Synthesis of Magnetic Nanoparticles for the removal of heavy metal ions from wastewaters

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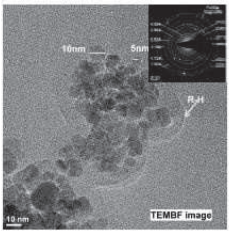
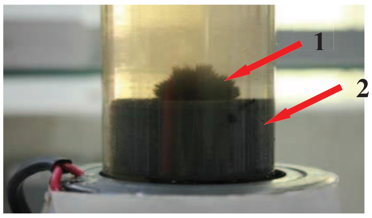
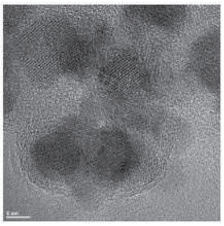
Abstract: The removal of heavy metals from waste waters became a necessity, due to their toxicity and persistence in the environment. Latest researches indicated that the use of magnetic nanoparticles in the removal of these pollutants from industrial waters represented a better option than ion exchange, filtration, membrane separation, or reverse osmosis, due to the fact that it was cost effective and easily to use. This paper presented the synthesis, characterization and adsorption efficiency of iron oxide nanoparticles covered with cationic resin for wastewater treatment. The magnetic nanoparticles were obtained by co-precipitation method, and then covered with cationic resin. The products (Fe_3O_4-T-RH) were then characterized by transmission electron microscopy (TEM) and X-Ray diffraction (XRD). The removal efficiency was tested on a column with magnetic separation. The results demonstrated the fast adsorption of heavy metal ions on magnetic nanoparticles and the possibility to remove with high efficiency the toxic materials from wastewaters.



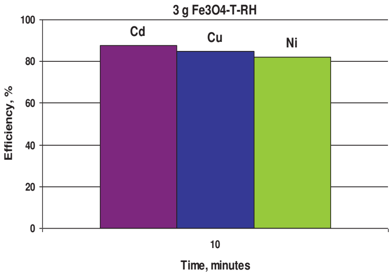
TEMBF image for coated magnetic nanoparticles



Recovery of coated magnetic nanoparticles (**1**) and magnetic core (**2**)



HRTEM image for coated magnetic nanoparticles



Metal ions removal efficiency for Cd, Cu, Ni on Fe_3O_4 –T-RH

1. Introduction

Contamination of waters with toxic metal ions is a severe environmental and public health problem. In order to treat the wastewaters, various techniques such as adsorption, precipitation, ion exchange, reverse osmosis, electrochemical treatments, membrane filtration, evaporation, flotation, oxidation and biosorption processes are extensively used [1-3]. Among these, adsorption is a conventional, but efficient, technique to remove toxic heavy metal ions and bacterial pathogens from waters.

Recently, magnetic nanoparticles received great considerations as a very efficient tool in many applications. Synthesis of magnetite (Fe_3O_4) nanoparticles has been considerably advanced not only for its fundamental scientific interest but also for many technological applications such as in magnetic resonance imaging, ferro-fluids for audio speakers, magnetic targeted drug delivery, and magnetic recording media [4]. In particular, the use of magnetite nanoparticles as adsorbents in water treatment provides a convenient approach for separating and removing the contaminants by applying external magnetic fields.

Recently, researchers have used magnetic Fe oxides at the nanometric scale to remove toxic heavy metal ions and organic pollutants from water [5]. This is because magnetic Fe oxide nanoparticles possess not only strong adsorption capacities but also magnetic properties that offer the capacity of being easily separated and collected by an external magnetic field [6-8]. Adsorption activity by magnetite nanoparticles for many heavy metal ions has been reported in the literature [9, 10]. Research regarding adsorption of Cr (VI) from single-component solutions onto magnetite nano-particles has also been reported [10, 11]. Recent studies have shown favorable responses of magnetite nanoparticles for the adsorption or reduction of several toxic metal ions (e.g., Ni^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, and Cr^{6+}) and the catalytic degradation of certain organic contaminants [10]. Metal ions (Cu^{2+}, Ni^{2+} and Cr^{6+}) from multi-component solution were adsorbed with good results onto magnetite nanoparticles under acidic or basic conditions [11]. The novelty of this paper consists in coating of the magnetic nanoparticles with cationic resin. In this way, the nanoparticles are more stable while retaining their magnetic and adsorption properties.

This paper presents the synthesis and characterization of cationic resin coated iron nanoparticles. We prepared Fe_3O_4 nanoparticles (NP) by co-precipitation of ferrous ion (Fe^{2+}) and ferric ion (Fe^{3+}) with NaOH solution. The iron solutions were strongly stirred in water, after adding NaOH solution. The precipitates were separated by magnetic decantation or slow filtration after which the batch was washed several times with distilled water and ethanol [12]. The iron nanoparticles were coated by the cationic resin of Amberlite IR-120 type (R-TH). The nanoparticles were characterized and tested for their adsorption efficiency.

