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

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Graphical abstract

- 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 favors 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.
Highlights

- Imo-Fe\textsubscript{50} & Imo-Fe\textsubscript{25} composites showed high efficiency for Cu-Cd-As removal.
- Size of magnetite was lower in Imo-Fe\textsubscript{25} than Imo-Fe\textsubscript{50}.
- Magnetic behavior of nanocomposites was confirmed.
- Arsenate was removed faster than Cu & Cd by both nanocomposites.
- Arsenate favoured the removal of Cu & Cd by both nanocomposites.
Abstract

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

Keywords: Adsorption; Imogolite; Nanocomposite; Trace Elements; Water Treatment.
1. Introduction

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

The World Health Organization (WHO) indicates that the concentrations of these elements in water for human consumption should not exceed 1.5 mg·L\(^{-1}\) for Cu, and 0.01 mg·L\(^{-1}\) for Cd and As [22].

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

Imogolite, a nanotubular aluminosilicate, is found in the inorganic phase of soils of volcanic origin, and it has shown a high ability for the removal of pollutants due to its wide versatility, high adsorption capacity, and easy functionalization [27–32]. Imogolite’s stoichiometry is (OH)\(_3\)Al\(_2\)O\(_3\)SiOH, with 100 nm length, and average outer and inner diameters of 2.0 and 0.9 nm, respectively [33,34]. This aluminosilicate has a marked superficial differentiation, where aluminol groups (\(\equiv\)Al-OH (pK\(_{a1}\)=9.9 and pK\(_{a2}\)=11.9)) predominate on the outer surface, while silanol groups (\(\equiv\)Si-OH (pK\(_{a1}\)=-2.77 and pK\(_{a2}\)=6.77)) constitute the inner surface [18,35]. The differential pKa values owing to the unique aluminol and silanol structures, as mentioned above, allow imogolite having positive charges on its outer surface over wide pH values, while on the inner surface the predominant charge is negative. The behavior of the surface groups of imogolite would facilitate the simultaneous removal of anions and cations, respectively, a phenomenon recently described in the literature [18,35,36]. Despite of the surface properties and flexibility of synthesis, imogolite was scarcely used in
decontamination studies, with the adsorption of Ni$^{2+}$, and degradation of azo compounds by means of Photo-Fenton reactions standing out, using Ge-imogolite and Fe-imogolite, respectively, whose nanostructures were isomorphic with that of imogolite [31,37]. A recent study by Arancibia-Miranda et al., showed that the functionality of imogolite with Fe-oxides favored the removal kinetics of arsenate, besides facilitating an energy-neutral separation of the adsorbent due to magnetic characteristics [28]. Currently there is no information on the variation of the ability to remove pollutants in multi-component systems by imogolite where the chemical properties of pollutants can give rise to synergistic or antagonistic effects in the contaminant removal performance [38].

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

2. Materials and methods

2.1 Reagents

The imogolite sample used in this study was prepared using tetraethyl orthosilicate, (99.995%, Sigma–Aldrich), NaOH (99.996%, Merck), and Al(NO$_3$)$_3$·9H$_2$O (99.998%, Merck). The oxidic coatings of Fe was synthesised using KNO$_3$ (99.998%, Merck), FeSO$_4$·7H$_2$O (99.998%, Merck) and NH$_4$OH (99.997%, Sigma–Aldrich). In adsorption studies, solutions of Cd(NO$_3$)$_2$, Cu(NO$_3$)$_2$ and As (As$_2$O$_5$ in H$_2$O) were prepared from commercial standards (Titrisol®).
2.2 Synthesis of imogolite

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

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

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

2.4 Characterization

The products were characterized by transmission electron microscopy (TEM), and isoelectric point (IEP), electrophoretic mobility (EM), and Brunauer–Emmett–Teller (BET) specific surface area (SSA) measurements. Fe-containing samples were additionally characterized by Mössbauer spectroscopy, and vibrating-sample magnetometry (VSM) and SQUID magnetometer.
The samples were observed with a Zeiss EM 910 transmission electron microscope (Zeiss, Germany) using 80 kV-acceleration potential. Sample suspension was deposited on a thin layer of carbon, and the solvent was dried via vacuum evaporation. The carbon film was then transferred to a perforated Cu support grid for collecting the images.

The SSA of imogolite and both nanocomposites was measured by the N$_2$ method of Brunauer-Emmett-Teller (BET), and pore size was calculated from the Barrett, Joyner and Halenda (BJH) analysis of N$_2$ adsorption/desorption isotherms at 77 K using an automatic analyser (Quantachrome Nova Station A, Quantachrome, USA, Florida).

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

The IEP was determined by measuring the EM (at pH = 5 to 11) under constant stirring of suspensions on a Zeta Meter 4.0 apparatus (Zeta-Meter, USA, Stauton). About 100 mg of each sample was suspended in 200 mL of a solution with an ionic strength of 1.0x10$^{-3}$ M (KNO$_3$). The IEP was obtained from the EM vs. pH graph as the pH at which EM = 0. The Helmholtz-Smoluchowski equation was applied for the conversion of EM to zeta potential (ZP), when this parameter was required [41].

