Enhanced Removal of Mercury and Lead by a Novel and Efficient Surface-functionalized Imogolite with Nanoscale Zero-valent Iron Material

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Enhanced removal of mercury and lead by a novel and efficient surface-functionalized imogolite with nanoscale zero-valent iron material

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A novel hybrid nanomaterial, nanoscale zero-valent iron (nZVI)-grafted imogolite nanotubes (Imo), was synthesized via a fast and straightforward chemical procedure. The as-obtained nanomaterial (Imo-nZVI) was characterized using transmission electron microscopy (TEM), electrophoretic mobility (EM) and vibrating sample magnetometry (VSM). The prepared Imo-nZVI was superparamagnetic at room temperature and could be easily separated by an external magnetic field. Sorption batch experiments were performed in single- and multicomponent system and showed that Hg$^{2+}$ and Pb$^{2+}$ could be quantitatively adsorbed at pH 4.0 with maximum adsorption capacities of 62.3 and 73.8 mg·g$^{-1}$, respectively. It was observed that the functional groups in Imo-nZVI interact preferentially with analytes according to Misono Softness parameter. The higher performance of Imo-nZVI compared with Imo and nZVI is related to the increased adsorption sites in the functionalized nanomaterial. The sorption equilibrium data obeyed the Langmuir model, while kinetic studies demonstrated that the sorption processes of Hg$^{2+}$ and Pb$^{2+}$ followed the pseudo-second-order model. This study suggests that the Imo-nZVI composite can be used as a promising sorbent and provides a simple and fast separation method for the removal of Hg and Pb ions from contaminated water.

**Keywords:** Imogolite; Nanoscale zero valent iron (nZVI); Hybrid material; Neurotoxic metals (Hg and Pb) removal
1. Introduction

Nanoscale zero-valent iron (nZVI) has recently emerged as powerful and versatile sorbents for potential use in environmental engineering. Because of their special physicochemical properties, such as a high surface-to-volume ratio, magnetism and in situ reactivity, nZVI materials have attracted substantial interest in the scientific community. nZVI has shown application in a wide array of environmental treatments, such as soil, sediment, and groundwater remediation (Crane & Scott 2012, Li et al. 2006, Stefaniuk et al. 2016, Yan et al. 2010). However, nZVI forms aggregates due to van der Waals and magnetic forces, which decrease its efficiency by reducing its surface area and producing a less negative oxidation–reduction potential (Shi et al. 2011). Different approaches based on immobilization techniques have been developed for nZVI stabilization. Diatomite, zeolites, montmorillonite or cellulose have been used as matrices to increase the stability of nZVI (Arancibia-Miranda et al. 2016, Bossa et al. 2017, Dror et al. 2012, Kim et al. 2013, Suazo-Hernández et al. 2020, Suazo-Hernández et al. 2019, Zou et al. 2016). Furthermore, the sorption capacity of nZVI can also be improved by synergistically combining it with other nanomaterials. In this sense, inorganic nanotubes based on aluminosilicates, called imogolite (Imo), have attracted much research attention due to their one-dimensional structure, mechanical resistance and reactive surfaces (Arancibia-Miranda et al. 2020, Arancibia-Miranda et al. 2015). Imogolite is a hydrated aluminosilicate with the chemical formula \((\text{OH})_3\text{Al}_2\text{O}_3\text{SiOH}\) (Craddock et al. 1972). Characterized as a nanotubular structure, imogolite has a variable length from 100 nm to several microns, an internal diameter of 1 nm, and an external diameter of 2 nm for natural Imo, whereas synthetic Imo has a diameter in the range of 2.3-2.7 nm according to the synthesis method (Arancibia-Miranda et al. 2013b). Imogolite is amphoteric because the inner surface of nanotubes is lined with isolated silanol \((\equiv\text{SiOH})\) groups, and the outer
surface of nanotubes is covered with both Al–O–Al and Al–OH–Al groups, determining the superficial properties of this material (Arancibia-Miranda et al. 2017). Because of its high dispersibility in water and the amphoteric character of Imo, which is strongly influenced by the pH of the medium (Arancibia-Miranda et al. 2015), cations should be able to interact with the inner surface and anions with the outer surface of the nanotubes (Bonelli 2016). Due to the special properties of imogolite, this nanomaterial has attracted substantial interest in the scientific community because of its potential application in the removal of cations and anions from polluted water (Arancibia-Miranda et al. 2020, Bonelli 2016, Levard et al. 2009).

In this work, we propose the functionalization of imogolite with nZVI as a strategy to obtain a powerful and new sorbent nanomaterial with magnetic properties. The combination of both nanomaterials can be synergistically used to enhance the extraction efficiency of certain analytes (Bonelli 2016). In this context, recent research has shown that the high reactivity of nZVI promotes the stabilization of potential contaminants through multiple processes, such as adsorption, reduction, oxidation, precipitation and coprecipitation (Jiang et al. 2018, Lu et al. 2016). However, it is important to consider that mechanisms of removal for nZVI are dependent on conditions of the media (pH and redox potential ($E_{\text{h}}$)), but also on the type, chemical status, and nature of the analyte. In this sense, the sorption preferences and specific interactions between the substrate and the analyte are dependent on (i) the hydrolysis constant of the metal ion (considering the presence of $\equiv X$-OH and $\equiv X$-O-OH groups), (ii) polarizability, (iii) ionic and hydrated radius, and (iv) trend to form covalent bonds. In this context, Sposito (1989) postulated a relationship for an atom, defined as the Misono softness parameter, to form covalent bonds according to its ionic radius and ionization potential (Sposito 1989). A large Misono softness value for an atom indicates its preference for electrostatic and inner-
sphere surface complexation reactions. In this work, the removal of Hg and Pb from water samples was studied. Hg and Pb have long been a worrying issue due to their high neurotoxicity and widespread occurrence (Charlet et al. 2012, Jaishankar et al. 2014). The potential health risks from low levels of Hg and Pb are a subject of intense debate. Therefore, removal of these two metals from water samples is a current challenge. Taking these factors into consideration, along with the potential advantages resulting from the combination of imogolite and nZVI, synthesis and characterization of the hybrid nanomaterial and kinetic extraction studies of Hg\(^{2+}\) and Pb\(^{2+}\) are presented.

