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Mobility of Heavy Metals in Aquatic Environments Impacted by Ancient Mining-Waste

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Abstract

The mobility of heavy metals in aquatic environments, impacted by discharges from mining waste, is one of the major processes causing metal pollution mainly by arsenic (As), cadmium (Cd), lead (Pb), zinc (Zn) and iron (Fe), which could be risky for biota and human health. The heavy metals contained in mining waste constituted by large amounts of sulfides can reach the aquatic compartments by acid mine drainage and runoff and eventually become deposited in sediments and associated with colloidal material, being this one of the main reservoirs and ways of transport. However, the mobility of heavy metal is influenced by their specific chemical properties and undergo several physicochemical phenomena as sorption, oxidation–reduction, hydrolysis and this can be influenced by water flow, the size and composition of geological material. Hence, this work aims to review the processes and mechanism involved in the fate and transport of heavy metals from mining-waste to aquatic compartments and the methods used for identification of the specific chemical species associated with their mobility and ecological risk.

Keywords: mobility, heavy metals, mining-waste, hardpads, acid mine drainage, sediments

1. Introduction

Heavy metals in aquatic environments have mainly a natural origin due to the geological parent material (lithogenic), they can be incorporated into different materials as silicates, carbonates, oxides, hydroxides, and sulfides structures and as a native element. They also could result from anthropogenic sources including deposition of particles ($<30\text{ }\mu\text{m}$ in diameter) and precipitation containing heavy metals, fertilizers application, the use of agrochemicals, spilled of wastewater and mining waste [1, 2]. Among anthropogenic sources, ancient mine residues, has a

high impact and pose a threat to the environment and health as a consequence of the rustic extraction method and their high content of heavy metals such as arsenic (As), lead (Pb), cadmium (Cd), mercury (Hg), copper (Cu), zinc (Zn) and Iron (Fe), which can cause high damage to aquatic biota and human health [3, 4].

Metals are partitioned among the various aquatic environmental compartments (water, suspended solids, sediments and biota) and can occur in dissolved, particulates or complex form. The metals and metalloids can reach the aquatic environments from mining waste as metallic ions and complexes in dissolved solid formed either by weathering, erosion and run off processes. Once a metal reaches an aquatic reservoir, it does not suffer any degradation, rather they are accumulated in sediments and depending on their chemical form it can increase or reduce their toxicity, bioavailability, and solubility [5–7].

Sediments are considered a main sink and means of transport of organic and inorganic pollutants in aquatic environments. It has been found that they have a great capacity to adsorb metals and metalloids present in the aqueous phase and reduce their mobility in the aquatic environment [3, 8, 9]. Among different particles size that constitute sediments, metals are mainly associated with the smallest particles of colloidal size ranging from 0.001 to 0.1 μm in diameter due to their largest surface area and most likely as a consequence of occurrence of ionic exchange sites linked to several chemical species such as humus Fe, Al and Mn, oxyhydroxides, aluminosilicates and some moderately soluble salts such as calcium carbonate (CaCO_3).

The mobility of trace elements, from the vadose zone to the aquifers and in rivers and tributaries, also influenced by sorption, oxidation–reduction, hydrolysis, and complexation and chelation processes, determining the transport of highly toxic metals and metalloids in aquatic environments [1]. Adsorption is likely the most important process that determines the mobility of traces metals in aquatic environments, since it supports ions at the interface between the solid and the aqueous phase, the clay and humus material with a negative charge on its surface adsorbs cations, while oxyhydroxides with varying charges on their surface can adsorb cations and anions, respectively.

Hence, this work aims to review the processes and mechanism involved in the dynamics (fate and transport) of heavy metals from mining-waste to aquatic compartments and the methods used for identification of chemical species associated with their mobility and ecological risk.

2. Processes involving in mobility of heavy metals in natural waters

The mobility of metals and metalloids in aquatic compartments is a very complex phenomenon as it involves a great variety of physical, chemical and biological processes mainly determined by pH values, precipitation and dissolution of secondary minerals, sorption–desorption reactions, hydrolysis processes, by oxidation–reduction processes and co-adsorption processes, for instance: graphene oxide a very soluble chemical specie, it is commonly found in aquatic environments, adsorbed on inorganics contaminants such as the hematite and goethite, which co-adsorbed graphene oxide about 92% at pH 3–5 [10].

