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Synthesis of Multicomponent Nanoparticles for Immobilization of Heavy Metals in Aqueous Phase

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Abstract

This study is focused on the preparation of multicomponent nanoparticles (MCNPs) used to remediate artificial and real mine tailings. The nanoparticles were synthesized with 0.035 M or 0.007 M of sodium sulfate, 0.5 M of iron chloride and 0.8 M of sodium borohydride. Characterization of nanoparticles performed with a Transmission Electron Microscope (TEM), X-ray diffractometer (XRD), Fourier Transform Infrared Spectrometer (FTIR), and X-ray Photoelectron Spectrometer (XPS) demonstrated, these materials are in the nanoscale range, contain zero valent iron Fe(0) and iron sulfide (FeS) and are structurally modified after treatment. Simultaneous removal of heavy metals was carried out under oxidizing and reducing conditions using MCNPs reaching an efficiency of more than 98% for all of them. Kinetics conducted under oxidizing condition, pH 3 and 0.035 M sodium sulfate shows that the highest removal of heavy metals from artificial mine tailings was achieved after 160 min of treatment although steady state was reached in 240 mins. Results of kinetic tests fit very well to a pseudo-second-order model, while the isothermal equilibrium adsorption tests were adjusted to a Freundlich isotherm. Also, nanoparticles showed a high adsorption capacity (~140 mg/g) when they were in contact with 200 mg Cu^{2+}/L. Finally, multicomponent nanoparticles tested with real mine tailings in the presence of other competing chemicals results in heavy metals removal over 90%.

Keywords

Multicomponent, Nanoparticles, Removal, Heavy metals, Mine tailing

Introduction

Mining is an important economic activity worldwide, but it has generated a huge pollution in the environment, mainly because of poor exploitation processes and wrong disposal of mine tailings [1-3]. Actually, the delivery of hazardous contaminants to the ecosystem, especially heavy metals into the water streams is a great concern (EPA, 2012). Chemical characterization of mine tailings has found the presence of heavy metals such as Hg^{2+}, As^{5+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Ni^{2+}, Mn^{2+}, and others [4]. Due to the recognized toxicity of heavy metals, the exposure to these elements, even in trace concentrations, is considered to be harmful to living beings [5, 6]. These pollutants can be assimilated through inhalation, ingestion and skin adsorption, bringing about serious illnesses, like cancer, neurological, endocrinological and immunological dysfunction, Alzheimer, among others [7]. The toxicity of heavy metals is attributed to their physicochemical properties. Generally, these pollutants are highly soluble in water, especially at low pH, spreading out more easily in water streams [8]. Additionally, heavy metals are persistent and cannot be rapidly degraded in nature [9], accumulating in living

tissues until getting hazardous concentrations [7, 10, 11]. Similarly, because of its persistence in the environment, heavy metals are likely to sediment at the bottom of lakes, rivers, lagoons, and oceans, causing adverse effects on ecosystems, altering their normal conditions. Thus, provoking death of aquatic species, and even passing through the trophic chain [12, 13]. Owing to the environmental and health concerns, many conventional techniques have been developed to remediate media contaminated with heavy metals; even though with limited performance in terms of effectiveness and removal efficiency. For example, microbial cells have been used as bioaccumulators of soluble and particulate heavy metals from industrial wastes with high efficiency [14-17]; however, these metals could be released back into the liquid phase when the biomass is degraded. Current techniques make use of nanoparticles or composite materials for remediation of heavy metals in water. Nevertheless, almost all approaches rely on the functionalization of nanoparticles with different reactive groups or loading nanostructures on supporting materials to provide them, with the capability of capturing the heavy metals [18-21]. Besides all these preparation techniques are complex. Multicomponent nanoparticles, prepared and characterized by Kim et al. (2011) [22] have shown good performance for TCE and pesticides degradation. However, from the best of our knowledge, there is no study related to the application of these nanoparticles in the simultaneous removal of heavy metals from the aqueous phase.