2. **Experimental**

2.1. **Instrumentation**

Elemental detection was performed using a PerkinElmer 5100ZL atomic absorption spectrometer (PerkinElmer, Norwalk, CT, USA) equipped with a pyrolytic graphite tube and a transversely heated graphite atomizer Zeeman-effect background correction system (PerkinElmer, Norwalk, CT, USA). Hg and Pb electrodeless discharge lamps (EDL) operated at currents of 170 mA and 360 mA (modulated operation) and wavelengths of 253.7 nm and 283.3 nm, respectively, with a spectral bandpass of 0.7 nm, were used. All measurements were made based on absorbance signals with an integration time of 5 s.

A centrifuge (model 5810, Eppendorf, Germany) was used to accelerate the phase separation process. A reciprocating shaker (Boeco, Hamburg, Germany) was used to mix the reagents. A Horiba F-51 pH meter (Kyoto, Japan) was used for pH determinations.

2.2. **Reagents**
All reagents were of analytical grade, and the presence of Hg was not detected within the working range. A 1000 μg mL⁻¹ Hg²⁺ stock solution was prepared from mercury(II) nitrate (Merck, Darmstadt, Germany) in 0.1 mol L⁻¹ HNO₃ (Ultrex® II Mallinckrodt Baker, Phillipsburg, NJ, USA). Lower concentrations of Hg²⁺ were prepared by diluting the stock solution with 0.1 mol L⁻¹ HNO₃. A 1000 μg mL⁻¹ Pb²⁺ stock solution was prepared from lead(II) nitrate (Merck, Darmstadt, Germany) in 0.1 mol L⁻¹ HNO₃. Stock solutions of 150 mg L⁻¹ Mg(NO₃)₂ (Merck) and 2500 mg L⁻¹ NH₄H₂PO₄ (Merck) were prepared and used as chemical modifiers. These solutions were prepared in 0.1% (v/v) HNO₃. A KNO₃ (Merck) solution (2 mol L⁻¹) was used to adjust the ionic strength. Ultrapure water (18 MΩ cm) was obtained from a Millipore Continental Water System (Bedford, MA, USA).

For the synthesis of Imo, the reagents used were tetraethyl orthosilicate (99.995%, Sigma–Aldrich), NaOH (99.996%, Merck), and Al(NO₃)₂·9H₂O (99.998%, Merck). The coating procedure involved the use of Fe(NO₃)₃·6H₂O (99.998%, Merck), NaBH₄ (99.997%, Sigma–Aldrich) and absolute ethanol (Merck). In sorption studies, KNO₃ (99.998%, Merck) was used. When needed, reagent grade solvents were considered. Ultrapure water (18 MΩ cm) was obtained from a Millipore Continental Water System (Bedford, MA, USA). All reactions were conducted at ambient conditions.

### 2.3. Synthesis of imogolite

Imo was prepared according to the procedure described by Arancibia-Miranda et al. (Arancibia-Miranda et al. 2011).

### 2.4. Synthesis of nZVI and nZVI functionalized imogolite
nZVI was synthesized according to Arancibia-Miranda et al. procedure.[7] The new Imo-
nZVI was obtained as follow: the coating process had a theoretical 2:1 mixture of Imo/Fe
(w/w), obtained by dissolving 24.41 g of Fe(NO$_3$)$_3$·6H$_2$O in 100 mL of EtOH:H$_2$O
(90:10) in a 500 mL round bottom flask. Then, Imo (2.50 g) suspended in 100 mL of
EtOH:H$_2$O (9:1) was added. The suspension was stirred for 3 h, leading to a lighter
orange-red solution. The NaBH$_4$ reducing agent (20.0 g) dissolved in 100 mL of H$_2$O was
immediately added at room temperature, causing the solution to turn black within 30-60
s, and the reaction mixture was stirred for approximately 1 h under a N$_2$ atmosphere. The
product was collected in a Falcon tube and centrifuged. The supernatant was removed,
and the precipitated product was cleaned with an ethanol EtOH:H$_2$O (9:1) solution several
times. Finally, the product was frozen with liquid N$_2$ and lyophilized.

**Characterization**

The products were characterized by X-ray diffraction (XRD), transmission electron
microscopy (TEM), electrophoretic mobility (EM) and vibrating sample magnetometry
(VSM). The samples were studied on a diffractometer (Shimadzu XRD-6000) at 1.5418
Å with CuKα radiation in the 2θ region of 5–80°. A Zeiss EM 910 transmission electron
microscope using an 80 kV acceleration potential on carbon substrates was prepared as
follows: A drop of the sample suspended in water was transferred onto the face of a
freshly cleaved sheet of mica, and the solvent was allowed to evaporate.

The magnetic response of the samples was investigated with a vibrating sample
magnetometer (VSM) operated at room temperature with a maximum magnetic field of
1.2 Tesla and a sensitivity of $10^{-4}$ emu. The isoelectric point (IEP) was determined by
measuring the zeta potential of particles on a Zeta Meter ZM-4.0 apparatus.

Approximately 30 mg of each sample was suspended in 200 mL of a solution with an
ionic strength of 0.01 mol·L\(^{-1}\) (KNO\(_3\)), and the EM was determined as a function of pH.

The IEP was obtained from the EM versus pH graph as the pH at which EM = 0. The specific surface areas (SSAs) of imogolite, nZVI and Imo-nZVI were measured by the N\(_2\) method of Brunauer-Emmett-Teller (BET), and pore size was calculated from Barrett, Joyner and Halenda (BJH) analysis of N\(_2\) adsorption/desorption isotherms at 77 K using an automatic analyzer (Quantachrome Nova Station A, Quantachrome, USA, Florida).

