich					Langmuir-Freundlich				
	Q <sub>sat</sub>	K	n	r <sup>2</sup>	RMSE	Q <sub>sat</sub>	K	n	r <sup>2</sup>	RMSE	Q <sub>sat</sub>	K	n	r <sup>2</sup>	RMSE
<b>Copper (Cu)</b>															
Imogolite	52.0 (4.1)*	1.5 (0.34)	0.5 (0.0)	0.985	0.092	31.8 (2.5)	3.8 (1.0)	0.7 (0.1)	0.991	0.231	132.6 (9.1)	0.6 (0.0)	0.4 (0.1)	0.970	0.069
Magnetite	61.2 (5.9)	2.6 (0.7)	0.6 (0.2)	0.989	0.108	42.4 (1.9)	8.9 (2.4)	0.8 (0.1)	0.902	0.115	151.9 (19.9)	0.9 (0.1)	0.5 (0.0)	0.993	0.074
Imo-Fe <sub>25</sub>	105.6 (10.3)	1.5 (0.3)	0.7 (0.1)	0.989	0.142	54.9 (3.2)	13.7 (1.9)	0.9 (0.1)	0.989	0.099	157.9 (20.9)	0.9 (0.1)	0.5 (0.1)	0.973	0.103
Imo-Fe <sub>50</sub>	131.7 (12.9)	1.5 (0.5)	0.7 (0.1)	0.990	0.170	67.1 (5.9)	18.0 (0.8)	0.9 (0.1)	0.992	0.187	169.3 (22.9)	1.1 (0.1)	0.5 (0.1)	0.976	0.123
<b>Cadmium (Cd)</b>															
Imogolite	30.5 (3.1)	3.9 (1.0)	2.2 (0.4)	0.993	0.145	19.2 (1.0)	7.8 (1.1)	2.1 (0.3)	0.993	0.075	76.6 (6.7)	4.2 (0.3)	0.8 (0.1)	0.955	0.092
Magnetite	52.8 (2.9)	3.8 (0.5)	1.0 (0.2)	0.992	0.099	30.5 (1.2)	5.0 (0.6)	1.2 (0.1)	0.998	0.122	86.4 (9.7)	0.8 (0.1)	0.9 (0.1)	0.986	0.088
Imo-Fe <sub>25</sub>	60.2 (3.4)	5.3 (0.8)	1.2 (0.2)	0.996	0.078	39.3 (1.9)	5.4 (0.7)	1.5 (0.2)	0.993	0.101	87.1 (3.6)	7.4 (0.9)	1.0 (0.0)	0.955	0.143
Imo-Fe <sub>50</sub>	68.8 (2.9)	11.1 (1.0)	1.5 (0.3)	0.990	0.085	51.9 (2.4)	6.2 (0.6)	1.7 (0.6)	0.994	0.152	92.5 (3.9)	8.6 (1.9)	1.2 (0.0)	0.956	0.084

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744 \* Values in parentheses correspond to standard errors.

745 **Table 3.** Related parameters for the adsorption of arsenic on imogolite, magnetite, Imo-Fe<sub>25</sub> and Imo-Fe<sub>50</sub>.

	Single-component					Multi-component				
	Langmuir-Freundlich					Langmuir-Freundlich				
	<b>Q<sub>sat</sub></b>	<b>K</b>	<b>n</b>	<b>r<sup>2</sup></b>	<b>RMSE</b>	<b>Q<sub>sat</sub></b>	<b>K</b>	<b>n</b>	<b>r<sup>2</sup></b>	<b>RMSE</b>
Imogolite	186.7 (33.3)*	3.8 (0.7)	1.3 (0.4)	0.989	0.112	98.7 (11.7)	15.5 (1.8)	1.3 (0.39)	0.990	0.099
Magnetite	285.9 (27.2)	8.4 (1.7)	1.7 (0.3)	0.990	0.078	139.4 (9.7)	15.6 (1.8)	1.4 (0.39)	0.991	0.099
Imo-Fe <sub>25</sub>	335.9 (11.2)	31.3 (9.8)	1.7 (0.3)	0.991	0.075	175.5 (8.36)	48.7 (7.66)	1.6 (0.27)	0.989	0.101
Imo-Fe <sub>50</sub>	472.9 (32.9)	32.9 (3.50)	1.8 (0.2)	0.989	0.111	251.6 (6.7)	103.9 (23.9)	1.7 (0.2)	0.991	0.101

746

747 \* Values in parentheses correspond to standard errors.