Materials and Methods

Materials

Chemicals were purchased from Fisher Scientific: Ferric chloride ($FeCl_3.6H_2O$, 99.8%), sodium sulfate (Na_2SO_4, 99.9%), sodium borohydride ($NaBH_4$, > 98%) ascorbic acid (USP/FCC), hydrochloric acid (HCl, 37.3%), nitric acid (HNO_3, 69.5%), sodium hydroxide (NaOH, 98%), 55 buffer solution (0.2 M Sodium acetate, 96%), and potassium iodide (KIO_3, 99%) from Himedia.

General procedure for preparation of the multicomponent nanoparticles

The MCNPs were prepared using a modified method developed by Kim et al. [22]. In a typical procedure, solutions of 0.5 M $FeCl_3.6H_2O$ and 0.8 M $NaBH_4$ + 0.035 M or 0.007 M Na_2SO_4 were prepared using DI water purged with nitrogen for 15 min. Then, 5 mL of the latter solution was added drop wise to the mixture of 50 mL of $FeCl_3$ contained in a flask attached to a vacuum line. This mixture was placed under vigorous stirring using an orbital shaker for 15 min at ambient temperature. During this process, the color of the iron solution changes from yellowish to blackish color, indicating the formation of MCNPs. The resulting product, multicomponent nanoparticles, was centrifuged at 7000 rpm for 2 min and washed several times with nitrogenized deionized water. The purified nanoparticles were lyophilized for 16 h and stored in an air-free bottle for further characterization.

Characterization

Transmission electron microscope images were recorded digitally (Tecnai G2 Spirit TWIN, FEI, Holland). XRD studies on thin films of the nanoparticle were carried out using a diffractometer (EMPYREAN, PANalytical) with a θ–2θ configuration (generator–detector), wherein a copper X-ray tube emitted a wavelength of λ =1.54 A°. FTIR attenuated total reflection spectra were recorded on a Spectrum Two IR spectrometer (Perkin Elmer, USA) to detect the different functional groups involved in the capture of heavy metals by the multicomponent nanoparticles. XPS spectra were recorded on an AXIS ULTRA equipped with Magnetic Immersion Lens and Charge Neutralization System with a new Spherical Mirror Analyzer and monochromatic source (Al Kα) operated at 150 W (15 kV, 10 mA).

Removal of heavy metals

Batch kinetic tests for heavy metals removal by nanoparticles were carried out using 100 mL Boeco bottles under oxidant environment and pH 3 ± 0.2. The removal was initiated by mixing 5 or 9 mL of MCNPs with 50 mL of artificial aqueous mine tailings, which resulted in concentrations of 5.3 mg/L Cu^{2+}, 4.99 mg/L Zn^{2+}, 4.24 mg/L Mn^{2+}, 2.48 mg/L Ni^{2+}, 2.98 mg/L Pb^{2+}, 4.1 mg/L Ag^+, and 0.99 mg/L As^{5+}. These initial concentration values are within the range of reported heavy metal levels in aqueous mine tailings [23, 24]. Bottles were placed in a water bath and agitated for 4 hours at 25 °C. During the test, 10 samples of 2 mL of treated aqueous phase were filtered with a 0.2 μm PVDF filter for heavy metals analyses. In addition, kinetic tests for each heavy metal in the presence of high concentration of other metals were performed under otherwise same experimental conditions. To test pH effects, the removal experiments were performed at an initial pH of 3, 5, 7, and 9, adjusted with 0.1 N NaOH and/ or 0.1 N HCl and by adding 0.2 M of sodium acetate buffer to the glass bottles. Samples of 5 mL were collected after completing the treatment (4 hours), filtered, and analyzed for heavy metals. Tests under reductive conditions were carried out in 80 mL glass vials filled with 64 mL of artificial mine tailing containing MCNPs and sealed with Teflon-lined caps. Additionally, we have also performed adsorption isotherm measurements using different concentrations of Cu (2, 4, 6, 8, 10, 15, 20, 50, 100 and 200 mg/L) and 9 mL of MCNPs. The amount of Cu^{2+} adsorbed per unit mass of wet nanoparticles was calculated through the Equation 1:

$$q_t = \frac{(c_o - c_t)v}{m} \text{-----------------------------}(1)$$

Where q_t (mg/g) corresponds to the amount of Cu^{2+} adsorbed per gram of wet nanoparticles at time t (min), C_0 (mg/L) is the initial concentration of Cu^{2+} in the solution, C_t(mg/L) refers to the concentration of Cu^{2+} at a time t, m (g) is the mass of the multicomponent nanoparticles used in tests and V(L) refers to the initial volume of the stock solution [25].