### 2.5. Sorption studies

Batch adsorption of Pb\(^{2+}\) and Hg\(^{2+}\) was studied in 40 mL polypropylene centrifuge tubes containing 10 mg of imogolite and Imo-nZVI in 10 mL of a Hg\(^{2+}\) or Pb\(^{2+}\) solution in 0.01 mol·L\(^{-1}\) KNO\(_3\), respectively. The dependence of metal adsorption as a function of time was studied in a solution of Pb or Hg containing 60 mg·L\(^{-1}\) in equilibrium with 10 mg of imogolite and Imo-nZVI. The samples were equilibrated using a reciprocating shaker for 300 min. The temperature for the experiments was 298 K, and the pH condition was 3.0 ± 0.2 for both metals (see Table S1). The samples were centrifuged at 10,000 rpm for 10 min, and the supernatant was filtered through 0.22 mm Millex-GX membranes and analyzed by ETAAS. The amount of adsorbed metals was determined from the difference between the initial and final concentrations in solution, according to Eq. (1).

\[
q_t = \frac{(C_o - C_t)V}{M} \quad (1)
\]

where \(C_o\) and \(C_t\) are the initial metal concentrations in mg·L\(^{-1}\) and at time \(t\), respectively; \(V\) (L) is the volume; and \(M\) (g) is the mass of the substrate.

### 2.6. Sorption kinetics models

*Pseudo-first-order model (PFO)*

In this model, the kinetic rate equation is given by:
\[
\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2}
\]

where \( q_e \) and \( q_t \) correspond to the amount adsorbed and in equilibrium at time \( t \), expressed in mg·g\(^{-1}\), respectively, and \( k_1 \) is the pseudo-first-order adsorption rate constant (min\(^{-1}\)), which is a combination of the adsorption (\( k_a \)) and desorption (\( k_d \)) constants (Boparai et al. 2011, Lagergren 2013, Manquián-Cerda et al. 2017, Rudzinski & Panczyk 2000). Integration of this equation from \( t = 0 \) to \( t = t \) and \( q = 0 \) to \( q = q \) gives:

\[
\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \tag{3}
\]

**Pseudo-second-order model (PSO)**

In this case, the driving force \( (q_e - q_t) \) is proportional to the portion of activated sites available on the sorbent (Ho & McKay 2000, Rao et al. 2006, Rudzinski & Plazinski 2008). The kinetic rate equation follows the expression:

\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{4}
\]

Rearranging the variables in this equation and integrating between times 0 and \( t \) and the corresponding boundary conditions 0 and \( q \) gives:

\[
\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{1}{q_e} t \tag{5}
\]

The initial adsorption rate of the system can be estimated by this model and determined by \( h = k\cdot q_e^2 \), obtained directly from the intercept of the curve.

**Elovich equation**

This model is used to describe the chemisorption processes on heterogeneous surfaces; it considers that adsorption takes place in two stages: a fast reaction, mainly associated with the movement of the adsorbate over outer active sites, and diffusion (slow) into and out of the adsorbent pores (Arancibia-Miranda et al. 2020, Arancibia-Miranda et al. 2015, Chien & Clayton 1980, Wu et al. 2001, 2009). This model is expressed as:
\[
\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (6)
\]
The constant \(\alpha\) (mg·g\(^{-1}\)·min\(^{-1}\)) is regarded as the initial rate, and parameter \(\beta\) (g·mg\(^{-1}\)) is an indication of the number of sites available for adsorption, which is related to the extent of surface coverage and activation energy for chemisorption. Given that \(q_t = 0\) at \(t = 0\), the integrated form is:

\[
q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (7)
\]

Parameters \(\alpha\) and \(\beta\) are obtained from the slope and intercept of the \(q_t\) vs. \(\ln t\) plot, respectively.

**Intraparticle diffusion model (Weber-Morris model)**

Webber-Morris’s pore-diffusion model is a single-resistance model derived from Fick’s second law of diffusion (Cáceres-Jensen et al. 2013, Cheung et al. 2007, Weber & Morris 1963). If the sorption process is considered to be influenced by diffusion in the sorbent and by convective diffusion in the sorbate solution, then the mathematical dependence of sorbate uptake, \(q_t\), at \(t^{1/2}\) is given by the equation:

\[
q_t = k_{int} t^{1/2} + C \quad (8)
\]

where \(k_{int}\) (mg·g\(^{-1}\)·min\(^{-1/2}\)) is the intraparticle diffusion constant and \(C\) is a constant related to the thickness of the surface layer; the higher the value of \(C\) obtained from the \(q_t\) vs. \(t^{1/2}\) plot, the greater the boundary layer effect, which is related to intraparticle diffusivity.

**Langmuir Isotherm**

This model assumes that the analyte is adsorbed in a determined number of active sites, forming a monolayer. The Langmuir equation is described by

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (9)
\]
where $q_m$ (mg·g$^{-1}$) is the maximum adsorption capacity, $q_e$ (mg·g$^{-1}$) is the amount of analyte adsorbed, $K_L$ is the Langmuir constant and $C_e$ is the equilibrium molar concentration of the analyte (mg·L$^{-1}$).

3. Results and discussion

3.1. Characterization of the composite

The samples were analyzed by X-ray diffraction to evaluate the changes generated from the coating process of imogolite with nZVI and Hg and Pb removal in single and multicomponent systems (Fig. S1). For imogolite, four broad peaks were identified at 21.0, 12.0, 3.4, and 2.2 Å, corresponding to the (hkl) (100), (110), (001), and (211) planes, respectively. According to previous reports, these planes are associated with monoclinic or hexagonal packaging (Arancibia-Miranda et al. 2013a, Kang et al. 2014). In the case of nZVI, diffraction peaks at $2\theta = 45.0^\circ$ (corresponding to the 110 plane) and $2\theta = 65.5^\circ$ (corresponding to the 200 plane) were observed, which also correspond to elemental Fe (Arancibia-Miranda et al. 2016, Kanel et al. 2005, Zhang et al. 2011). Fe oxide diffraction peaks were determined in nZVI, corresponding to magnetite and maghemite. The diffractogram of composite Imo-nZVI showed bands attributed to imogolite and nZVI, with clear differences in the degree of crystallinity of the peak in comparison to the starting materials. No signs of Fe oxides were observed in the composite, suggesting that nZVI oxidation did not occur or that the percentage of Fe oxide was less than the detection capacity of the XRD equipment. The process of Hg and Pb removal in single and multicomponent systems caused significant changes in the degree of crystallinity of the composites, altering the structure of the immobilized nZVIs in imogolite. After the removal process (single and multicomponent), the corrosion products magnetite (Fe$_3$O$_4$) and lepidocrocite ($\gamma$-FeOOH) (Baltazar et al. 2014, Kanel et al. 2005) were identified.
Both species are byproducts of the energetically favorable redox reactions between the nZVI and the analytes, as is described in equations 10 and 11.