748



749 **Supporting Information:**

750 **Mechanistic insights into simultaneous removal of copper, cadmium and arsenic from**  
751 **water by iron oxide-functionalized magnetic imogolite nanocomposites**

752  
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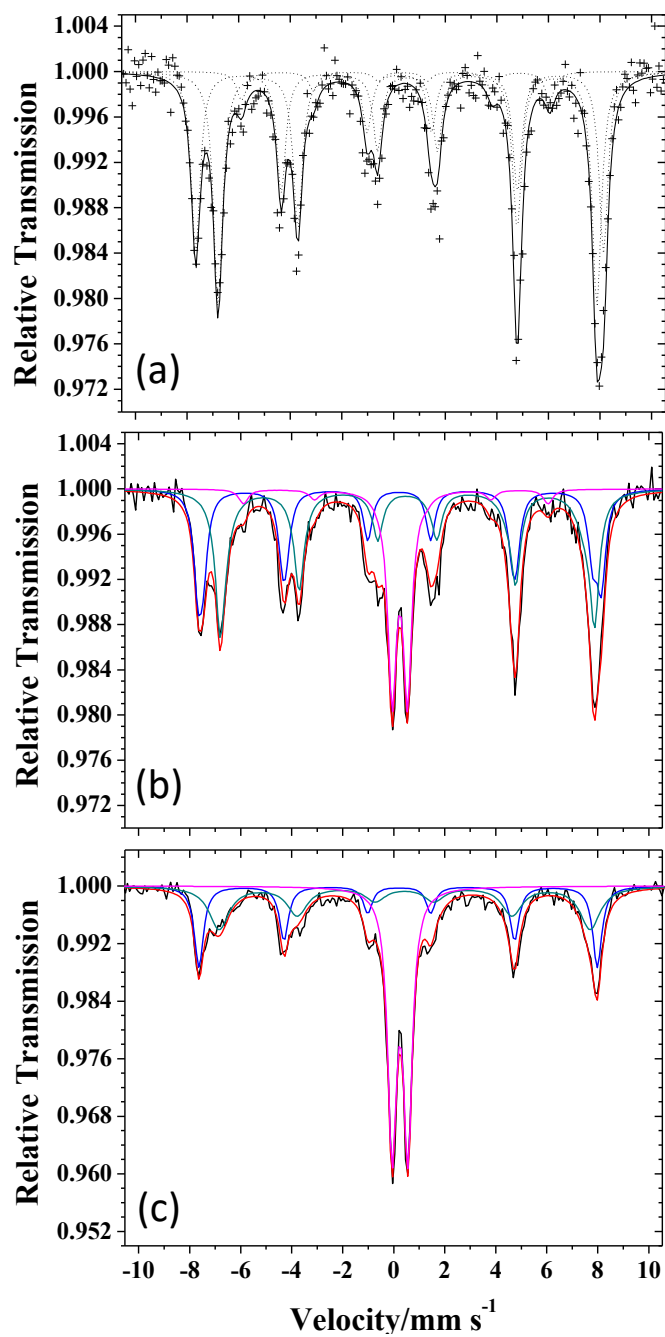
768 Dr Binoy Sarkar; Lancaster University; e-mail: [b.sarkar@lancaster.ac.uk](mailto:b.sarkar@lancaster.ac.uk), and