Chemical and physical analyses

Heavy metals such as Pb^{2+}, Ag^+, Ni^{2+}, Mn^{2+}, Zn^{2+} and Cu^{2+} were analyzed with an atomic absorption spectrometer, Perkin Elmer AA 800, using standardized methods [26]. Arsenic was quantified using a Flow Injection Analysis System (FIAS) coupled to AA 800 and a discharge lamp. For the operation of FIAS system, it was used a solution of 10% v/v of HCl as carrier and a solution of 0.2% w/v $NaBH_4$ + 0.05% NaOH

as reducing agent. For this analysis, samples of artificial and real mine tailings were pretreated with a solution of potassium iodide and ascorbic acid 5% to reduce all the As species to As^{3+}. For FIAS-absorption spectrometer the calibration curve with a correlation index, R ≥ 99%, was obtained before analyzing the samples. For the analysis of anions, an ion chromatograph Dionex ICS 1100 was used, equipped with a guard column AG14 and an analytical column AS14, both of 4 mm, and a sample loop of 50 μL. A solution of 35 mM sodium hydroxide was used as eluent. Physicochemical properties of real mine tailings such as dissolved oxygen, conductivity and pH were determined using a Mettler Toledo multiparameter.

Figure 1: TEM images of MCNPs prepared using 0.035 M Na_2SO_4, 0.035 M $FeCl_3.6H_2O$ and 0.8 M $NaBH_4$.
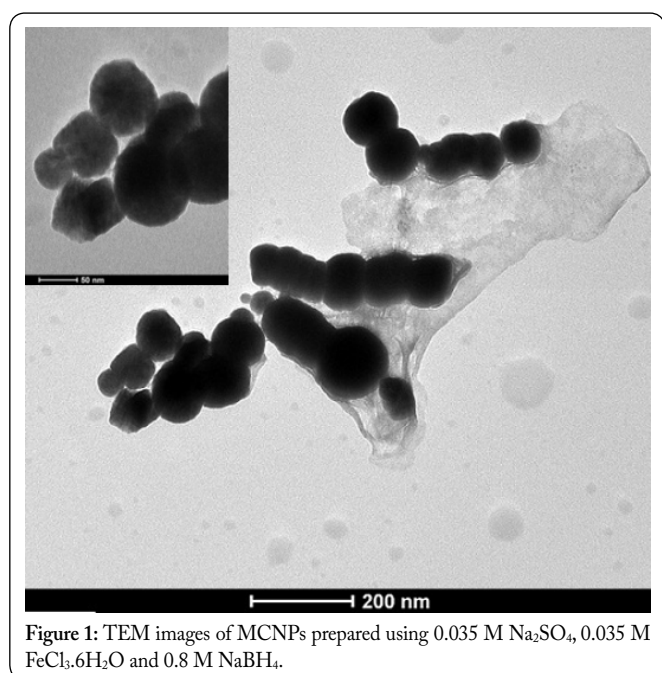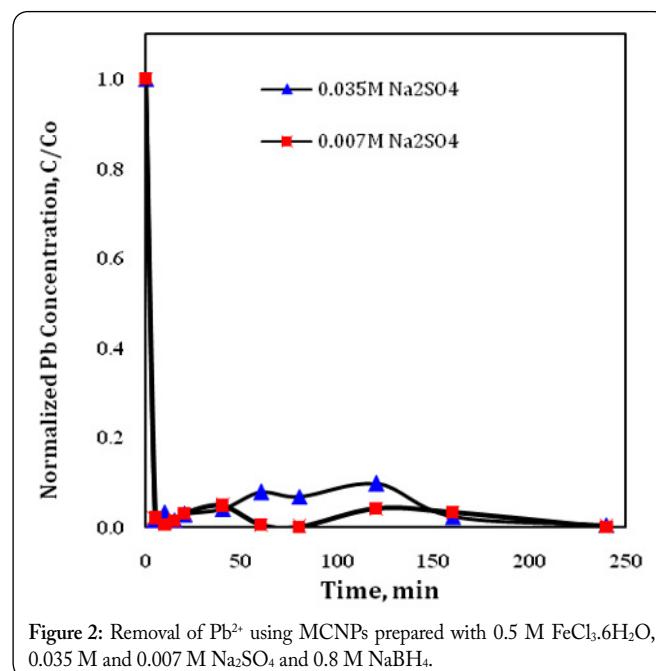
Results and Discussion