The magnetic response was investigated with a vibrating sample magnetometer (VSM) (homemade) operated at room temperature with a maximum magnetic field of 1.2 Tesla, and a sensitivity of 10$^{-4}$ emu.

2.5 Batch adsorption experiments
The adsorption kinetics were carried out at 25±2 °C. Working solutions of the TEs were prepared by dilution in Milli-Q water of stock solutions of 1000 mg·L⁻¹ of Cd²⁺, Cu²⁺ and As (arsenate), from commercial standards (Titrisol®). In the kinetic studies, 50 mg of samples were added to 20 mL of the TE solutions (Cd and Cu: 50 mg·L⁻¹, and arsenate: 350 mg·L⁻¹; pH=5.0±0.2) using 1.0x10⁻³ M KNO₃ as the background electrolyte. The concentration of TEs in the suspension was determined at 5, 10, 20, 30, 45, 60, 90, 120, 150, and 180 min intervals after separation of the solids as described later.

In the one-component adsorption isotherm studies, 50 mg of the samples were added to 20 mL of solution containing Cd or Cu (0–100 mg·L⁻¹) or arsenate (0–200 mg·L⁻¹), at pH =5.0±0.2 using 1.0x10⁻³ M KNO₃ as the background electrolyte with a stirring time of 180 min. The concentration ranges of contaminant elements were chosen to simulate real mining wastewater concentrations of these elements often encountered in Chile [14,18]. The effect of competition of different TEs alone was assessed only in the studies of adsorption isotherms, using a mixture containing, for each TE, the same concentration considered in one-component systems [11]. The adsorption experiments were carried out at 25±2 °C. The adsorption of the adsorbates in multi-component systems considered the presence of Cu and Cd at similar concentrations (0-100 mg·L⁻¹, treatment 1), and the adsorption of those metals at the same previous concentrations was also evaluated, but in the presence of arsenate (0-100 mg·L⁻¹, treatment 2). The pH of each suspension was adjusted to 5.0±0.2 by the addition of HNO₃ or KOH (1.0x10⁻¹ mol·L⁻¹).

The samples were centrifuged at 10,000 rpm for 30 min followed by filtration of the supernatant through 0.22 μm Millex-GX membranes. Elements in the clear supernatant were then analysed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, Perkin Elmer Optima 2000). Eq. 1 gave the amounts of adsorbed ions, as the difference between their initial and final concentrations in solutions.
where, $C_0$ and $C_t$ are respectively the initial and equilibrium concentrations of TEs (mg·L$^{-1}$) at time “$t$”, $V$ (L) is the volume, $M$ (g) is the mass of the adsorbent, and $C_t$ is the amount adsorbed (mg·g$^{-1}$). All the adsorption tests were carried out in triplicate, and average values were reported.

2.6 Theory

The pseudo-first order model (PFO), pseudo-second order model (PSO), and intraparticle diffusion model, were used to analyse the adsorption kinetics of Cd, Cu, and arsenate on imogolite, Imo-Fe$_{25}$ and Imo-Fe$_{50}$ [10,18,42,43].

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

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

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

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

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

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

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

$$C_t = k_{int}t^{1/2} + C \quad (Eq. 4)$$
where, $k_{\text{int}} \text{ (mg·g}^{-1} \cdot \text{min}^{-1/2})$ is the intraparticle diffusion constant, and $C \text{ (mg·g}^{-1})$ is a constant related to the thickness of the surface layer [18,47]. The higher the value of $C$, the greater the boundary layer effect, which is related to intraparticle diffusivity.

2.7. Residual error analysis

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

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

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

3. Results and Discussion

3.1 Sample characterization

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

The nanocomposites obtained were characterized morphologically using TEM (Fig. S2), estimating their dimensions from measures of multiple particles as 70 to 90 nm, with a mean
value of 82±3 nm. In the case of imogolite, dispersed nanotubular structures were seen, due to the fact that the nanotubes were highly dispersed at the pH (pH=4.00±0.20) at which the measurements were made [48]. The average outer diameter of imogolite was 2.11±0.02 nm, while its length was greater than 500 nm, in agreement with previous observations [18,28,49], with a low by-product content. No morphological changes were seen in imogolite due to the effect of Fe-oxide coverage, but the synthesis conditions of the Fe-oxide caused a high agglomeration in the nanotubes (Fig. S2). The Fe-oxide supported on the Imo-Fe$_{25}$ nanocomposite showed a diameter distribution between 16 and 46 nm, with a mean value of 36±4 nm. In the case of Imo-Fe$_{50}$, the dimensions of the Fe-oxide nanoparticles were found between 20 and 50 nm, with a mean value of 44±3 nm [21]. The distribution of Fe-oxide immobilized on the surface of the imogolite was sensitive to the degree of coverage, finding greater homogeneity of the oxides in the Imo-Fe$_{25}$ nanocomposite compared to Imo-Fe$_{50}$. This phenomenon was similar to what was described in clay minerals covered with nZVI particles [24,50], associated with limited Fe$^{3+}$ adsorption sites that imogolite possessed. IEP values calculated from the EM measurements [21] were 10.1, 6.4, 8.9, and 7.7, respectively, for imogolite, magnetite, Imo-Fe$_{25}$, and Imo-Fe$_{50}$ (Fig. 1). According to Eq. 6, the apparent surface coverage (ASC) of Fe-oxide on the imogolite surface was worked out by considering the zero point charge (ZPC; of magnetite), the molecular weights of imogolite (M$_s$=198.08 g·mol$^{-1}$) and iron oxide (M$_M$=231.54 g·mol$^{-1}$), as well as the IEP of both the nanocomposites [21].