\[
nZVI + Pb^{2+} \rightarrow Fe^{2+} + Pb^0 \quad (E^o = 0.32 V) \quad (10)
\]

\[
nZVI + Hg^{2+} \rightarrow Fe^{2+} + Hg^0 \quad (E^o = 1.30 V) \quad (11)
\]

However, according to the significant differences in the standard redox potential for \( Pb^{2+}/Pb^0 \) (-0.12 V) and \( Hg(II)/Hg(0) \) (0.86 V) couples with respect to the \( Fe^0/Fe^{II} \) (-0.44 V) couple, the removal of \( Hg^{2+} \) occurs preferentially by a reductive precipitation at the nZVI surface (Lagergren 2013), whereas that removal process of \( Pb^{2+} \) occurs by sorption with partial chemical reduction (Noubactep 2008).

It is important to highlight that in the multicomponent system, the samples have a lower degree of crystallinity, which shows that the presence of both metals significantly alters the surface of nZVI.

The morphologies of the samples were obtained through a detailed microscopic analysis (Fig. 1). The dimensions of imogolite were determined by images retrieved by HR-TEM. The external diameter was approximately 2 nm, with a length that exceeded 500 nm. For nZVI, two clearly defined areas were observed. The first area presented a higher degree of crystallinity located in the nucleus, corresponding to metallic Fe, while on the external surface, there was a second amorphous area associated with iron oxides, a process widely described in the literature. The coating process of imogolite with nZVI showed a heterogeneous distribution, in which areas with a high presence of agglomerated nZVI are highlighted. This is due to the synthesis conditions of nZVI, where the acid character of Fe (Lewis acid) favors positive charges at superficial sites of imogolite, decreasing the adsorption of this cation, which occurs at sites of greater specificity, a phenomenon.
similar to that reported by Arancibia-Miranda et al., 2014. The dimensions of nZVI were also sensitive to the process of its immobilization in imogolite, and the size was 20% lower than that of nZVI synthesized without support.

The surface behavior of the study materials was described through measurements of zeta potential (ZP) (Fig. 2), a technique that is sensitive to the changes that a surface can suffer in its composition. The isoelectric point is considered an indicative parameter of what occurs on the surface of imogolite due to being coated with nZVI. Imogolite has a pH-sensitive surface charge and is positive over a wide pH range with an IEP value of 10.5, which favors anion adsorption (Arancibia-Miranda et al. 2011). On the other hand, this parameter of nZVI reached a value of 7.7, which is characteristic of this type of material. The coating process with nZVI caused a drastic change in the IEP value of Imo-nZVI, which presented a value of 8.3, in addition to a decrease in the magnitude of the generated surface charge. The decrease in the IEP value observed in the composite reduces the potential electrostatic impediments in the processes of divalent ion sorption, as occurs in imogolite. The textural properties of the samples (Table 1) show that as a result of coating, the SSA and pore volume decrease while the pore diameter increases.

The hysteresis curve of presorption Imo-nZVI shows a typical ferromagnetic curve with a saturation magnetization ($M_s$) of 16.5 emu·g$^{-1}$ and a coercive field ($H_c$) of 100 Oe (Fig. S2). The Pb postsorption magnetization curve presents a decrease in $M_s$ to 7 emu·g$^{-1}$. This decrease in magnetization is attributed to the amount of Pb that has been absorbed by the Imo-nZVI nanoparticles, which does not contribute to the magnetization of the sample. A much larger decrease in $M_s$ is observed for the postsorption samples with Hg and Pb-Hg, with values of 0.6 emu·g$^{-1}$ and 0.56 emu·g$^{-1}$, respectively. The coercivity of the postsorption samples remains close to 100 Oe in all samples. This perturbation on the
magnetic properties of the materials under study could be related to the different corrosion products from nZVI, which has less magnetic character than Fe⁰.

3.2. Adsorption kinetics

The effect of the contact time on the removal of Hg²⁺ and Pb²⁺ in single and multicomponent systems was evaluated for the different materials by means of removal kinetics. In the case of imogolite, an equilibrium time was achieved at 60 minutes for both single- and multicomponent systems. For nZVI and Imo-nZVI, equilibrium was reached after 30 minutes in all the studied systems (Fig. 3). Pb²⁺ removal was slightly higher than Hg²⁺ removal in all the systems under study.

3.3. PFO and PSO models

Kinetic models of pseudo first order (PFO) and pseudo-second order (PSO) (Fig. 4) were used to describe the kinetic behavior of the experimental data. The PFO model showed the least adjustment of these data (Table 2). This behavior could be explained by the theoretical fundamentals that differentiate both models. For example, in the case of the PFO model, high levels of adjustment are observed when the analyte is monovalent, which is removed by direct interaction between this species and a surface active site of the substrate. For the PSO model, this condition occurs when an ion is attracted at two active sites in the substrate. The removal of divalent cations is explained by this model, favoring a chemical-type interaction (chemisorption), probably forming bidentate complexes (Table 2).

The sorption capacities (qₑ) of imogolite obtained from the PSO model (Eq. 5) for Pb²⁺ and Hg²⁺ were 44.9 and 39.4 mg·g⁻¹, respectively, in single-component systems. However, as a result of the competition between cations, a reduction of more than 10%
was observed in the sorption capacity of imogolite in multicomponent systems. In the case of nZVI, the removal of these metals was higher in both systems under study. This is because this nanoparticle has multiple mechanisms of removal (adsorption, precipitation, coprecipitation, and oxidation-reduction), unlike imogolite, for which adsorption is the only mode of removal. The functionalization of imogolite with nZVI improved the removal capacity of both Hg$^{2+}$ and Pb$^{2+}$ compared to the starting materials, where the $q_e$ values in the case of Pb$^{2+}$ in single and multicomponent systems were 78.0 and 72.4 mg·g$^{-1}$ and 81.0 and 77.7 mg·g$^{-1}$, for Hg$^{2+}$, respectively. The removal rates of both metals obtained from the PSO model (Eq. 5) show that the functionalization process generates an increase in this parameter, which is up to 2.3 times greater than that observed for imogolite and nZVI. The initial velocity (h), calculated from the PSO model, showed that Pb$^{2+}$ is removed by Imo-nZVI in early sorption stages compared to Hg$^{2+}$.