Characterization of MNPs

Size characterization of MCNPs, demonstrated that there is no significant difference when using 0.007 and 0.035 M of sodium sulfate during preparation of nanoparticles. TEM images of MCNPs have shown almost the same diameter on average size of 24-42 nm (Figure 1). Nevertheless, the nanosized particles indeed influence the physical and chemical properties of the nanoparticles and therefore the surface electronic structure [27, 28]. The high reactivity of the atoms on the surface of nanoparticles due to a decrease in size, confer to electrons more energy because of quantum confinement [29]. Also, reactivity depends on the amount of Fe(0) and FeS formed during the preparation of MCNPs. In this study, it was used approximately 27.9 g/L of Fe(III) and 1.12 or 0.224 g/L of sulfur in the preparation of the particles. XRD spectrum of nanoparticles shows peaks corresponding to Fe(0) and a small amount of FeS precipitates, as depicted in Figure S1 (Supporting Information). In regard to the stability of these nanoparticles, it can be implied they are greatly stable in aqueous solutions. Results on pH measurements of the nanoparticles solutions, exhibited a value of around 9.90. At

this pH there is an absence of hydrogen ions (H⁺) preventing early oxidation of nanoparticles [30]. Lu et al. (2007) [29] reported that nanoparticles were more stable at pH over 8. In addition, when these nanoparticles are manufactured under reducing conditions, dissolved oxygen is as low as 0.02 mg/L. This, in turn, contributes to the stability of the nanoparticles since FeS does not react with oxygen to produce oxidized nanoparticles [31]. On the other hand, the high conductivity of the nanoparticles solution (~36 mS/cm) may produce a strong flow of electrons at the nanoparticles surface, suggesting an increase of its roughness that contributes to a higher surface area, and therefore, higher reactivity [22].

Kinetic study

Figure 2 shows the reaction kinetics of Pb^{2+} removal from artificial mine tailing using Fe/FeS nanoparticles prepared with 0.035 M or 0.007 M Na_2SO_4. The highest removal of this heavy metal occurred after approximately five minutes of reaction (Figure 2). However, Pb^{2+} reached a complete steady state after 160 mins. Most of the heavy metals utilized in this study (Mn^{2+}, Zn^{2+}, Cu^{2+}, Ag^+, Ni^{2+}) attained a steady condition after approximately 40 min, only As^{5+} reached this condition at 160 min (data not shown in Figure 2). Results of kinetic tests of all heavy metals did not evidence a significant difference on removals using multicomponent nanoparticles with different concentrations of sodium sulfate (0.035 M and 0.007 M) (data not shown). These experimental values fit a pseudo-second-order model [Equation 2].

Figure 2: Removal of Pb^{2+} using MCNPs prepared with 0.5 M $FeCl_3.6H_2O$, 0.035 M and 0.007 M Na_2SO_4 and 0.8 M $NaBH_4$.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{--------------------------(2)}$$

Where k_2 (g/mg.h) is the pseudo-second-order rate constant, q_e is the amount of metal adsorbed (mg/g) at equilibrium and q_t is the amount of the adsorption (mg/g) at any time t(h) [25]. Table S1 (Supporting Information) summarizes the calculated q_e values, pseudo-second-order rate constants k_2 and correlation coefficient values. The q_e and k_2 are

calculated from de slope and the intercept of the plots of t/q_t versus t according to the Equation 2. All fitting curves exhibit good linearity with a correlation coefficient nearly equal to unity ($R^2 \sim 1.0$) as shown in Figure 3. This behavior suggests that chemical adsorption is the main mechanism for removal of heavy metals from artificial mine tailing [32, 33].