$$ASC = \frac{\text{IEP}_S-\text{ZPC}}{\left(\frac{1}{M_s^{-1}}-\frac{1}{M_M^{-1}}\right)\left(\text{ZPC}-\text{IEP}_M\right)+\frac{1}{M_M^{-1}}-\left(\text{IEP}_S-\text{IEP}_M\right)} \cdot 100 \quad \text{(Eq. 6)}$$

The Fe-oxide coating was close to 20 (Imo-Fe$_{25}$) and 32 mass% (Imo-Fe$_{50}$), lower than stoichiometrically planned (25 and 50 mass%). However, the ASC for Imo-Fe$_{25}$ was closer to the theoretical value, indicating that the coverage process was more homogeneous when a lower Fe percentage was used. This was due to the finite number of sites where Fe could be
adsorbed on imogolite, a result consistent with what was seen in the microscopic analysis (Fig. S2). These results suggested that higher concentrations of Fe might form multilayers, affecting the proportional variations of IEP and ASC [28,51].

The microporous structure of imogolite, Imo-Fe25, and Imo-Fe50 was studied by N2 adsorption-desorption, and it was found that the SSA of imogolite (350 m²·g⁻¹) [52,53] decreased significantly in both the nanocomposites, and was 15% lower for Imo-Fe25, and 35% lower for Imo-Fe50, compared to the pristine imogolite (Table S2) [54].

Differences in the size and distribution of magnetite as a consequence of Fe concentrations applied in the coverage process caused changes in the magnetic behaviour of the nanocomposites too (Fig. S3). A saturation of magnetization was obtained after an applied magnetic field of 8000 kOe, and it was 92.14 emu·g⁻¹ for magnetite, but decreased drastically in the nanocomposites, with values of 6.82 emu·g⁻¹ for Imo-Fe25, and 11.23 emu·g⁻¹ for Imo-Fe50 [24,28,55]. The coercive fields (Hc) were 53.05 Oe for Imo-Fe25, and 57.89 Oe for Imo-Fe50, while this parameter for pure magnetite was 142.81 Oe. The remanence data indicated that this parameter was significantly greater in magnetite (∼11 emu·g⁻¹) with respect to the nanocomposites, and it was about 25 times greater compared to that obtained for Imo-Fe25 (0.33 emu·g⁻¹) and Imo-Fe50 (0.56 emu·g⁻¹). Despite the evident differences in the magnetic parameters between magnetite and both the nanocomposites, the values obtained, mainly the saturation magnetization, allowed classifying them as clearly magnetic materials (Fig. S3).

Evolution of the coercive field as a function of temperature for Imo-Fe25 and Imo-Fe50 showed increased values at decreased temperatures. For Imo-Fe25, the increase in coercivity was evident at temperature close to 75 K, while for Imo-Fe50 this parameter increased to approximately at 100 K. These results supported that the magnetite nanoparticles constituting the nanocomposites were smaller in Imo-Fe25 than Imo-Fe50, because at
temperatures exceeding 100 K the magnetization of Imo-Fe$_{25}$ was more unstable than Imo-Fe$_{50}$ (Fig. S3).

3.2 Kinetic adsorption

3.2.1 Cadmium and copper

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

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

The diffusion of Cu and Cd on both nanocomposites was compared by the intraparticle diffusion model proposed by Weber and Morris [18,24,47], finding differences in the values of the parameters given by this model (Table 1). The differences possibly were as a consequence of the imogolite-Fe oxide surface coverage process (Fig. 3). The multiple curves seen in Fig. 3 indicated that the adsorption took place by three probable steps [56]. The first one was a surface adsorption or film diffusion (step I). Adsorption through an intraparticle diffusion mechanism was evidenced by the second linear zone of the graph (step II), while the last step corresponded to adsorption on the inner sites of the adsorbent (step III). By means of this model, it could be inferred that the adsorption of Cu and Cd on imogolite and
both nanocomposites took place at the first stage through surface diffusion, where the largest proportion of these elements was adsorbed, with the highest adsorption values obtained with Imo-Fe_{25} and Imo-Fe_{50} \cite{18,24,47}.