The degree sorption/desorption of metals depend on time of contact between sorbate and sorbent and oxide aging due to the weathering. The adsorption and precipitation can be simultaneous but can dominate a mechanism due to reaction conditions and metal involved. When the precipitate consists of species derived from both aqueous solution and dissolution of the mineral, it is referred to as a coprecipitate [7].

Overall, Zn, Cd, Cu and Al cations have high concentrations in acidic water and undergone high mobility, while oxyanions such as SO_4^{2-} , AsO_4^{3-} , MoO_4^{2-} , CrO_4^{2-} increase their mobility when water is neutral or alkaline [4, 11].

2.1 Cation exchange adsorption

Non-specific or cation exchange adsorption, also known as physical adsorption, is an electrostatic phenomenon that occur on the surface of clays (kaolinite, illite, montmorillonite, vermiculite, smectite and chlorite) and it is caused by the weathering of olivine, augite, pyroxene, mica and feldspar. Structure of clays are characterized by thick microcrystalline sheets composed of tetrahedral layers of silica and octahedral layers of aluminum in 1: 1 or 2:1 proportion [1].

Cation exchange is carried out by less selective outer-sphere clusters. The cations are bound to the surface of the negatively charged clay through weak covalent bonding independent of the aqueous pH value. This type of phenomenon is reversible in nature, and occurs very quickly, typically controlled by diffusion and electrostatic reactions, while the smallest ions of the aqueous phase are exchanged for larger ions on the surface of clay, for example, Mg^{2+} exchange Al^{3+} and Al^{3+} exchange Si^{4+} . The number of cations reversibly adsorbed per unit weight of adsorbent (e. g. clay) is called cation exchange capacity (CEC) [2].

2.2 Specific adsorption

The specific adsorption is also known as chemisorption or surface complexation. It is mainly carried out in oxides of Fe, Al, and Mn. The ions, either cations or anions, are highly bonded on the surface of the oxides by covalent bonding with oxygen atom or OH groups. The Fe or Mn oxide are electrically charged by the adsorption or release of H^+ ions, from the oxygen atoms at the interface between the mineral and the solution. Because oxides are amphoteric chemical compounds, they have negative and positive charges on their surface, and the net charge is largely symmetric about at zero point, at a characteristic pH value. The pzc, stand for zero point of charge varies between several oxides compound; Fe oxides have a pzc between pH 7.0 and 8.5 which implies a positive charge on their surface. While the pzc of Mn oxides varies between pH 1.5 and 4.6, which indicates that they have a net negative charge on their surface [1]. It is carried out on the surface of Fe and Mn oxides with variable charges and complexation with MO functional groups, by weak electrostatics charges with pH-dependent bonding.

2.3 Hydrolysis

In pure water at 25°C, $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$ and pH = 7.0 (neutral pH); when dissolving NaCl in water there is no an appreciable hydrolysis reaction and the pH of the solution remains at a value of 7.0. However, when ammonium chloride (NH_4Cl) is added to the water, pH drops below 7.0, it means that $[\text{H}_3\text{O}^+] > [\text{OH}^-]$, and when sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$) is dissolved in water, pH increases above 7.0, it means that $[\text{OH}^-] > [\text{H}_3\text{O}^+]$. In general, salts containing an ion of an alkali or alkaline earth metal (except Be^{2+}) do not significantly hydrolyze; thus, when a substance is added to water and dissociated, one of its ions causes a change in the pH of water ($\text{pH} \neq 7$), it is at that moment when we speak of a hydrolysis reaction. In fact, all positive ions react with water to produce an acidic solution [12, 13].

In deposits of tailings containing high levels of sulfides such as pyrite and pyrrhotite, during complex oxidation process, Fe^{2+} dissolves and when reacting with water, carries out a hydrolysis reaction, increasing the acidity of the medium by decreasing the pH value [Eq. (1)] [8, 9]. Likewise, when Fe^{2+} is oxidized to Fe^{3+} and pH values >5 , a hydrolysis reaction occurs, releasing H^+ and ferric hydroxide (reaction 2) that generates an oxyhydroxide [4]. However, the increase in acidity in a mining waste, even though it reaches the aquatic environment, does not necessarily implies that the water has low pH values since the presence of carbonate minerals can neutralize the acidity.