Figure 3: Pseudo-second-order kinetic studies of heavy metals removal using MCNPs 0.35 M Na$_2$SO$_4$.
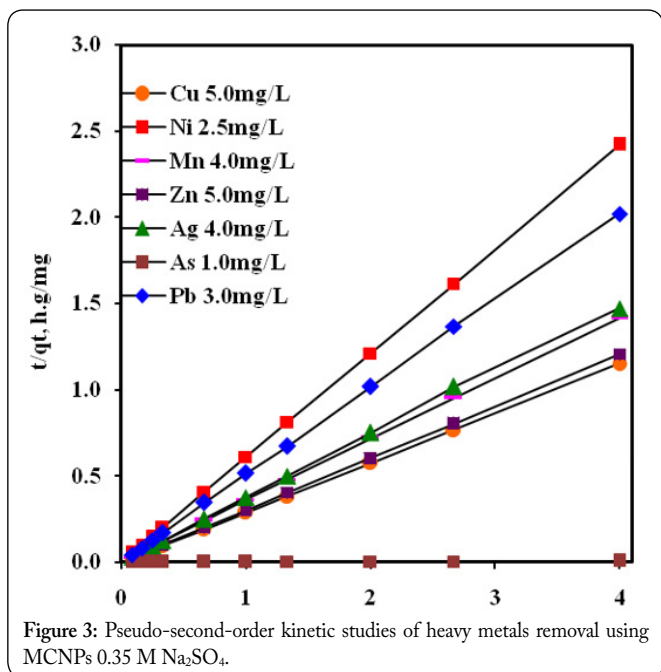
Adsorption capacity study

The adsorption capacity of multicomponent nanoparticles, using different concentrations of Cu^{2+}, showed almost instantaneous removals in the first five minutes with any desorption throughout the test as shown in Figure S2 (Supporting Information). The removal efficiency and adsorption capacity of the multicomponent nanoparticles, increased progressively from 98.59% and 1.51 mg/g to 99.91% and 135.64 mg/g for 2 and 200 mg/L of Cu^{2+}, respectively. This behavior could be credited to an enhancement in the Brownian motion, propitiating higher collisions among copper ions dissolved in water and a better diffusion of them towards multicomponent nanoparticles [25, 34].
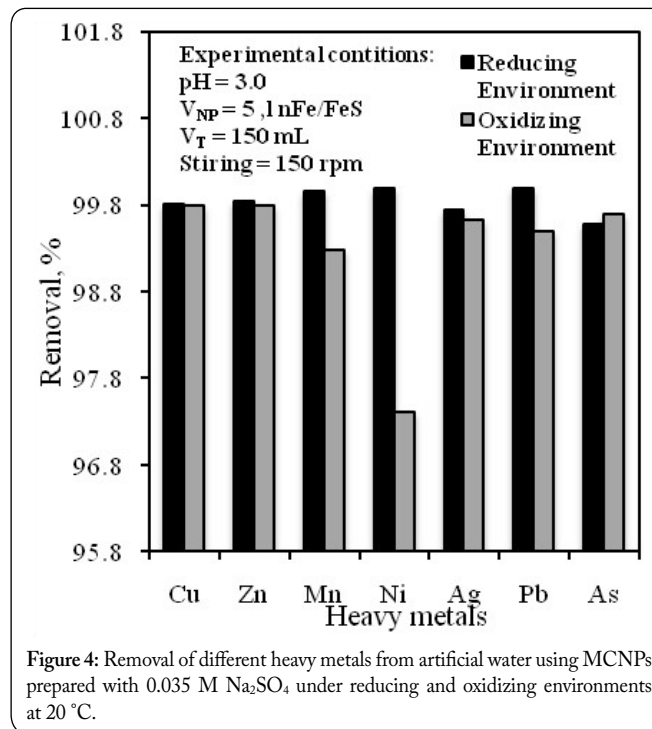
Adsorption isotherms study

Isotherm tests were conducted to describe the adsorption behavior of the multicomponent nanoparticles when removing Cu^{2+}. Results of adsorption tests fit well Freundlich isotherm model (Equation 3), exhibiting a correlation coefficient value of 0.988 as shown in Figure S3 (Supporting Information).