3.4. Adsorption mechanisms

The sorption mechanisms of Hg and Pb analytes in imogolite, nZVI and Imo-nZVI were analyzed using the Elovich equation and Weber-Morris models (Fig. 5).

Elovich equation

The Elovich equation (Eq. 7) is a widely used model in various systems whose reactive sites are energetically heterogeneous. The $\alpha$ parameter, associated with the initial rate of adsorption, was higher in single-component systems for all the substrates studied, indicating that the presence of both cations (Hg$^{2+}$ and Pb$^{2+}$) generated a strong competition for the active sites available in each material, explaining the lower values of $\alpha$ in multicomponent systems (Table 3). The desorption constant obtained from this model ($\beta$) was lower in the single-component systems, indicating that the different
available active sites can remove metals, observing the following decreasing order for both metals Imo-nZVI > nZVI > imogolite (Fig. 5). However, in competition, this parameter increases, showing that the removal of these analytes occurs in sites of greater specificity.

**Intraparticle diffusion kinetic model**

As previously discussed (Table 3), the immobilization of nZVI in imogolite generated changes in textural properties, which could generate changes in the overall removal rate of Hg\(^{2+}\) and Pb\(^{2+}\). The data were adjusted using the Weber-Morris model (Eq. 8) to determine these changes and whether intraparticle diffusion is the limiting step of the global speed for the removal process (Table 3). In general, multilinearity was observed for all the systems under study. Reductive precipitation and surface sorption are the main removal mechanism, with percentages greater than 90\% (q\(_e\)-1 values) of the analytes in all the systems evaluated (Fig. 5), which is consequence of new sites of adsorption (Fe-OH and Fe-O-OH) that provides the surface-functionalized imogolite with nZVI. C is related to the thickness of the limiting layer associated with instantaneous adsorption. This parameter was lower in multicomponent systems, which implies that accessibility to the active sites where sorption occurs is dependent on the composition of the solution, showing higher values for Hg. This result could be associated with the chemical characteristics of this element (i.e., ionic radius, polarizability, and electronegativity).

**Isotherm sorption**

The isotherms were studied for all elements in the single and multicomponent systems (Fig. 6, Table 4) at pH 4.0, considering a range of concentrations of Hg\(^{2+}\) and Pb\(^{2+}\) between 1 and 50 mg·L\(^{-1}\). In general, the curves of the isotherms showed an "L"-type shape, which indicates good affinity between the substrate and the analytes, as well as a
greater removal capacity in the single-component systems. However, in nZVI and the nanocomposite, the removal was greater than that in imogolite because in both substrates, the interactions are favored due to the displacement of the IEP and decrease in ZP. The experimental data were adjusted using the Langmuir model (Eq. 9), where \( q_{\text{max}} \) corresponds to the maximum removal capacity (mg·g\(^{-1}\)) and \( K_L \) is the Langmuir constant associated with the removal capacity (L·mg\(^{-1}\)).

All the materials in the single and multicomponent systems showed higher values of \( q_{\text{max}} \) and \( K_L \) for Pb\(^{2+}\) than for Hg\(^{2+}\). The values of \( q_{\text{max}} \) for Pb\(^{2+}\) and Hg\(^{2+}\) in the single and multicomponent systems had the same descending sequence: Imo-nZVI>nZVI>> Imogolite. Regarding the adsorption intensity (\( K_L \)), the nanocomposite showed an increase in this parameter, reaching 1.2 and 1.4 times higher values in comparison to nZVI and imogolite, respectively, probably associated with the decrease in the size of nZVI immobilized on the surface of imogolite (Table 4).

According to Misono softness parameters (\( Y\text{Hg}^{2+}=4.24 \) and \( Y\text{Pb}^{2+}=3.58 \)) (Misono et al. 1967), the functional groups of nZVI favored a stronger interaction with Hg\(^{2+}\) than Pb\(^{2+}\), due to the fact that Fe has a borderline character on the Misono softness scale. This observation is in agreement with the \( K_L \) value, which is a measure of the metal ion affinity to the adsorption sites on materials, which is enhanced in multicomponent systems (Table 4). The free energy (\( \Delta G^\circ \)) was determined for each material in the systems under study at a temperature of 25 °C and pH = 4.0 through the following equation: \( \Delta G^\circ = -RT\ln K \), where \( R \) is the gas constant (8.134 J mol\(^{-1}\)·K\(^{-1}\)) and \( T \) the temperature (K) using the Langmuir isotherms (Table S1). However, Zhou & Zhou (2014) reported that \( K_L \) cannot be used directly to obtain this parameter because it is expressed as L·mg\(^{-1}\). The standard equilibrium constant (\( K^\circ \)) using the Langmuir equation was calculated to avoid this problem using the equation \( K^\circ = K_L \cdot 10^3 \cdot 55.5 \) and replaced in the Gibbs free energy.
equation. The data obtained from this equation determined negative values of $\Delta G^\circ$ for the removal of Pb$^{2+}$ and Hg$^{2+}$ for imogolite, nZVI and the nanocomposite, both for single and multicomponent systems (Table S1). Hence, the process of removing Pb$^{2+}$ and Hg$^{2+}$ is spontaneous and thermodynamically favorable.

**Role of imogolite as a support for nZVI and its effects on the removal of Pb$^{2+}$ and Hg$^{2+}$.**

The structural and surface characteristics of imogolite describe how this nanotubular aluminosilicate significantly favors the removal of neurotoxic metals, such as Pb$^{2+}$ and Hg$^{2+}$, in single and multicomponent systems when it is used as a support for nZVI. Several investigations have shown that in situ synthesis of nZVI in different substrates, such as activated carbon, zeolite, kaolinite, and montmorillonite, causes a decrease in size and increase the removal capacity of nZVI; however, the impact of this process in imogolite has important nuances to take into account:

Due to the variable charge of imogolite, which is positive with ZP values higher than 25 mV between pH 3 and 7, the formation of nZVI occurs mainly at the edges of the nanotube, indicating that the surface sites have higher sensitivity to changes in pH, which are neutral or negatively charged according to the synthesis conditions of nZVI, favoring the adsorption of Fe$^{3+}$ and generating nuclei of attraction for other iron ions.