2.4 Oxidation-reduction

Sulfide minerals in mining waste pose several relative resistances to weathering (**Table 1**) [9]. However, due to physicochemical processes, the weathering process presents alterations that influence the composition of water that can drain or percolate in the mining waste.

The oxidation of sulfur minerals is due frequently to their deposition in aerated places where sulfide minerals are thermodynamically unstable. Therefore, pyrite and pyrrhotite, which generally dominate sulfide deposits are the first sulfides to undergo oxidation [Eqs. (3) and (4)] due to their chemical composition. During oxidation process, one mole of pyrite and pyrrhotite with atmospheric oxygen, is the main electron acceptor, and water form Fe^{2+} , 4 and 2 moles of acid, respectively [9]. However, sphalerite, chalcopyrite, galena and arsenopyrite also contribute to the generation of acid drainage [4, 14].

Mineral	Formula	Resistances
Pyrrhotite	$Fe_{(1-x)}S$	<div>Low</div> <div>↓</div> <div>High</div>
Galena	PbS	
Sphalerite	$(Zn, Fe)S$	
Bornite	Cu_5FeS_4	
Pentlandite	$(Fe, Ni)_9S_8$	
Arsenopyrite	FeAsS	
Marcasite	FeS_2	
Pyrite	FeS_2	
Chalcopyrite	$CuFeS_2$	
Magnetite	Fe_3O_4	
Molybdenite	MoS_2	

Table 1.
Relative resistances of sulfide minerals and magnetite in oxidized tailings taken from [9].

Heat is released when oxidation reaction of metal sulfides occurs. When pyrite is oxidized and form acid, this reaction releases 1440 KJ.mol^{-1} , heat that is hardly released by an oxidation reaction [15]. The heat generated by that exothermic reaction of pyrite, as long as there is high permeability in the tailings cover, it transports oxygen by convection, increasing oxidation rate of sulfides. However, when a reservoir is saturated with water, advective transport is reduced and the main oxygen transport mechanism is diffusion [14, 16]. In addition, oxygen can be supplied by wind in lateral parts of deposit, where oxygen can migrate upward or reach basal regions by advection, convection and diffusion, [17]. Therefore, low concentrations of oxygen are due to its high consumption in oxidation of sulfides minerals and to a limited supply due to the low permeability that governs waste materials.

When the cover of the tailings dam is depleted in oxygen and the air supply is insufficient, high oxidation of sulfides causes water to be characterized by $\text{pH} < 3$, high concentrations of sulfates and metals, for instance Zn, Fe, Pb. Under these scenarios, Fe^{3+} ion remains in solution and becomes the dominant oxidant of metal sulfides, generating acidity in the environment, Eqs. (5) and (6) show generation of acid from oxidation of pyrite and pyrrhotite [9].

2.5 Geological factors influencing mobility of heavy metals

Geological formations are volumes of rocks confined to a certain space, they are formed by different types of rocks (igneous, sedimentary, and metamorphic) of different nature, they can enclose mineral deposits of great economic value. Metallic mineral deposits are generally enriched in sulfides such as: pyrite (FeS_2), pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$), sphalerite (ZnS), chalcopyrite (FeCuS_2), arsenopyrite (FeAsS), galena (PbS) and cubanite (CuFe_2S_3). From the metallurgical method, the recovery of high economic value metals such as Pb, Zn and Cu is carried out, releasing to the environment waste ground material commonly called “tailings” enriched in gangue minerals that do not represent any economic interest for its exploitation as: pyrite (FeS_2), arsenopyrite (FeAsS), pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$), calcite (CaCO_3), quartz (SiO_2) and K feldspars (AlSi_3O_8) [3, 18].

Once the deposition of tailings is concluded, either if oxygen and water flow through pores or if there is ferric ion, oxidation of sulfides occur, generating acidity through the release of protons H^+ (Eqs. (7)–(10)). In deposit of tailings, As is associated with pyrite, Zn and Cd with sphalerite, and they are released when these minerals are dissolved. Despite that galena has a reactivity similar sphalerite, it does dissolve very slowly because secondary mineral of anglesite (PbSO_4) generally precipitates on its edges, which avoid its dissolution even in highly oxidized environments removed from sphalerite. Cu in acidic environments is released from chalcopyrite, while Co and Ni are generally derived from the oxidation of pyrite and pyrrhotite [3, 9].