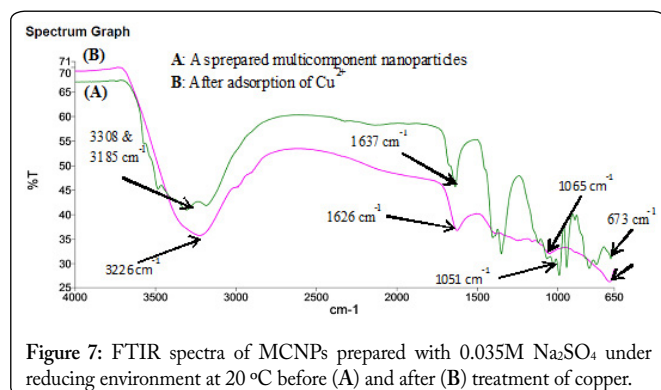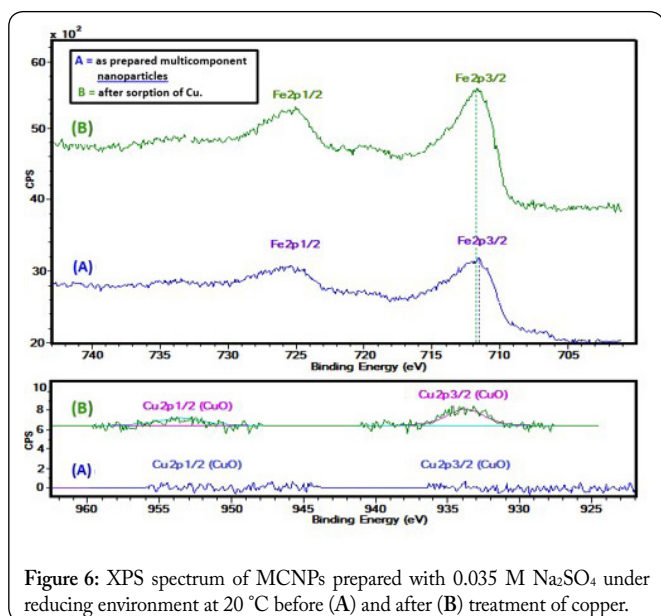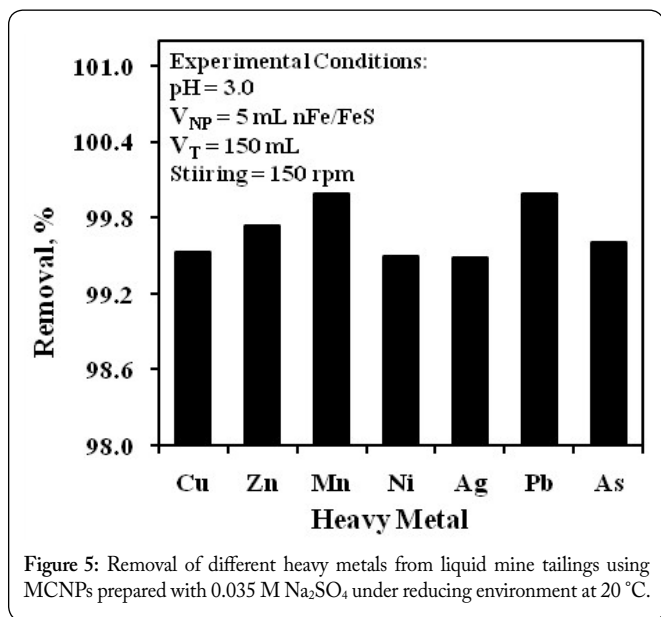$$q_e = KC_e^{1/n}$$ -------------------------- (3)

Where, q_e (mg/g) and C_e (mg/L) are the amount of pollutant adsorbed and the concentration in the aqueous phase and K and n are constants for Cu adsorption on MCNPs at 25 °C. The elevated correlation coefficient obtained with Freundlich model suggests that adsorption of heavy metals may occur on a rough surface of nanoparticles as described above. In other words, there is a heterogeneous distribution of the active sites on the surface of the nanoparticles where the metals are bound [25]. Furthermore, having adjusted the adsorption isotherm

data to a Freundlich model, it reinforces the fact that sodium sulfate contacted with borohydride promotes the precipitation of FeS on the surface Fe(0) core of nanoparticles, contributing to their roughness [22].

Figure 4: Removal of different heavy metals from artificial water using MCNPs prepared with 0.035 M Na$_2$SO$_4$ under reducing and oxidizing environments at 20 °C.