3.2.2 Arsenate

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

In general, the surface coverage process of imogolite with Fe-oxide gave rise to a synergic effect on the removal of the adsorbates. There could even be a blockage of the inner surface of imogolite by Fe^{3+} used during the synthesis of magnetite, which mainly affected the removal of Cu and Cd. The blockage of inner surfaces by Fe^{3+} contributed to the variation of surface charges of the nanocomposites, and the high affinity of Fe-oxides for arsenate (log K (((FeO)\_2AsO_4)^{3+})=27.1) compared to the affinity that arsenate had with Al (log K (AlO_4AsH_2)=9.72) \cite{58,59}.

3.3 Adsorption isotherms

The removal of Cu, Cd and arsenate by imogolite, magnetite, Imo-Fe_{25}, and Imo-Fe_{50} was analysed by the Langmuir-Freundlich (Eq. 7) isotherm model \cite{10,60}.

$$ q = \frac{Q_{sat}(K\cdot C_e)^m}{(K\cdot C_e)^m+1} \quad \text{(Eq. 7)} $$
The Langmuir-Freundlich parameters were obtained by nonlinear least-square regression analysis, in which $Q_{\text{sat}}$ is the adsorption capacity of the system (mg of adsorbate·g$^{-1}$ adsorbent), $K$ correspond to the affinity constant for adsorption (L·mg$^{-1}$), $C_e$ (mg·L$^{-1}$) is the equilibrium adsorbate concentration, and $m$ is the index of heterogeneity.

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

### 3.3.1 Adsorption of copper and cadmium

In general, the adsorption of Cu and Cd on both the nanocomposites was higher than on imogolite and magnetite, for all the treatments. The maximum adsorption of Cu and Cd on Imo-Fe$_{50}$ (Table 2) suggested that an increased ASC of Fe-oxide favored the adsorption of both adsorbates, most likely due to the decrease of the electrostatic repulsion, and because of the presence of new functional groups (≡Fe-OH). These behaviors could be confirmed by the reduction of EM values at working pH ranges with increasing Fe-oxide coverages, from EM=2.78 (+33.30 mV) for imogolite to EM=2.32 (+27.79 mV) for Imo-Fe$_{25}$, and EM=1.58 (+18.93 mV) for Imo-Fe$_{50}$ [41]. The relative reduction of surface positive charge resulted in a reduction of electrostatic repulsion, consequently increasing the adsorption of Cu and Cd (Fig. 4) [21]. Furthermore, all the materials showed a high capacity for removing Cu than Cd. This was reflected by the values of $C_m$, which were 50% greater for Cu than those determined for Cd (Table 2). However, the adsorption intensity of Cd, as reflected by the values of $K$, was greater than Cu for all the studied substrates (Table 2), showing that Cd was adsorbed on the high energy sites. The shapes of the adsorption curves in one-component systems were different for each metal; in the case of Cu, they were of the $L$ type, while for Cd they were of
the $S$ type, reflecting different interactions that occurred between the surface sites of
imogolite or nanocomposites and the adsorbates [37,60–62].

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

The presence of arsenate in the solution substantially changed the removal of both the metals
(Fig. 4c and f), showing an increase of the adsorption capacity for Cu and Cd on the studied
materials. The increase was predominant in case of the nanocomposites where the presence of
magnetite influenced this phenomenon (Table 2). This behavior could be explained by the
fact that arsenate was adsorbed more readily than both metals, as determined in the kinetic
studies, generating a kind of functionalization of the adsorbent’s surface that changed the
system’s surface charge, making it less negative. This likely allowed to overcome the
electrostatic barrier generated between arsenate and the surface of the adsorbents [10,63,64].
The types of curves of both metals in the presence of arsenate did not show large variations
compared to the Cu/Cd multi-component system, but the affinity constant $K$ showed an
increase of greater than 10% due to the presence of arsenate.