The high density and magnetic and hydrophilic properties of nZVI prevent it from being suspended, leading to rapid agglomeration and oxidation in aqueous systems, reducing the removal capacity of different analytes (Peng et al. 2018). In contrast, the behavior of imogolite is opposite to that described for nZVI since it remains in a stable suspension, even under conditions of unfavorable pH and ionic strength, due to its low density and
because water can structure itself in different ways in the pores of imogolite, which allows
the Imo-nZVI composite to be in suspension under conditions when nZVI is not.
Immobilization of nZVI on imogolite increases the reactivity of the material adding a new
type of surface active sites with functional groups such as $\equiv$Fe$^{(II)}$-OH, $\equiv$Fe$^{(II)}$-OOH,
$\equiv$Fe$^{(III)}$-OH, and $\equiv$Fe$^{(III)}$-OOH, generated through the oxidation of the nZVI. These
functional groups could preferentially react with Hg$^{2+}$ or Pb$^{2+}$ according to the softness
of the analytes and the polarizability of the Fe(II)/Fe(III) group. Thus, hard Pb$^{2+}$ would
interact preferentially with more polarized $\equiv$Fe$^{(III)}$-OOH and $\equiv$Fe$^{(III)}$-OH groups whereas
softer Hg$^{2+}$ would interact with $\equiv$Fe$^{(II)}$-OH and $\equiv$Fe$^{(II)}$-OOH groups (Fig. 7).

**Conclusions**

The hybrid nanomaterial (Imo-nZVI) synthesized in this work represents a very
interesting type of material because of its exceptional properties and potential use in a
wide range of application fields. The synergistic combination of both components was
efficiently tested as a sorbent material for neurotoxic metals removal. Based on the speeds
and removal capacities obtained, Pb$^{2+}$ was preferably removed by all materials, even in
systems that coexisted with Hg$^{2+}$. The process of immobilizing nZVI in imogolite caused
an increase of the speed and removal capacity of both metals compared to the starting
materials because the nZVI present in the nanocomposite is smaller than free nZVI. The
PSO and Langmuir models showed a better adjustment of the experimental data for all
the cases under study, which suggests that the removal process is produced by
chemisorption. The free energy associated with the removal of Pb$^{2+}$ and Hg$^{2+}$ indicates
that this process is spontaneous in all materials and is more favorable in nZVI. The
excellent percentage of recovery for Pb$^{2+}$ and Hg$^{2+}$ from water matrices and the magnetic
properties of Imo-nZVI make it a promising material for environmental applications.
Declarations

Ethics approval and consent to participate
Not applicable

Consent for publication
Not applicable

Availability of data and materials
Not applicable

Competing interests
The authors declare that they have no competing interests

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Authors' contributions
All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Estefanía M. Martinis and Nicolás Arancibia-Miranda. Material characterization and sorption kinetic data analysis were performed by Juliano C. Denardin, Raul Calderón, Cristóbal Flores, Karen Manquián-Cerdae and Tamara Maldonadoe. The first draft of the manuscript was written by Estefania M. Martinis and Nicolás Arancibia-Miranda. and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Figure Captions

Fig. 1. Morphology of the samples obtained by HR-TEM.

Fig. 2. ZP vs. pH plot of synthetic Imo, nZVI, and Imo-nZVI.

Fig. 3. Effect of contact time on the removal of heavy metals from each sample.

Fig. 4. Kinetic models of pseudo first-order (PFO) for (a) Imo, (b) nZVI, and (c) Imo-nZVI and pseudo second-order (PSO) for (d) Imo, (e) nZVI, and (f) Imo-nZVI.

Fig. 5. Fits of the experimental data to the Elovich equation for (a) imogolite, (b) nZVI, and (c) Imo-nZVI and Weber-Morris model for (d) Imo, (e) nZVI, and (f) Imo-nZVI.

Fig. 6. Langmuir isotherm for the adsorption of Pb$^{2+}$ and Hg$^{2+}$ in single (S) and multicomponent (M) systems on nZVI, Imo, and Imo-nZVI.

Fig. 7. Schematic representation of the possible interactions that occur on the surface of the Imo-nZVI. The affinity and intensity of removal of Pb$^{2+}$ and Hg$^{2+}$ with the different groups of the nanocomposite is conditioned by the magnitude of the Misono softness parameters ($Y_{Hg^{2+}} = 4.24$ and $Y_{Pb^{2+}} = 3.58$) and the possibility they have of interacting with functional groups with similar characteristics.
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 6
Fig. 7

**Removal mechanism:**
- Adsorption in aluminol group.
- Adsorption and/or partial reduction in Fe^{III-}OOH and Fe^{III-}OH
- Sorption preferably in Fe^{III-}OOH > Fe^{III-}OH

**Removal mechanism:**
- Adsorption in aluminol group.
- Reduction in Fe^{III-}OOH and Fe^{III-}OH
- Sorption preferably in Fe^{III-}OH > Fe^{III-}OOH
| Parameters                                      | Imogolite | nZVI | Imo-nZVI |
|------------------------------------------------|-----------|------|----------|
| Specific surface area (m²·g⁻¹)                   | 310       | 87   | 234      |
| External surface area (m²·g⁻¹)                    | 180       | 35   | 133      |
| Micropore volume x10⁻³ (cm³·g⁻¹)                  | 20        | 1.5  | 26       |
| Micropore area (m²·g⁻¹)                           | 66        | 17   | 50       |
| Pore Volume (cm³·g⁻¹)                             | 0.25      | 0.18 | 0.22     |
| Pore diameter (Å)                                 | 10        | 18   | 13       |
Table 2. Kinetic parameters predicted from pseudo first and pseudo second-order models. Standard error for each parameter is included in parenthesis.