Study of simultaneous removal of heavy metals from the aqueous phase

Despite good removal of heavy metals achieved on tests conducted with artificial mine tailing samples under different pH, redox potential, and concentrations of sodium sulfate, certain values have shown to be better than the others. For instance, using 0.035 M of sodium sulfate in the preparation of MCNPs resulted on better removals than employing 0.007 M. Sodium sulfate concentration has been demonstrated to be directly proportional to roughness as well as to the increase of surface area of multicomponent nanoparticles [22]. Also, under reducing conditions and 0.035 M Na$_2$SO$_4$, removal of toxic metals (~99%) was slightly enhanced compared to the under oxidized environment (~97%) (Figure 4). Reduced conditions provided a favorable setting for the removal of heavy metals because oxygen was not present in solution [35]; thus nanoparticles were not easily oxidized and did not lose their reactivity. Tests using MCNPs prepared with 0.035 M of sodium sulfate applied to real mine tailings contaminated with heavy metals showed also high efficiency to immobilize the metallic elements (Figure 5). More than 99% of removal was achieved for the majority of toxic metals from the liquid phase. Therefore, the property of the nanoparticles that causes high removal of heavy metals from water is its chemical composition: Fe(0) and FeS. It is obvious that the active groups of the multicomponent nanoparticles chemically immobilize the toxic metals (Figure 6). Clearly, XPS spectra show peaks related to the formation of CuO with binding energies of 953.8 and 934.1 eV for Cu2p$_{1/2}$ and Cu2p$_{3/2}$, respectively. Chemical sorption of heavy metals on MCNPs is also

Figure 5: Removal of different heavy metals from liquid mine tailings using MCNPs prepared with 0.035 M Na₂SO₄ under reducing environment at 20 °C.

Figure 6: XPS spectrum of MCNPs prepared with 0.035 M Na₂SO₄ under reducing environment at 20 °C before (**A**) and after (**B**) treatment of copper.

Figure 7: FTIR spectra of MCNPs prepared with 0.035M Na₂SO₄ under reducing environment at 20 ºC before (**A**) and after (**B**) treatment of copper.

confirmed by FTIR tests performed on samples containing fresh and after treatment multicomponent nanoparticles (Figure 7). As seen in Figure 7, the graphical representations of both samples reveal a decrease of frequency from 3308 to 3226 (-OH stretching), 1637 to 1626 (H-H bonding/bending vibration of water). Changes on peaks from 1403 to 1120 may imply the existence of residual hydroxyl groups on the

surface of MCNPs. This can be assumed due to the formation of complex of Sulfur-OH-Cu^{2+} and Sulfur-O-Cu^{2+} during the adsorption of Cu^{2+}. At 1349 cm^{-1} the intensity of the band is increased after adsorption. It seems that adsorption induces the increase of the amount of hydroxyl groups, which may arise from the formation of surface precipitate of $Cu(OH)_2$. The other peaks shifted as compared with those of fresh MCNPs, indicating a strong interaction between the multicomponent nanoparticles and the copper cation. Also, scientific literature describes the formation of metal sulfides when metals are contacted with the fraction of FeS [36]. The excellent removal of arsenic from the aqueous phase (> 98%) accomplished is this study is essentially due to different reactions that arsenates bear when contacted with elemental iron of nanoparticles. According to Ramos et al. [37], Arsenic(V) in the presence of elemental iron nanoparticles is reduced to As^0 or As^{3+}. Also, it may form complex Fe-oxide-As^{3+} or develop complexes with iron hydroxides. Moreover, Li & Zhang [38] reported that redox mechanisms are dominant when elements such as Zn^{2+}, Pb^{2+}, Cu^{2+}, As^{5+} are brought into contact with zero valent iron nanoparticles and reduced to Zn^0 and Pb^0, or are immobilized by the hydroxides or oxides.

