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Optimized Synthesis of Multicomponent Nanoparticles for Removing Heavy Metals from Artificial Mine Tailings

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Abstract

Treatment of artificial mine tailings with multicomponent nanoparticles (MCNPs) has reached removals higher than 99.00% for Pb, Zn, Ag, Cu, As and Ni using a standardized laboratory procedure. However, it is believed that the amount of reactants can be optimized and make it a profitable technique. In this study, the amount of NaBH4 and $FeCl_3$ was reduced in 90.00% and in 99.50%, respectively, without affecting the removal of heavy metals from the artificial mine tailings. This new procedure utilized only 25 mL of 1.0 mM $FeCl_3$, 25 mL of 0.7 mM Na_2SO_4 and 3 mL of 0.8M $NaBH_4$ prepared with nitrogenized water. Size and spherical shape of nanoparticles obtained with Transmission Electron Microscopy showed no difference compared to the particles prepared with the former procedure. Also, removals of Cu, Zn, Ni in 5 minutes were higher than 99.50%. Thus an enhanced procedure for fabrication of the multicomponent nanoparticles was developed. This procedure moreover of achieving an excellent removal of heavy metals may end up as a profitable remediation technique.

Keywords: Mine tailing; Multicomponent nanoparticles; Heavy metals

Introduction

Pollution caused by various human activities is creating environmental and human health problems [1,2]. Although mining is an important economic activity worldwide it has generated a huge pollution in the environment, mainly because of poor exploitation processes and wrong disposal of mine tailings [3-5]. In Ecuador, mining problems are mainly related to the small and artisan scale works with an epicenter in the area of Zaruma-Portovelo [6]. Over the years, this activity has generated pollution with heavy metals, arsenic and cyanide in the nearby rivers. Lack of rules for the proper management of tailings and mine closure has deteriorated the landscape of the mining area [7]. 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 [8-11]. 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 [12-15]. Treatment of artificial mine tailings with MCNPs has achieved removals higher than 99.00% for Pb, Zn, Ag, Cu, As and Ni when using a standardized laboratory procedure [16]. However this procedure uses high amount of chemicals [17]. In this study we optimized the amount of reactants and make the technique profitable.

Materials and Methods

Materials

Chemicals were purchased from Fisher Scientific: Ferric chloride ($FeCl_3.6H_2O$), sodium sulfate (Na_2SO_4), sodium borohydride ($NaBH_4$), hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH). Reference standards were purchased from AccuStandard, Inc., 1000 µg/mL AccuTrace for each heavy metal. Artificial mine tailings were prepared with 1000 mg/L stock solutions of cupric sulfate pentahydrate ($CuSO_4.5H_2O$), cadmium sulfate ($CdSO_4$), zinc sulfate heptahydrate ($ZnSO_4.7H_2O$), nickel sulfate (II) hexahydrate ($NiSO_4.6H_2O$), silver nitrate ($AgNO_3$); which resulted in concentrations of 4.59 mg/L Cu^{2+}, 4.23 mg/L Zn^{2+}, 2.87 mg/L Cd^{2+}, 2.43 mg/L Ni^{2+} and 6.66 mg/L Ag^{+}.

Preparation of the multicomponent nanoparticles

The fabrication of nanoparticles, employing the optimized procedure, used 3 mL of 0.8M $NaBH_4$, 25 mL of 1.0

mM $FeCl_3.6H_2O$ and 25 mL of 0.7 mM Na_2SO_4. The latter solution was mixed and purged with nitrogen for 1 minute in a 250 mL Erlenmeyer flask. Then, 3 mL of $NaBH_4$ was promptly added to the mixture with a micropipette and the content was homogenized with slow shaking (30 rpm). During the evolution of the reaction, there was a color change from yellowish to blackish indicating the formation of MCNPs. For the characterization of nanoparticles, we first concentrated the particles. With this purpose, we prepared nanoparticles in 15 Erlenmeyer flaks. Then, the content of the first flask was dispensed into a Falcon tube and centrifuged at 3000 rpm for 20 min and the supernatant was removed. Thereafter, the second flask was added to the tube with the remaining semisolid and it was again centrifuged at 3000 rpm for 20 minutes. This procedure was repeated

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up to the 15th flask. Finally, the semisolid remaining in the tube was lyophilized overnight and stored in an air-free bottle for further characterization.