3.3.2 Adsorption of arsenate
The adsorption isotherms of arsenate on imogolite, Imo-Fe$_{25}$, and Imo-Fe$_{50}$ are shown in Fig.
5. The Langmuir-Freundlich model showed the best fit of the experimental data ($r^2 \geq 0.955$)
(Table 3). For the two studied systems, single- and multi-components, the curves of the
isotherms were of the $S$ type, showing a good affinity between different substrates and
arsenate. The adsorption capacity ($Q_{sat}$) was greater for the magnetic materials than for
pristine imogolite (Table 3), indicating that the adsorption of arsenate was strongly
influenced by the type of surface of the substrates. The presence of Cd and Cu affected the
adsorption capacity for arsenate of the materials, showing an approximately 20% decrease
compared to the one-component system. This behavior could be due to the possible changes
in adsorption rates, which would occur when all adsorbates were present in the system,
enabling Cd and Cu to occupy surface sites of the adsorbents at times similar to that of
arsenate [65,66]. The values of the affinity constants $K$ obtained from the Langmuir-
Freundlich model turned out to be highly sensitive to the coverage process as well as to the
presence of the bivalent metals, showing an increased magnitude on Imo-Fe$_{25}$ and Imo-Fe$_{50}$
compared to imogolite. This effect was slightly greater in the magnetic materials when the
three adsorbates coexisted, suggesting that in the competitive system, arsenate (an oxyanion)
was adsorbed through a ligand exchange mechanism on the specific surface sites present in
imogolite and magnetite. Similar results were reported in case of clay minerals and
nanoparticles, where the pH and variation of surface charge favored such adsorption
mechanism [10,63,64].
3.4 Environmental implications and physicochemical properties of magnetite-imogolite nanocomposites

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

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

The data obtained from the adsorption studies, mainly from the isotherms, showed that in imogolite there were at least four kinds of adsorption sites which held variable selectivity for metals [68–70]. These sites could be categorized as follows: preferential sites for Cu, preferential sites for Cd, preferential sites for arsenate, and non-preferential sites for Cu, Cd or arsenate. In this context, our results showed that in multi-component systems (in which Cu and Cd coexisted), imogolite had a marked preference for Cu over Cd. The decrease of the
adsorption capacity of Cu in the competitive system was 12% compared to the single component system, while that for Cd exceeded 41% in the same case. These differences might be associated with the chemical characteristics of each metal ion, where the ionic radius, polarizability, and electronegativity (EN) would condition their affinity towards \( \equiv \text{Al-OH} \) and \( \equiv \text{Si-OH} \) groups. This has been seen in similar systems where the most adsorbed 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 behavior was similar to that found for imogolite, but the Fe-oxide coverage process caused a slight decrease in the Cd adsorption difference between the single- and multi-component systems. This was probably caused by electrostatic effects, presence of \( \equiv \text{Fe-OH} \) groups, and changes in the porosity of the nanocomposites [10,15,57].

The presence of arsenate in the competitive system altered the general adsorption behavior of Cu and Cd on different substrates, which was evidenced by the increase of the value of constant \( K \) (Table 2). The adsorption of arsenate modified the affinity and selectivity of the original active sites of imogolite and nanocomposites, which might have reduced the density of common sites for Cu and Cd, but generated specific sites for each metal. This would also affect the macroscopic behavior of the adsorption, as observed by the changes of values of the adsorption constants and types of isotherm curves [47, 58-60].

4. Conclusions

The Fe oxide-functionalized magnetic imogolite nanocomposites showed better TE removal capabilities than the pristine imogolite, and the removal capacity varied according to the amount of magnetite contained in the nanocomposites. Due to an increasing coverage with Fe oxide, there was a decrease of IEP, which was associated with a reduction of the positive surface charge at equilibrium pH for both the nanocomposites, as compared to the pristine imogolite. The reduction of positive surface charge favored the adsorption of cationic
adsorbates (Cd$^{2+}$ and Cu$^{2+}$) due to a smaller electrostatic repulsion between the adsorbent and adsorbates, and through complexing the adsorbates on the surface functional groups. The adsorption studies showed that the composition of the equilibrating solution strongly influenced the adsorption of Cu, Cd, and arsenate on imogolite as well as on its magnetic nanocomposites (Imo-Fe$^{25}$ and Imo-Fe$^{50}$). The presence of arsenate favored the removal of divalent metals such as Cu and Cd. This study showed that Imo-Fe$^{25}$ and Imo-Fe$^{50}$ were efficient nanocomposites for the removal of trace elements such as Cu, Cd, and arsenate, even in systems where there was competition for the adsorption sites. These new adsorbents are thus a group of promising and efficient materials for TE removal from aqueous solutions, which could be used in conventional filter systems.

Acknowledgments

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References


kinetic model for the formation and growth of single-walled metal oxide nanotubes,


**Figure captions**

**Fig. 1.** Electrophoretic mobility vs. pH plots of imogolite, magnetite, Imo-Fe$_{25}$ and Imo-Fe$_{50}$.

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

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

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

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

**Table titles**

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

**Table 2.** Related parameters for the adsorption of Cu and Cd on imogolite, magnetite, Imo-Fe$_{25}$ and Imo-Fe$_{50}$.

**Table 3.** Related parameters for the adsorption of arsenic on imogolite, magnetite, Imo-Fe$_{25}$ and Imo-Fe$_{50}$.
Fig. 1.
Fig. 2.
Fig. 3.
Fig. 4.

![Graph showing As removal vs. Equilibrium Concentration for different materials.](image)
Fig. 5.