| Parameters       | Pb²⁺ (single component) | Pb²⁺ (multi component) |
|------------------|-------------------------|-------------------------|
|                  | Imogolite   | nZVI      | Imo-nZVI | Imogolite   | nZVI      | Imo-nZVI |
| $q_{exp}$ (mg·g⁻¹) | 44.84 (3.26) | 63.66 (6.12) | 77.67 (6.89) | 38.75 (3.42) | 58.14 (5.55) | 73.70 (6.99) |
| $q_{exp}$ (%)     | 49.82 (3.33) | 70.73 (7.16) | 86.30 (7.99) | 43.06 (4.29) | 64.60 (6.07) | 81.89 (8.16) |
| $Pseudo-second$  | **Order**    | **Order**  | **Order**  | **Order**    | **Order**  | **Order**  |
| $q_{e}$ (mg·g⁻¹) | 47.90 (3.46) | 68.01 (6.66) | 81.96 (7.74) | 41.68 (4.09) | 62.54 (5.99) | 77.43 (7.99) |
| $k_2 \times 10^{-3}$ (g·mg⁻¹·min⁻¹) | 4.24 (0.26) | 2.98 (0.12) | 3.01 (0.41) | 4.34 (0.29) | 2.90 (0.11) | 2.68 (0.31) |
| $h$ (mg·g⁻¹·min⁻¹) | 9.73       | 13.78      | 20.22      | 7.54       | 11.34      | 16.07      |
| $r^2$            | 0.972      | 0.977      | 0.987      | 0.969      | 0.983      | 0.977      |

| Models           | Hg²⁺ (single component) | Hg²⁺ (multi component) |
|------------------|-------------------------|-------------------------|
|                  | Imogolite   | nZVI      | Imo-nZVI | Imogolite   | nZVI      | Imo-nZVI |
| $q_{exp}$ (mg·g⁻¹) | 38.25 (3.44) | 60.41 (7.11) | 75.83 (6.95) | 33.24 (3.81) | 55.41 (5.26) | 72.20 (8.01) |
| $q_{exp}$ (%)     | 42.50 (3.98) | 67.12 (6.14) | 84.26 (7.33) | 36.93 (3.06) | 61.57 (5.17) | 80.22 (7.94) |
| $Pseudo-second$  | **Order**    | **Order**  | **Order**  | **Order**    | **Order**  | **Order**  |
| $q_{e}$ (mg·g⁻¹) | 40.36 (4.46) | 63.74 (6.53) | 81.01 (8.03) | 34.92 (3.80) | 58.21 (5.11) | 77.66 (7.26) |
| $k_2 \times 10^{-3}$ (g·mg⁻¹·min⁻¹) | 6.54 (0.51) | 4.14 (0.46) | 2.50 (0.22) | 5.95 (0.61) | 3.57 (0.41) | 2.33 (0.29) |
| $h$ (mg·g⁻¹·min⁻¹) | 10.65    | 16.82      | 16.41      | 7.26       | 12.10      | 14.05      |
| $r^2$            | 0.978      | 0.987      | 0.981      | 0.979      | 0.963      | 0.977      |
Table 3. Kinetic parameters predicted from the linear analysis of Elovich and intraparticle diffusion kinetic models. Standard error for each parameter is included in parenthesis.

| Elovich Equation | Pb$^{2+}$ (single-component) | Pb$^{2+}$ (multi-component) |
|------------------|-----------------------------|-----------------------------|
|                  | Imogolite | nZVI | Imo-nZVI | Imogolite | nZVI | Imo-nZVI |
| $\alpha$         | 9.09 (0.51) | 16.39 (2.01) | 18.94 (1.71) | 8.50 (1.10) | 11.54 (0.83) | 11.99 (1.21) |
| $\beta$          | 0.06 (0.00) | 0.07 (0.01) | 0.07 (0.00) | 0.06 (0.01) | 0.07 (0.00) | 0.10 (0.01) |
| RMSE             | 0.41 | 5.75 | 0.51 | 18.00 | 1.03 | 11.58 |
| $r^2$            | 0.993 | 0.937 | 0.990 | 0.773 | 0.993 | 0.937 |

| Elovich Equation | Hg$^{2+}$ (single-component) | Hg$^{2+}$ (multi-component) |
|------------------|-----------------------------|-----------------------------|
|                  | Imogolite | nZVI | Imo-nZVI | Imogolite | nZVI | Imo-nZVI |
| $\alpha$         | 16.94 (1.24) | 18.84 (2.31) | 24.35 (2.63) | 13.64 (0.11) | 14.17 (2.03) | 19.52 (0.19) |
| $\beta$          | 0.05 (0.00) | 0.05 (0.01) | 0.06 (0.00) | 0.09 (0.00) | 0.10 (0.02) | 0.14 (0.00) |
| RMSE             | 1.41 | 40.51 | 16.43 | 1.70 | 62.46 | 2.49 |
| $r^2$            | 0.990 | 0.773 | 0.937 | 0.993 | 0.773 | 0.990 |

| Intraparticles Diffusion | Pb$^{2+}$ (single-component) | Pb$^{2+}$ (multi-component) |
|--------------------------|-----------------------------|-----------------------------|
|                          | Imogolite | nZVI | Imo-nZVI | Imogolite | nZVI | Imo-nZVI |
| $q_{eq}$                 | 28.84 (3.23) | 48.18 (3.99) | 66.47 (7.99) | 36.30 (4.01) | 58.84 (5.29) | 69.00 (7.03) |
| $k_{int1}$               | 0.10 (0.02) | 0.16 (0.02) | 0.36 (0.05) | 0.31 (0.02) | 0.52 (0.04) | 0.25 (0.03) |
| $C_1$                    | 13.3 (1.20) | 25.4 (1.99) | 33.1 (4.29) | 20.21 (2.54) | 33.03 (3.54) | 35.1 (3.43) |
| $r^2$                    | 0.951 | 0.951 | 0.857 | 0.950 | 0.950 | 0.954 |

| Intraparticles Diffusion | Hg$^{2+}$ (single-component) | Hg$^{2+}$ (multi-component) |
|--------------------------|-----------------------------|-----------------------------|
|                          | Imogolite | nZVI | Imo-nZVI | Imogolite | nZVI | Imo-nZVI |
| $q_{eq}$                 | 34.29 (4.01) | 52.00 (5.78) | 74.82 (7.09) | 41.04 (4.21) | 58.57 (5.99) | 73.96 (8.01) |
| $k_{int1}$               | 0.21 (0.01) | 0.31 (0.04) | 0.21 (0.01) | 0.14 (0.05) | 0.20 (0.01) | 0.69 (0.01) |
| $C_1$                    | 17.35 (2.23) | 27.15 (2.27) | 72.7 (5.99) | 22.3 (3.01) | 31.1 (3.02) | 41.3 (4.12) |
| $r^2$                    | 0.859 | 0.856 | 0.951 | 0.864 | 0.954 | 0.950 |
Table 4. Parameters of Langmuir isotherm models for Pb\(^{2+}\) and Hg\(^{2+}\) adsorption on imogolite, nZVI and Imo-nZVI in single and multi-component systems. Standard error for each parameter is included in parenthesis.