2. Experimental

2.1 Preparation of magnetic nanoparticles coated with cationic resin

All commercial reagents were pure analytical grade (Merck). Distilled water was used. The magnetic NP were prepared using 0.4 mol/L $Fe(NO_3)_3 \times 9H_2O$ and 0.4 mol/L $FeCl_2 \times 9H_2O$ mixed with 0.5 mol/L NaOH at a molar ratio of 1:2 at room temperature. The reaction mixture was maintained at pH=10 for 3h. The precipitate was separated by centrifugation and washed several times with distillated water. The final pH was 7. The magnetite nanoparticles were dried into oven at 60 ^{o}C [13]. Working installation is presented into Figure 1.

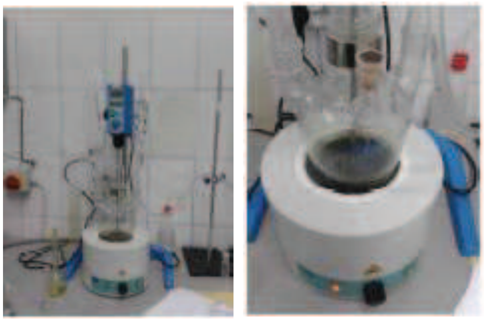


Figure 1: Installation for magnetite preparation

The iron nanoparticles coated with cationic resin were obtained during a 24 hours process, when magnetite and cationic resin were mechanically stirred. The first step was to prepare the cationic resin by washing for 8 hours in ethyl alcohol and then drying at 60^0C. We used the Amberlite IR-120 type resin, with yellowish-brown spherical molecular shape, dimensions ranging from 0.3 to 1.1 mm and a wet total capacity of 1.9 mM/ml. After the preparation phase, the resin was brought in contact with 50 ml of Fe_3O_4 solution for 24 hours, then washed with a mixture of water-alcohol (20:80 vol.) and dried at 55^0C for 6 hours. Magnetic nanoparticles coated with cationic resin type were obtained.

2.2 Characterization of the nanoparticles

The material used as adsorbents, Fe_3O_4–R-TH, was characterized by X-ray diffraction (XRD) and transmission (TEM) and scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectra (EDS) methods. A Panalytical X'Pert PRO MPD X-ray diffractometer with high-intensity Cu–Ka radiation (l = 1.54065 A) and 2q range from 10 to 90° was used to obtain XRD patterns. To evaluate the average dimension of the crystallites, the Debye–Scherrer equation was used:

$$D = \frac{K\lambda_{Cu-K\alpha}}{\cos\theta FWHM} \quad [1]$$

where D is the crystallite dimension, K is a coefficient (0.89), $\lambda_{Cu\text{-}Ka}$ is the wavelength of the radiation from the diffraction tube, FWHM is the full width at half maximum of diffraction in the 2θ scale (rad), and θ is the diffraction Bragg angle. The TEM images were obtained on a TECNAI F30 G$_2$STWIN high-resolution transmission electron microscope with 1-A line resolution.

2.3 Adsorption studies

All stock standard solution for Cd, Cu, Ni were prepared from Merck reagent-grade solutions by dissolving them into ultrapure water. The working plan was as follows: 50 ml of multi-component solution (Cd, Cu, Ni) with initial concentration of 1000 mg/L were mixed with 3 g of magnetite covered with cationic resin. The final working concentration was 50 mg/L for each analyzed metal ion. Schematically, the preparation method for the solutions is presented in fig. 2.

The adsorption studies were performed by measuring the initial and final concentrations of the metal on a GBC 932 AB Plus spectrometer (flame atomic absorption spectrometry) with spectral domain between 185 and 900 nm.

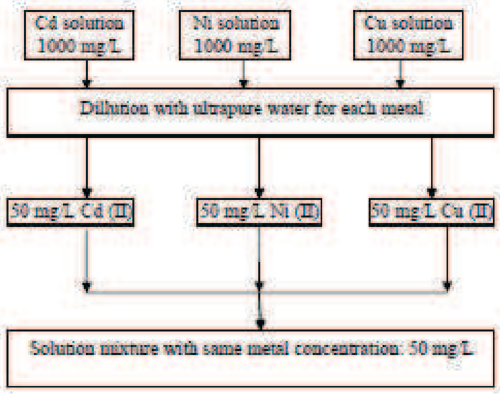
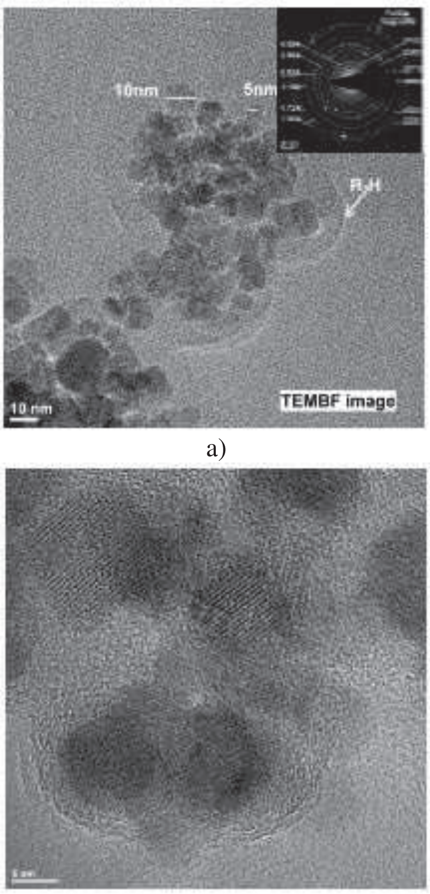


Figure 2: Flowchart illustrating the solution mixtures obtaining with the same metal concentrations (50 mg/L).