Physical characterization

Transmission electron microscope images were recorded digitally (Tecnai G2 Spirit TWIN, FEI, Holland). XRD studies on thin films of the nanoparticles 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°.

Removal of heavy metals

Tests to evaluate the removal of heavy metals using the synthetized nanoparticles were carried out by adding 5 mL of fresh MCNPs and 50 mL of artificial aqueous mine tailings into 50 mL falcon tubes and the content was stored overnight at room temperature. The supernatant was filtered through a 0.2 µm PVDF filter and analyzed for heavy metals with atomic absorption spectrometry. In addition, the heavy metals removal capacity was evaluated at 5, 20, 40, 60, 120 and 150 minutes, under otherwise the same experimental conditions.

Chemical analyses

Heavy metals such as cadmium, silver, nickel, zinc and copper, and arsenic were analyzed with an atomic absorption spectrometer, Perkin Elmer AA800, and Flow Injection Analysis System (FIAS) coupled to the AA800. Standardized methods were used for heavy metals analysis [18]. Energy dispersed X-Ray Analysis (EDX) of the nanoparticles was performed with Scanning Electron Microscope (SEM, Tescan MIRA 3).

Results and Discussion

Characterization of MCNPs

Energy dispersed X-Ray analysis demonstrates that MCNPs are mainly composed of iron (90.57%) and a low content of sulfur (1.81%) (Table 1) while the Scanning Electron Microscopy (SEM) mapping shows a homogeneous distribution of sulfur (S) and iron (Fe) in a sample of fresh nanoparticles (Figure 1). It is noteworthy to observe that the sulfur content is not the same compared to EDS analysis. This result may be associated with the deposit of iron sulfides on the surface of the zero valent iron core as seen on the transmission electron micrographs (Figure 2a). Also, the XRD spectrum confirms the presence of zero valent iron in the nanoparticles (Figure 3). Peaks at 2θ 44.79, 65,11 and, 82, 42 are related to zero valent iron [19]. On the other hand, the spherical shape of nanoparticles imaged with the Transmission Electron Microscopy (Figure 2b) shows no difference compared to the particles prepared with the former procedure. However, reducing the concentration of the reactants to millimolar scale provides the stability of the particle's system thus avoiding the agglomeration and precipitation of the nanoparticles.

Removal of heavy metals from artificial mine tailings

In this study, the amount of $NaBH_4$ and $FeCl_3$ was reduced to 90.00% and 99.50%, respectively. From the results it is clearly seen that there is not any decrease on the removal of heavy metals from artificial mine tailings when adding the same percentage in volume (10%) of MCNPs synthesized by the former procedure (>95%) [17]. Batch tests showed that removals higher than 99.50% were achieved for Cu (5 mg/L), Zn (5 mg/L), Cd (3 mg/L) and Ag (4 mg/L) in 5 minutes (Figure 4). Even with the addition of only 2% of MCNPs in volume, removals exceeded 99% for Cu. However, the removal of metals such as Ni (<70%) and Mn (<20%) was significantly affected. Therefore, the volume of the multicomponent nanoparticles appears to be dependent on the chemical composition of the mine tailings to be treated. In addition, the presence of the heavy metals in the multicomponent nanoparticles was verified with EDS analysis. Peaks on the Figure 5 show metallic contaminants in the precipitates formed after treatment.

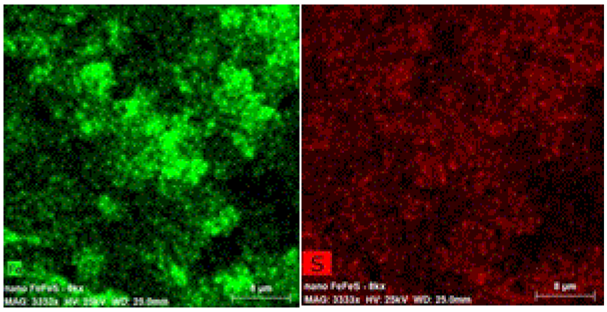

Figure 1: Scanning Electron Microscopy mapping of iron (green) and sulfur (red) present in fresh multicomponent nanoparticles.