If the oxidation of sulfides remains, the acidity would increase at pH <4, generating acid mine drainage (AMD). However, if the mineralogy of the encasing rock has enough carbonate as calcite (CaCO₃), hydroxide and silicate, when dissolution occurs, acid is consumed and neutralization of the AMD is completed [Eq. (11)], originating secondary gypsum precipitates and other metal sulfates [9, 11].

However, when acidity-consuming minerals are insufficient, neutralization is not achieved, so continuous generation of AMD dissolves mineral phases, causing supersaturation of ions with high electrical conductivity and generating the precipitation of secondary minerals such as oxyhydroxides of Fe³⁺ (goethite), hydroxysulfates (jarosite, scorodite and beudantite). Those highly oxidized tailings, are rich in sulfides; the precipitation of these minerals' forms cemented layers known as hardpads, of low porosity and high density that serve as hydraulic barriers and temporary sinks of metals and metalloids, where the precipitation of beudantite and scorodite limits the mobility of As and Pb, and Fe oxyhydroxides adsorb Cd, Pb, Cr, Zn (despite their high mobility) and As where substitution process in jarosite is common [3, 6, 8]. Although Fe oxyhydroxides have a high adsorption capacity for highly toxic metals, it decreases as increasing crystallinity, the larger grain size the lower surface area. Although high concentrations of metals and metalloids reach the aquatic environment by runoff, their mobility will depend on the nature of the sediments and minerals that predominate in the aquatic environment [9].

3. Chemical fractionation of heavy metals from sediments

In order to obtain information about mobility and potential toxicity of heavy metals or their potentially dangerous effects on the environment, it is necessary to implement a methodology that determines speciation or fractionation of those metals in sediments [19]. Different schemes of chemical fractionation [20] have

Fraction	Reagent or solution	Conditions	Geochemical fraction
Water soluble elements and adsorbed by electrostatic force (F1)	16 mL 1 M of MgCl ₂	Shakes for 1 hour at room temperature	Salts soluble in water and adsorbed by electrostatic force
Elements associated with carbonates (F2)	16 mL of NaOAc 1 M, adjusted to pH 5 with HOAc	Shakes for 2 hours at room temperature	Associated with secondary carbonates
Elements associated with oxihidroxidos (F3)	40 mL of NH ₂ OH.HCl 0.04 M in HOAc al 25% v/v	90°C with occasional shakes for 4 hours	Oxihidroxidos of primary and secondary
Elements associated with organic matter and sulfides (F4)	6 mL of HNO ₃ 0.02 M and 10 de H ₂ O ₂ 30% (pH 2 with HNO ₃)	85°C for 2 hours	Organic matter and sulfides
Residual (F5)	20 mL of HF and 4 mL of HClO ₄ , 20 of HF and 2 of HClO ₄ , HCl 12 N	The mixture is heated to dryness	Primary minerals such as silicates and quartz

Table 2.
Sequential chemical extraction methodology from Tessier 1979.

been used to identify and quantify concentrations of heavy metals and metalloids present in different fractions. However, the sequential extraction that suggests Tessier 1979, is one of the most used. Each fraction or extract corresponds to the metals associated with water or reagent (acid), Tessier method suggested five chemical fractions: exchangeable fraction (F1), fraction of carbonates (F2), reducible fraction or oxyhydroxides of Fe and Mn (F3), Oxidizable fraction or organic matter and sulfides (F4) and residual fraction (F5) that are extracted with different reagents, under different physicochemical conditions (**Table 2**) [20–22].

4. Discussion

Metals are transported from tailings deposit to the stormwater system through runoff in the soluble or particulate form. Depending on physicochemical conditions of aqueous medium and nature of metal, these can be adsorbed to the colloidal material, precipitate, solubilize or to be complexed. When sequential chemical extraction is applied to sediments impacted by old mining wastes with high concentrations of minerals such as sulfides and significant amounts of carbonates and silicates, it has been determined that Zn, although it has been found in fractions F2 and F3, tends to be more abundant in F1, that is, it has high mobility and availability in the aquatic environment, Cu has more affinity for F3 and F4 fraction [3, 9, 19] and As is generally found adsorbed to the oxyhydroxide fraction [23]. Although in stormwater systems the highest concentrations of heavy metals are found in sediments, rather than in the soluble fraction, these can be available mainly due to changes in pH and cause great effects on aquatic organisms and on the health of the man [24]. On the other hand, the fractionation is also a useful tool to determine whether pollutants are of natural origin or anthropogenic. Heavy metals of origin anthropogenic are present mainly in the first fractions, while that the origin lithogenic are in the residual fraction [19].