769 Dr Nicolás Arancibia-Miranda; Universidad de Santiago de Chile; e-mail:

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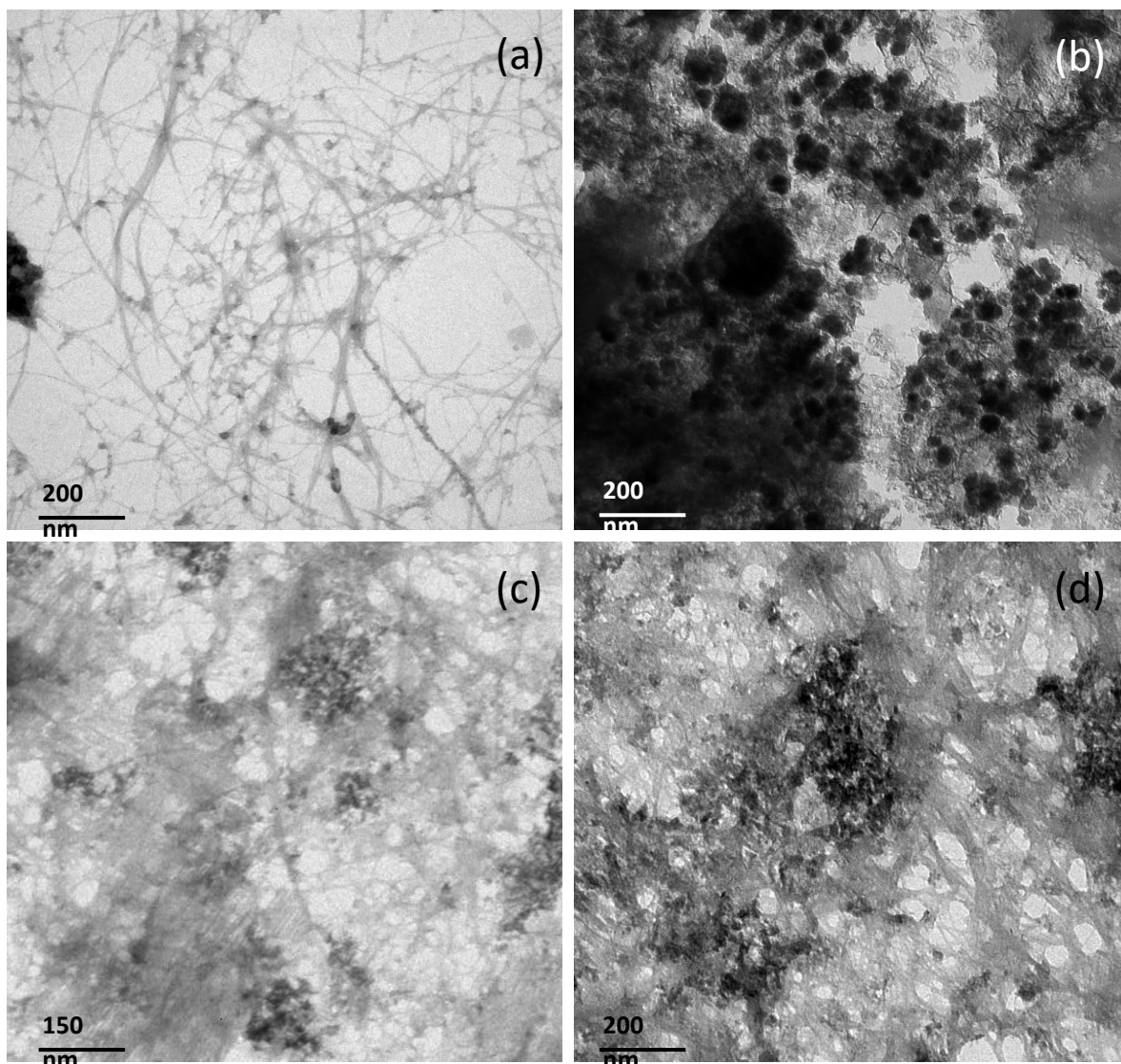
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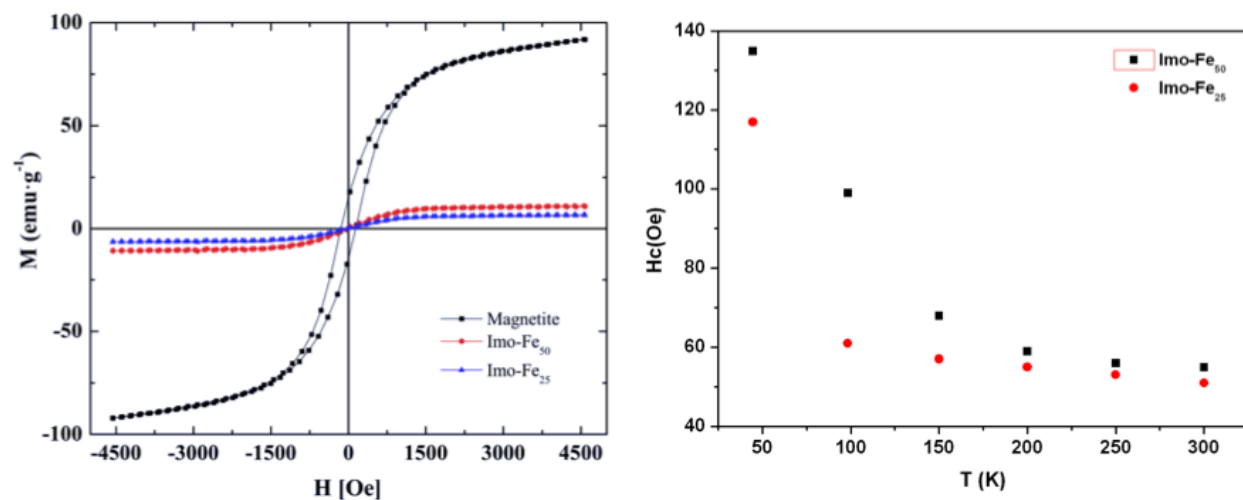
**Fig. S1.** 298 K-Mössbauer spectra at ambient temperature: (a) magnetite, (b) Imo-Fe<sub>25</sub>, (c) Imo-Fe<sub>50</sub>.