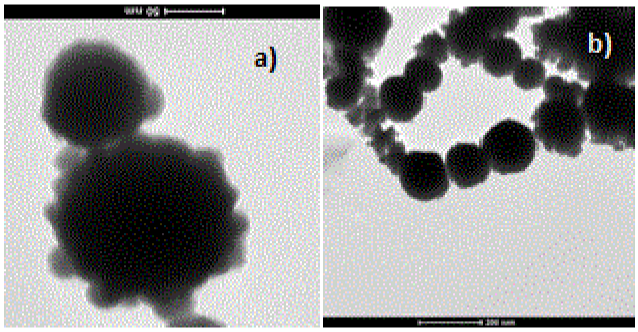

Figure 2: Transmission electron micrographs of multicomponent nanoparticles.

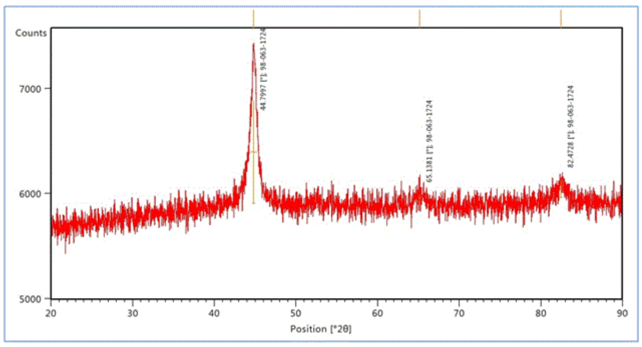

Figure 3: XRD spectrum of multicomponent nanoparticles.

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	O	Na	S	Fe
Mean value	7.38	0.24	1.81	90.57
Sigma	3.14	0.26	1.78	3.4
Sigma mean	0.32	0.03	0.18	0.34
		Error % on mean value	9.92	0.38

Table 1: Composition of multicomponent nanoparticles (%).

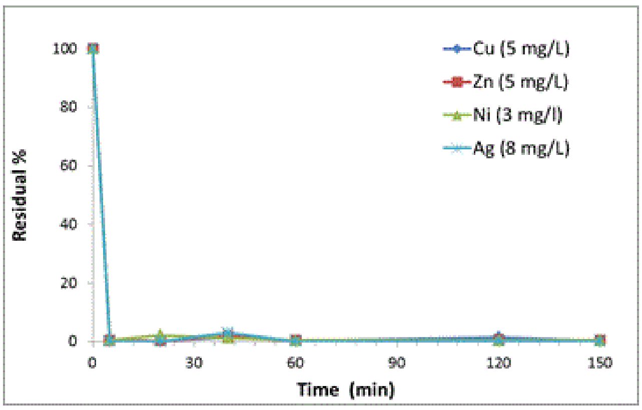

Figure 4: Heavy metals removal from artificial mine tailings.

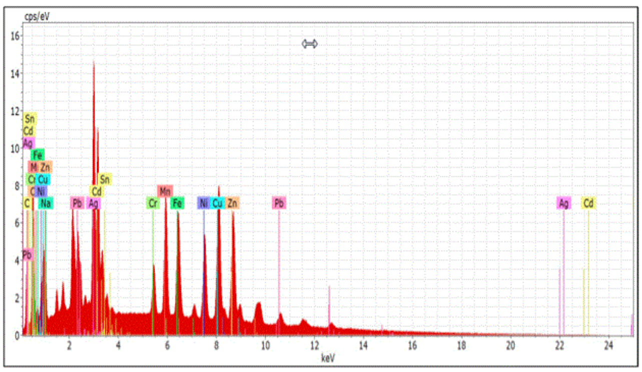

Figure 5: Chemical composition of the multicomponent nanoparticles after treatment.

Conclusion

The amount of $NaBH_4$ and $FeCl_3$ can be reduced to 90.00% and 99.50%, respectively; without affecting the removal efficiency of the heavy metals from artificial mine tailings when using 10% (v/v) of multicomponent nanoparticles.

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