| Parameters | Pb\(^{2+}\) (single-component) | Pb\(^{2+}\) (multi-component) | Hg\(^{2+}\) (single-component) | Hg\(^{2+}\) (multi-component) |
|------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
|            | Imogolite | nZVI | Imo-nZVI | Imogolite | nZVI | Imo-nZVI | Imogolite | nZVI | Imo-nZVI | Imogolite | nZVI | Imo-nZVI |
| qmax       | 68.84 (7.22) | 81.43 (8.31) | 94.77 (9.42) | 62.75 (7.01) | 70.65 (7.07) | 76.94 (7.13) | 56.99 (5.92) | 62.08 (6.61) | 72.66 (7.22) | 49.76 (7.22) | 56.00 (7.22) | 61.58 (7.22) |
| K\(_L\)    | 0.77 (0.08) | 2.92 (0.23) | 16.66 (1.72) | 0.73 (0.09) | 2.78 (0.25) | 31.50 (0.37) | 0.74 (0.07) | 5.55 (0.48) | 21.71 (3.01) | 0.93 (0.11) | 7.84 (0.80) | 54.02 (5.98) |
| r\(^2\)    | 0.989 | 0.991 | 0.998 | 0.969 | 0.996 | 0.977 | 0.990 | 0.993 | 0.979 | 0.974 | 0.996 | 0.987 |
Supporting information

Enhanced removal of mercury and lead by a novel and efficient surface-functionalized imogolite with nanoscale zero-valent iron material

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Fig S1. X-ray diffraction of imogolite (a), nZVI (b), Imo-nZVI (c), Imo-nZVI/Pb (d), Imo-nZVI/Hg (e), and Imo-nZVI/Pb-Hg (f).
Fig S2. Hysteresis curve of Imo-nZVI pre- and post-sorption of Hg, Pb and Pb-Hg (a).

Enlargement of the magnetization curves (b).
### Table S1. Speciation curve

| Species     | Log K  | Conc. [mol/l] |
|-------------|--------|---------------|
| Hg2++       | 0.000E0 | 0.182         |
| Hg2OH+      | -4900  | 0.00228       |
| K+          | 0.000E0 | 9.93          |
| KOH         | -14500 | 3.13E-11      |
| KNO3        | -150   | 0.0696        |
| NO3-        | 0.000E0 | 9.91          |
| Pb++        | 0.000E0 | 0.158         |
| PbOH+       | -7700  | 0.00000314    |
| Pb(OH)2     | -17100 | 1.25E-12      |
| Pb(OH)3-    | -28100 | 1.24E-20      |
| Pb2OH+++    | -6400  | 9.87E-09      |
| Pb3(OH)4++  | -23900 | 4.89E-21      |
| Pb4(OH)4++++| -20900 | 7.71E-22      |
| Pb6(OH)8++++| -43600 | 3.79E-40      |
| PbNO3+      | 1170   | 0.0231        |
| Pb(NO3)2    | 1400   | 0.000389      |
| OH-         | -14000 | 9.98E-09      |
| H+          | 0.000E0 | 1             |

### Table S2. ΔG values for the studied materials.
| Parameters       | \(\Delta G \text{ (J} \cdot \text{mol}^{-1}) \times 10^3\) | \(\text{Pb}^{2+}\) (single component) | \(\text{Pb}^{2+}\) (multi component) |
|------------------|-------------------------------------------------|--------------------------------------|-------------------------------------|
|                  | Imogolite nZVI Imo-nZVI Imogolite nZVI Imo-nZVI | Imogolite nZVI Imo-nZVI Imogolite nZVI Imo-nZVI | Imogolite nZVI Imo-nZVI Imogolite nZVI Imo-nZVI |
| \(\Delta G \text{ (J} \cdot \text{mol}^{-1}) \times 10^3\) | -45.2 -50.2 -54.5 | -45.3 -48.6 -52.9 | -45.7 -51.0 -55.8 | -45.1 -48.4 -53.5 |

868 869 870 871 872 873 874 875 876 877 878 879 880 881 882
Figure 1

Morphology of the samples obtained by HR-TEM.
Figure 2

ZP vs. pH plot of synthetic Imo, nZVI, and Imo-nZVI.
Figure 3

Effect of contact time on the removal of heavy metals from each sample.

Figure 4
Kinetic models of pseudo first-order (PFO) for (a) Imo, (b) nZVI, and (c) Imo-nZVI and pseudo second-order (PSO) for (d) Imo, (e) nZVI, and (f) Imo-nZVI.

Fig. 5

Figure 5

Fits of the experimental data to the Elovich equation for (a) imogolite, (b) nZVI, and (c) Imo-nZVI and Weber-Morris model for (d) Imo, (e) nZVI, and (f) Imo-nZVI.

Fig. 6
Figure 6

Langmuir isotherm for the adsorption of Pb2+ and Hg2+ in single (S) and multicomponent (M) systems on nZVI, Imo, and Imo-nZVI.

Fig. 7

Schematic representation of the possible interactions that occur on the surface of the Imo-nZVI. The affinity and intensity of removal of Pb2+ and Hg2+ with the different groups of the nanocomposite is conditioned by the magnitude of the Misono softness parameters (YHg2+ = 4.24 and YPb2+ = 3.58) and the possibility they have of interacting with functional groups with similar characteristics.

Supplementary Files

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