Effect of temperature

Tests conducted using MCNPs at different temperatures demonstrated that there is no need to raise the temperature in order to enhance heavy metals removal. On the contrary, it produces a small decrease on their removal (Figure S4). This could be related to the increase of nanoparticles size. It has been demonstrated, as the size of nanoparticles increases surface area and reactivity is reduced [28, 39]. However, a rapid physical adsorption of heavy metals on the surface of nanoparticles counterbalances the increase of particle size. Besides, results of kinetic tests showed a rapid adsorption of heavy metals, which is the main property of physisorption [30]. On the other hand, raising the temperature during the treatment could promote an increase of Brownian motion, that enhances the pollutant diffusion but it could also interfere with intermolecular weak forces (Van der Waals forces) causing the release of metallic ions from the surface of nanoparticles [30]. Nonetheless, if physisorption were the only adsorption mechanism in the treatment, there would be desorption of pollutants in the aqueous media due to high temperatures. Leakage of heavy metals was not observed on the removal tests on both the artificial and the real mine tailings. Therefore, chemical adsorption also plays an important role on the heavy metals uptake as it was explained above.

Effect of pH

Hydrogen potential (pH) is also one of the factors that, has great influence not only on the nanoparticle stability but also in the adsorption of heavy metals on solid surfaces (nanoparticles). At acidic pH there exists a negative interference with heavy metal uptake from water. Hydrogen ions compete for the reactive sites on the multicomponent nanoparticles [40]. Also, high concentration of H^+ the surface of nanoparticles is positively charged [41], inhibiting in some extent, adsorption of metallic ions due to electrostatic repulsion [42]. In this study the removal efficiency of heavy metals conducted under a pH of 3 is slightly lower compared to

the removal efficiency at higher pH values as shown in Figure S5 (Supporting Information). Nevertheless, the removal at pH 3 is not significantly lower compared to those at higher pH values of 5, 7, and 9. This can be attributed to the fact that at acidic pH, heavy metals are more soluble, offsetting to a certain level, the negative effects of competition between metallic cations and H$^+$. Soluble metals are found as free ions available for binding more easily to the reactive sites of the multicomponent nanoparticles [43]. Besides, at pH values greater than 5, ions H$^+$ are almost at equilibrium with ions OH$^-$, so there is less competition between hydrogen ions and heavy metals for binding the reactive sites of the nanoparticles [44]. As a result, the removal efficiency observed in these tests, revealed a slight enhancement at pH values of 5, 7, and 9 (Figure S5). Finally, at high pH values, namely 9, there are no hydrogen ions to compete with the pollutants. Indeed, high concentration of OH$^-$, negatively charges surface of the nanoparticles enhancing the attraction and adsorption of metallic cations; thus, increasing the removal efficiency [45].

Conclusion

- Novel multicomponent nanoparticles were successfully synthesized using sodium sulfate (Na$_2$SO$_4$) and without any stabilizing agent. The use of sodium sulfate in the synthesis of the multicomponent nanoparticles, allowed the manufacture of nanomaterials in an environmentally friendly approach since there is a lower release of hydrogen sulfide, a noxious gas to the environment and to the human health.

- The physicochemical characterization of multicomponent nanoparticles demonstrated that they are stable for a short time. Likewise, the size distribution reveals that they have an appropriate size within a range previously reported, as well as a great surface area, meaning they are suitable for obtaining high removal efficiency of heavy metals as observed in this work.

- The multicomponent nanoparticles demonstrated both rapid adsorption kinetics (within the first five minutes), and no desorption of heavy metals along the testing period, suggesting the occurrence of physical and chemical adsorption mechanisms for uptake of metals. Data of kinetic tests fit well on a pseudo-second-order model, thus confirming chemical adsorption for the removal of the pollutants. On the other hand, the isothermal adsorption of heavy metals onto the multicomponent nanoparticles follows a Freundlich isotherm model, indicating the presence of heterogeneous surface on the nanoparticles.

- Also, environmental conditions play a role in the removal of heavy metals using multicomponent nanoparticles. Tests conducted at different temperatures demonstrated good removal efficiencies between the toxic metals and the nanoparticles; however, at higher temperature the efficiency dropped about 1.6% due to Brownian motion. Hydrogen potential also influences the removal efficiency of heavy metals when using multicomponent nanoparticles for the uptake. Lower removal is achieved at acidic pH (pH 3) due to competition with hydrogen ions. While at basic pH the removal is higher because surface of nanoparticles is negatively charged, thus attracting heavy metals.

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