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

<table>
<thead>
<tr>
<th>Models</th>
<th>Cu</th>
<th>Cd</th>
<th>As</th>
<th>Cu</th>
<th>Cd</th>
<th>As</th>
<th>Cu</th>
<th>Cd-Fe&lt;sub&gt;25&lt;/sub&gt;</th>
<th>As</th>
<th>Cu</th>
<th>Cd-Fe&lt;sub&gt;50&lt;/sub&gt;</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{exp} (mg·g^{-1})$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pseudo-first order</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{m-cal} (mg·g^{-1})$</td>
<td>14.9</td>
<td>11.9</td>
<td>260.2</td>
<td>20.5</td>
<td>15.7</td>
<td>314.0</td>
<td>24.3</td>
<td>20.1</td>
<td>348.3</td>
<td>27.3</td>
<td>25.4</td>
<td>371.9</td>
</tr>
<tr>
<td>$k_1 (x10^3 min^{-1})$</td>
<td>2.8</td>
<td>3.7</td>
<td>109.4</td>
<td>4.8</td>
<td>3.1</td>
<td>95.8</td>
<td>7.1</td>
<td>3.8</td>
<td>97.2</td>
<td>7.5</td>
<td>4.8</td>
<td>112.8</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.983</td>
<td>0.984</td>
<td>0.967</td>
<td>0.995</td>
<td>0.980</td>
<td>0.981</td>
<td>0.985</td>
<td>0.985</td>
<td>0.979</td>
<td>0.985</td>
<td>0.984</td>
<td>0.981</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.21</td>
<td>0.13</td>
<td>4.53</td>
<td>0.25</td>
<td>1.65</td>
<td>4.03</td>
<td>0.33</td>
<td>0.81</td>
<td>3.99</td>
<td>0.37</td>
<td>1.2</td>
<td>4.92</td>
</tr>
<tr>
<td>Pseudo-second order</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{m-cal} (mg·g^{-1})$</td>
<td>12.7</td>
<td>9.1</td>
<td>237.2</td>
<td>17.9</td>
<td>13.1</td>
<td>285.4</td>
<td>21.7</td>
<td>17.4</td>
<td>317.7</td>
<td>24.7</td>
<td>22.7</td>
<td>342.3</td>
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<tr>
<td>$k_2 (x10^4 g·mg^{-1}·min^{-1})$</td>
<td>3.4</td>
<td>2.0</td>
<td>5.9</td>
<td>3.1</td>
<td>2.2</td>
<td>10.1</td>
<td>4.2</td>
<td>2.6</td>
<td>4.1</td>
<td>4.6</td>
<td>2.7</td>
<td>5.1</td>
</tr>
<tr>
<td>$h (mg·g^{-1}·min^{-1})$</td>
<td>0.07</td>
<td>0.05</td>
<td>39.99</td>
<td>0.13</td>
<td>0.05</td>
<td>131.30</td>
<td>0.25</td>
<td>0.11</td>
<td>48.53</td>
<td>0.34</td>
<td>0.17</td>
<td>70.53</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.993</td>
<td>0.991</td>
<td>0.994</td>
<td>0.993</td>
<td>0.988</td>
<td>0.994</td>
<td>0.990</td>
<td>0.991</td>
<td>0.997</td>
<td>0.991</td>
<td>0.992</td>
<td>0.996</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.19</td>
<td>0.88</td>
<td>3.44</td>
<td>0.14</td>
<td>0.11</td>
<td>0.22</td>
<td>0.12</td>
<td>0.21</td>
<td>3.22</td>
<td>0.34</td>
<td>0.33</td>
<td>4.63</td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_{e-2} (mg·g^{-1})$</td>
<td>4.1 (0.3)</td>
<td>3.0</td>
<td>29.6</td>
<td>4.4</td>
<td>5.9</td>
<td>21.4</td>
<td>2.9</td>
<td>5.6</td>
<td>32.1</td>
<td>2.8</td>
<td>5.9</td>
<td>45.0</td>
</tr>
</tbody>
</table>

*Values in parentheses represent standard deviation.
| $k_{int-2} \text{ (mg·g}^{-1} \cdot \text{min}^{1/2})$ | 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 (0.1) | 0.3 (0.0) | 3.1 (0.1) |
| $C_2 \text{ (mg·g}^{-1})$ | 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 |

* Values in parentheses correspond to standard errors.

# RMSE for intraparticle diffusion model was not calculated because the model does not give a relevant $q_{e-cal}$ value. An approximation could be made from the overall curve fitting, but that would be hardly feasible because the curve represents different diffusion processes.
Table 2. Related parameters for the adsorption of Cu and Cd on imogolite, magnetite, Imo-Fe$_{25}$ and Imo-Fe$_{50}$.