The old mining residues (tailings), that were deposited near the rivers; they are characterized by having large amounts of sulfides (mainly pyrite and pyrrhotite) with high concentrations of potentially toxic elements (PTEs) [25]. When the sulfides in the tailings are exposed to weathering by the presence of water, atmospheric and dissolved oxygen, oxidation process takes place [26]. The oxidation process, as undergo for pyrite is very complex, when the oxidation reaction is carried out, heat is released, which, by advection, can significantly improve transport of gas in the waste pile, increasing oxidation rate of sulfides [16]. Furthermore, oxygen can also enter lateral parts of reservoir upward and into basal regions. Nevertheless, in the rainy season, tailings deposits can become saturated with water, so diffusion is the main oxygen transport mechanism [14].

In oxidation of pyrite, Fe^{2+} dissolves and reacts with water through hydrolysis process, it generates acidity [9]. On the other hand, when the mining waste cover has insufficient atmospheric oxygen, a high oxidation of sulfides causes water to have a $\text{pH} < 3$, then under these acidic conditions, Fe^{3+} can remain in solution and become a dominant oxidant for the oxidation of pyrite [4]. The oxidation of pyrite, causes the dissolution of sulfides such as: sphalerite, pyrrhotite, arsenopyrite and chalcopyrite, although galena has reactivity similar to sphalerite, it does not dissolve easily since an anglesite (PbSO_4) edge is formed in galena that is almost insoluble in acidic environments.

If oxidation of sulfides continues at values $\text{pH} < 4$, the generation of AMD occurs, which can be neutralized if the encasing rock has enough carbonates, hydroxides, and silicates to consume the acidity generated [3]. However, if oxidation persists, and $\text{pH} < 3$, precipitation of secondary phases such as ferric

oxyhydroxides and gypsum takes place, which is accumulate, causing cementation and agglomeration of grains called “hardpan”, it decreases the porosity below the surface. The formation of hardpans limits water infiltration and vertical oxygen diffusion [27], for this reason they are considered hydraulic and diffusive barriers that protect the non-weathered material from oxidation [28]. In historical residues from New Zealand [29] they found that hardpan is mainly composed of very fine minerals (μm and nm) of Fe-As-S, in which the oxyhydroxides of As, bukovskyite $[\text{Fe}_2(\text{AsO}_4)(\text{SO}_4)(\text{OH}) \cdot 7\text{H}_2\text{O}]$ and scorodite $(\text{FeAsO}_4 \cdot 2\text{H}_2\text{O})$ are the most abundant. The formation of cement is facilitated in dry climates that allow the evaporation process that improves the cementation of minerals. Although, hardpans serve as sinks for PTEs, their function is not permanent, since their layers could undergo fracturing, and as consequence the infiltration of oxic surface water can cause oxidation of sulfides [30]. On the other hand, the aging of oxyhydroxides (ferrihydrite to goethite) reduces the adsorption capacity due to the increase in crystallinity [31].

Furthermore, precipitation of secondary minerals such as jarosite has a great synergistic capacity to simultaneously incorporate Pb (II) and As (V) in its structure, during mineral growth and mineral-water interactions; amount of As (V), which replaces SO_4 is greater when Pb (II) is also incorporated, in the same way amount of Pb incorporated in the structure is also greater when As (V) is incorporated, this simultaneity seems to confer less aqueous solubility to jarosite [32]. Despite presence of hardpans, if the oxidation of sulfides continues, acid dissolves mineral species that contain high concentrations of PTEs, and then are available to reach stream water through runoff. PTEs in surface waters are found in their different compartments. However, sediments are considered the main sink and transport medium, since, through adsorption, precipitation, co-precipitation and coadsorption they can remove highly toxic elements; the adsorption and coprecipitation in Fe minerals limit migration of pollutants in aquatic environments [33]. Although [34] have been found by SEM (Scanning Electron Microscope), that johansenite (manganese pyroxene) originates MnO which could be better adsorbent of PTEs than FeO.