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**Fig. S2.** TEM images of: (a) Imogolite, (b) magnetite, (c) Imo-Fe<sub>25</sub>, and (d) Imo-Fe<sub>50</sub>.

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782

783 **Fig. S3.** Magnetization response of Imogolite, Imo-Fe<sub>25</sub> and Imo-Fe<sub>50</sub> (Left). Evolution of the

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coercive field as a function of temperature for, Imo-Fe<sub>25</sub> and Imo-Fe<sub>50</sub> (Right).

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786

787 **Table S1.** 298 K Mössbauer fitted parameters for the a) nano-magnetite, (b) Imo-Fe<sub>25</sub>, (c) Imo-Fe<sub>50</sub>.

Sample	Assignment	$\delta/\text{mm s}^{-1}$	$\epsilon, \Delta/\text{mm s}^{-1}$	$\Gamma/\text{mm s}^{-1}$	$B_{hf}/\text{T}$	RA/%
Nano-magnetite	[MG]	0.332(7)	0.01(1)	0.41(2)	49.01(5)	40(2)
	{MG}	0.640(5)	-0.001(1)	0.41(2)	45.49(4)	51(2)
	$\alpha$ -FeOOH	0.32(4)	-0.27(8)	0.40(1)	37.0(3)	9(2)
Imo-Fe <sub>25</sub>	[MG]	0.318(4)	-0.042(9)	0.42(2)	48.72(4)	33(3)
	{MG}	0.590(3)	0.00*	0.68(6)	45.22(4)	40(2)
	(Super) paramagnetic Fe(III)	0.351(4)	0.71(5)	0.44(2)	--	18(5)
	(Super) paramagnetic Fe(III)	0.349(3)	0.50(1)	0.22(2)	--	9(5)
	[MG]	0.304(5)	-0.042(9)	0.42(2)	48.43(4)	28(1)
Imo-Fe <sub>50</sub>	{MG}	0.54(1)	0.00*	0.96(6)	45.02(1)	31(2)
	(Super) paramagnetic Fe(III)	0.355(4)	0.73(5)	0.49(2)	--	30(5)
	(Super) paramagnetic Fe(III)	0.356(3)	0.50(1)	0.23(4)	--	11(5)

788

789 **Table S2.** Specific surface area and porosity parameters of imogolite and Imogolite, Imo-Fe<sub>25</sub>  
 790 and Imo-Fe<sub>50</sub>.

	<b>Imogolite</b>	<b>Magnetite</b>	<b>Imo-Fe<sub>25</sub></b>	<b>Imo-Fe<sub>50</sub></b>
Specific surface area (m <sup>2</sup> ·g <sup>-1</sup> )	310	87	265	203
External surface area (m <sup>2</sup> ·g <sup>-1</sup> )	180	35	149	117
Micropore volume x10 <sup>-3</sup> (cm <sup>3</sup> ·g <sup>-1</sup> )	20	1.5	22	30
Micropore area (m <sup>2</sup> ·g <sup>-1</sup> )	66	17	53	46
Pore Volume (cm <sup>3</sup> ·g <sup>-1</sup> )	0.25	0.18	0.24	0.20
Pore diameter (Å)	10	18	11	15

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793 **Table S3.** Experimental maximums of Cu and Cd adsorption in different systems studied.

Sample	Single-component	Multi-component (Cu+Cd)	% Difference*	Multi-component (Cu+Cd+As)
Copper - Experimental Maximum Adsorption (mg/g)				
Imogolite	50.2	31.8	36.7	132.6
Magnetite	61.2	42.4	30,7	151.9
Imo-Fe <sub>25</sub>	105.6	54.9	48.0	157.9
Imo-Fe <sub>50</sub>	131.7	67.1	49.1	16.3
Cadmium - Experimental Maximum Adsorption (mg/g)				
Imogolite	30,5	19,2	37,0	76.6
Magnetite	52,8	30,5	42,2	86.4
Imo-Fe <sub>25</sub>	60,2	39,3	34,7	87.1
Imo-Fe <sub>50</sub>	68,8	51,9	24,6	92.5

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 795 \* Percentage difference of amount adsorbed between single and multi-component systems with  
 796 respect to single-component adsorption  
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