<table>
<thead>
<tr>
<th></th>
<th>Single-component</th>
<th>Multi-component (Cu+Cd)</th>
<th>Multi-component (Cu+Cd+As)</th>
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<tr>
<td></td>
<td>Langmuir-Freundlich</td>
<td>Langmuir-Freundlich</td>
<td>Langmuir-Freundlich</td>
</tr>
<tr>
<td></td>
<td>$Q_{sat}$</td>
<td>$K$</td>
<td>$n$</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Imogolite</td>
<td>52.0 (4.1)*</td>
<td>1.5 (0.34)</td>
<td>0.5 (0.0)</td>
</tr>
<tr>
<td>Magnetite</td>
<td>61.2 (5.9)</td>
<td>2.6 (0.7)</td>
<td>0.6 (0.2)</td>
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<tr>
<td>Imo-Fe$_{25}$</td>
<td>105.6 (10.3)</td>
<td>1.5 (0.3)</td>
<td>0.7 (0.1)</td>
</tr>
<tr>
<td>Imo-Fe$_{50}$</td>
<td>131.7 (12.9)</td>
<td>1.5 (0.5)</td>
<td>0.7 (0.1)</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Imogolite</td>
<td>30.5 (3.1)</td>
<td>3.9 (1.0)</td>
<td>2.2 (0.4)</td>
</tr>
<tr>
<td>Magnetite</td>
<td>52.8 (2.9)</td>
<td>3.8 (0.5)</td>
<td>1.0 (0.2)</td>
</tr>
<tr>
<td>Imo-Fe$_{25}$</td>
<td>60.2 (3.4)</td>
<td>5.3 (0.8)</td>
<td>1.2 (0.2)</td>
</tr>
<tr>
<td>Imo-Fe$_{50}$</td>
<td>68.8 (2.9)</td>
<td>11.1 (1.0)</td>
<td>1.5 (0.3)</td>
</tr>
</tbody>
</table>

* Values in parentheses correspond to standard errors.
Table 3. Related parameters for the adsorption of arsenic on imogolite, magnetite, Imo-Fe_{25} and Imo-Fe_{50}.

<table>
<thead>
<tr>
<th></th>
<th>Single-component</th>
<th></th>
<th>Multi-component</th>
<th></th>
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</thead>
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<tr>
<td></td>
<td>Langmuir-Freundlich</td>
<td></td>
<td>Langmuir-Freundlich</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( Q_{\text{sat}} )</td>
<td>( K )</td>
<td>( n )</td>
<td>( r^2 )</td>
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<tr>
<td>Imogolite</td>
<td>186.7 (33.3)*</td>
<td>3.8 (0.7)</td>
<td>1.3 (0.4)</td>
<td>0.989</td>
</tr>
<tr>
<td>Magnetite</td>
<td>285.9 (27.2)</td>
<td>8.4 (1.7)</td>
<td>1.7 (0.3)</td>
<td>0.990</td>
</tr>
<tr>
<td>Imo-Fe_{25}</td>
<td>335.9 (11.2)</td>
<td>31.3 (9.8)</td>
<td>1.7 (0.3)</td>
<td>0.991</td>
</tr>
<tr>
<td>Imo-Fe_{50}</td>
<td>472.9 (32.9)</td>
<td>32.9 (3.50)</td>
<td>1.8 (0.2)</td>
<td>0.989</td>
</tr>
</tbody>
</table>

* Values in parentheses correspond to standard errors.
Supporting Information:

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

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Fig. S1. 298 K-Mössbauer spectra at ambient temperature: (a) magnetite, (b) Imo-Fe$_{25}$, (c) Imo-Fe$_{50}$. 
Fig. S2. TEM images of: (a) Imogolite, (b) magnetite, (c) Imo-Fe$_{25}$, and (d) Imo-Fe$_{50}$. 
**Fig. S3.** Magnetization response of Imogolite, Imo-Fe\(_{25}\) and Imo-Fe\(_{50}\) (Left). Evolution of the coercive field as a function of temperature for, Imo-Fe\(_{25}\) and Imo-Fe\(_{50}\) (Right).
Table S1. 298 K Mössbauer fitted parameters for the a) nano-magnetite, (b) Imo-Fe$_{25}$, (c) Imo-Fe$_{50}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Assignment</th>
<th>$\delta$/mm s$^{-1}$</th>
<th>$\varepsilon$, $\Delta$/mm s$^{-1}$</th>
<th>$\Gamma$/mm s$^{-1}$</th>
<th>$B_{hf}$/T</th>
<th>RA/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano-magnetite</td>
<td>[MG]</td>
<td>0.332(7)</td>
<td>0.01(1)</td>
<td>0.41(2)</td>
<td>49.01(5)</td>
<td>40(2)</td>
</tr>
<tr>
<td></td>
<td>{MG}</td>
<td>0.640(5)</td>
<td>-0.001(1)</td>
<td>0.41(2)</td>
<td>45.49(4)</td>
<td>51(2)</td>
</tr>
<tr>
<td></td>
<td>$\alpha$-FeOOH</td>
<td>0.32(4)</td>
<td>-0.27(8)</td>
<td>0.40(1)</td>
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<td>9(2)</td>
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<tr>
<td>Imo-Fe$_{25}$</td>
<td>[MG]</td>
<td>0.318(4)</td>
<td>-0.042(9)</td>
<td>0.42(2)</td>
<td>48.72(4)</td>
<td>33(3)</td>
</tr>
<tr>
<td></td>
<td>{MG}</td>
<td>0.590(3)</td>
<td>0.00*</td>
<td>0.68(6)</td>
<td>45.22(4)</td>
<td>40(2)</td>
</tr>
<tr>
<td></td>
<td>(Super) paramagnetic Fe(III)</td>
<td>0.351(4)</td>
<td>0.71(5)</td>
<td>0.44(2)</td>
<td>--</td>
<td>18(5)</td>
</tr>
<tr>
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<td>(Super) paramagnetic Fe(III)</td>
<td>0.349(3)</td>
<td>0.50(1)</td>
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<td>9(5)</td>
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<td>Imo-Fe$_{50}$</td>
<td>[MG]</td>
<td>0.304(5)</td>
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<td></td>
<td>{MG}</td>
<td>0.54(1)</td>
<td>0.00*</td>
<td>0.96(6)</td>
<td>45.02(1)</td>
<td>31(2)</td>
</tr>
<tr>
<td></td>
<td>(Super) paramagnetic Fe(III)</td>
<td>0.355(4)</td>
<td>0.73(5)</td>
<td>0.49(2)</td>
<td>--</td>
<td>30(5)</td>
</tr>
<tr>
<td></td>
<td>(Super) paramagnetic Fe(III)</td>
<td>0.356(3)</td>
<td>0.50(1)</td>
<td>0.23(4)</td>
<td>--</td>
<td>11(5)</td>
</tr>
</tbody>
</table>
### Table S2. Specific surface area and porosity parameters of imogolite and Imogolite, Imo-Fe$_{25}$ and Imo-Fe$_{50}$.

<table>
<thead>
<tr>
<th></th>
<th>Imogolite</th>
<th>Magnetite</th>
<th>Imo-Fe$_{25}$</th>
<th>Imo-Fe$_{50}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area (m$^2$.g$^{-1}$)</td>
<td>310</td>
<td>87</td>
<td>265</td>
<td>203</td>
</tr>
<tr>
<td>External surface area (m$^2$.g$^{-1}$)</td>
<td>180</td>
<td>35</td>
<td>149</td>
<td>117</td>
</tr>
<tr>
<td>Micropore volume x10$^{-3}$ (cm$^3$.g$^{-1}$)</td>
<td>20</td>
<td>1.5</td>
<td>22</td>
<td>30</td>
</tr>
<tr>
<td>Micropore area (m$^2$.g$^{-1}$)</td>
<td>66</td>
<td>17</td>
<td>53</td>
<td>46</td>
</tr>
<tr>
<td>Pore Volume (cm$^3$.g$^{-1}$)</td>
<td>0.25</td>
<td>0.18</td>
<td>0.24</td>
<td>0.20</td>
</tr>
<tr>
<td>Pore diameter (Å)</td>
<td>10</td>
<td>18</td>
<td>11</td>
<td>15</td>
</tr>
</tbody>
</table>
**Table S3.** Experimental maximums of Cu and Cd adsorption in different systems studied.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Single-component</th>
<th>Multi-component (Cu+Cd)</th>
<th>% Difference*</th>
<th>Multi-component (Cu+Cd+As)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Copper</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Imogolite</td>
<td>50.2</td>
<td>31.8</td>
<td>36.7</td>
<td>132.6</td>
</tr>
<tr>
<td>Magnetite</td>
<td>61.2</td>
<td>42.4</td>
<td>30.7</td>
<td>151.9</td>
</tr>
<tr>
<td>Imo-Fe&lt;sub&gt;25&lt;/sub&gt;</td>
<td>105.6</td>
<td>54.9</td>
<td>48.0</td>
<td>157.9</td>
</tr>
<tr>
<td>Imo-Fe&lt;sub&gt;50&lt;/sub&gt;</td>
<td>131.7</td>
<td>67.1</td>
<td>49.1</td>
<td>16.3</td>
</tr>
<tr>
<td><strong>Cadmium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Imogolite</td>
<td>30.5</td>
<td>19.2</td>
<td>37.0</td>
<td>76.6</td>
</tr>
<tr>
<td>Magnetite</td>
<td>52.8</td>
<td>30.5</td>
<td>42.2</td>
<td>86.4</td>
</tr>
<tr>
<td>Imo-Fe&lt;sub&gt;25&lt;/sub&gt;</td>
<td>60.2</td>
<td>39.3</td>
<td>34.7</td>
<td>87.1</td>
</tr>
<tr>
<td>Imo-Fe&lt;sub&gt;50&lt;/sub&gt;</td>
<td>68.8</td>
<td>51.9</td>
<td>24.6</td>
<td>92.5</td>
</tr>
</tbody>
</table>

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