In the Yinma River, in Northeast China [35] they found that Pb and Cu had higher adsorption affinity to sediments than Ni and Cd, and they were adsorbed in higher concentrations to Fe and Mn oxyhydroxides, than in matter organic and residual (solid primary minerals). Cu in ferrihydrite is adsorbed by outer sphere interaction weak bonds (ion exchange) and by inner sphere interaction strong bonds (specific adsorption). However, the presence of organic carbon (OC) causes ferrihydrite, although it precipitates at a smaller size (5 nm to 1 nm), forms a layer or cover that inhibits adsorption of Cu, so Cu is contained mainly by coprecipitation, being trapped in cavities, when precipitation takes place [36]. In addition, it have been found that Cu is adsorbed to humic acids, by ionic bonding and complex formation through its carboxylic and phenolic functional groups, sorption capacity is mainly carried out at $\text{pH} < 4$, at higher pH, sorption could be complicated [37].

The mobility and fate of As in sediments and groundwater is strongly controlled by the sorption process, and its extent of adsorption is influenced by the presence of OM. Coprecipitation/preadsorption of HA in ferrihydrite inhibits As from binding to Fe oxyhydroxides because OM can compete with As for available binding sites, promoting the mobility of $\text{As (v)} > \text{As (III)}$ [38]. Likewise, the retention of As (III) and As (V) on goethite surfaces is reduced in the presence of (HA) and (FA) [39]. Furthermore, the sorption of As in sulfurous minerals also influences mobility, since it can co-precipitate in FeS_2 or precipitate in sulphides such as rejalgar (As_4S_4)

[40]. Several studies indicate that Zn and Cd are highly mobile, $Zn > Cd$; [41] found that Zn presented high correlation with aluminosilicates, and the adsorption results indicate that it is mainly adsorbed on clays through weak external sphere bonds. Aquatic environments commonly contain graphene oxide (a very soluble substance), which is characterized by its surface containing carboxyl groups that can form complexes with metal ions and coadsorb (approx 91%) to hematite and/or goethite at pH 3-5, decreasing its adsorption when it increases; this coadsorption is considered an irreversible process [10].

5. Conclusions

Ancient mining waste contains large amounts of sulfurous minerals with highly and concentrated toxic elements that, exposed to weathering, undergo hydrolysis and oxidation–reduction reactions and form AMD, that dissolves mineral phases and release As, Pb, Cd, Zn, Cu and Fe. AMD cause secondary minerals formation such as clays, gypsum, jarosite, ferrihydrite, hematite, among others; when minerals of ferric oxyhydroxide and gypsum are agglomerated and strongly cemented form hardpans that are important sinks mainly of As. Likewise, jarosite, during its growth, incorporates As (V) and Pb (II) in its structure simultaneously, achieving less aqueous solubility.

Due to AMD, the PTEs by runoff reach rainwater and, due to the prevailing pH, neutral to slightly basic in stream water currents, the highly concentrated metals and As are absorbed into the finest particles of the sediments (clays, oxyhydroxides and OM). Thus, the mobility and fate of As and metals in sediments and groundwater is strongly controlled by the sorption process, and extent of adsorption is influenced by the presence of OM. Metals such as As, Pb, Cd and Cu are adsorbed to oxyhydroxides by specific adsorption, by inner sphere strong bonds, causing reduced mobility. On the other hand, ion exchange, although it also takes place in most metals, is more representative of Zn, by outer sphere weak bonds, that cause high mobility. Cu, in the presence of OC, rather than adsorbed by internal sphere bonds, this is co-precipitated in the cavities of the ferrihydrite. Likewise, in sediments rich in sulfides, As can precipitate as realgar (As_4S_4) or co-precipitate in pyrite. The coprecipitated/preadsorbed HA in the ferrihydrite inhibit As binding, promoting the mobility of As (v) > As (III).

The risk that PTEs represent to human health can be inferred by their speciation or fractionation chemical perfil. Although sediments have high concentrations of toxic metals, only those found in fraction 1 and 2, soluble/interchangeable and carbonate, respectively, are those what present greater mobility, toxicity, and bioavailability in aquatic environments. However, the concentrations of As and metals in the distinct fractions could undergo changes mainly due to variations in the pH.

In addition, understanding of the physicochemical processes and mineralogy in tailings deposits could contribute to create more efficient protocol and alternatives to reduce mobility of PTEs in sediments and aquatic environments and consequently reduce effects on human beings.

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Conflict of interest

The authors declare no conflict of interest.

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