3. Results

3.1. Characterization of the magnetic nanoparticles

The TEM analysis indicates the presence of the nanomagnetite covered with cationic resin (Fe_3O_4-T-RH), as it can be seen in Fig. 3.a. The electron diffraction image (SAED) can be observed,. By analyzing the Miller indexes, the existence of the magnetite inside the cationic resin was demonstrated.



a)

b)

Figure 3: a) TEM with bright field image for magnetite covered with cationic resin and SAED associated image; b) HRTEM image.

The HRTEM analysis for Fe_3O_4-R-TH showed spherical particles of magnetite of about 10 nm that are wrapped in polymer, as shown in Fig. 3a. The EDS spectrum is shown in fig. 4.

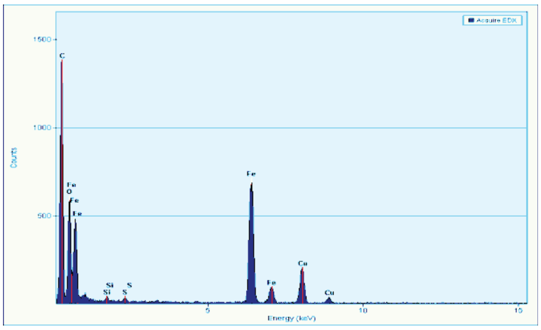


Figure 4: EDS spectrum

These results are in agreement with the XRD spectra obtained for coated and uncoated magnetic nanoparticles (not shown here). The X-ray diffraction spectrum of Fe_3O_4 (Figure 5) indicates a cubic spinel structure with a grain size of about 10 nm. Other phases, such $Fe(OH)_3$ or Fe_2O_3, which are the common products in chemical co-precipitation process, were not detected.

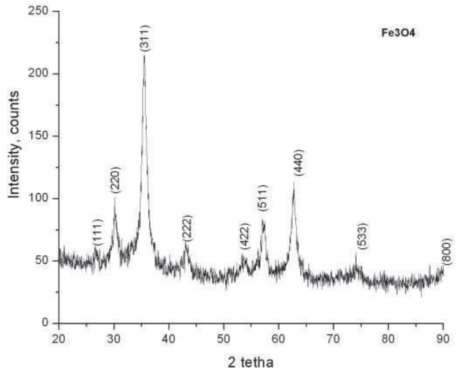


Figure 5: XRD for Fe_3O_4 nanoparticles

3.2. Adsorption studies

The removal efficiency of the nanoparticles covered with cationic resin was tested on a column with solenoid and a magnetic core in order to create a magnetic field for nanoparticles recovery (fig. 6).

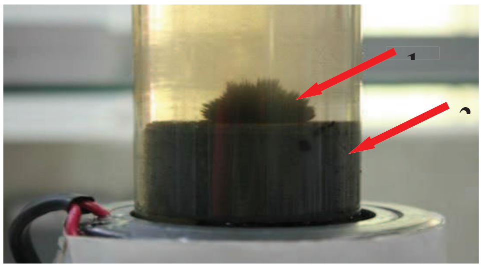


Figure 6: Recovery of the nanoparticles on the magnetic core: 1 – nanoparticles covered with cationic resin; 2 – magnetic core.

The initial concentrations for each metal were 50 mg/L. The contact time was 10 minutes. After the analysis of the solution by atomic adsorption spectrometry, it can be observed a very good removal efficiency of the metal ions, thus 87.5% for Cd, 84.6% for Cu and 82.2% for Ni (fig. 7). It worth mentioning the fast adsorption capabilities of coated magnetic nanoparticles.

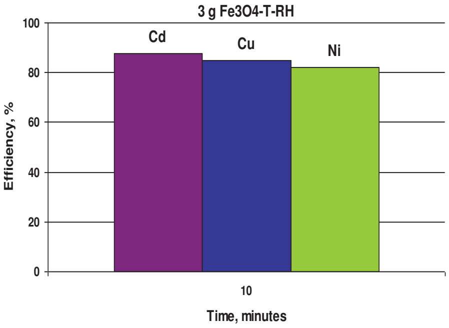


Figure 7: Metal ions removal efficiency for Cd, Cu, Ni on Fe_3O_4 –T-RH

The removal tendency is due to the ion exchange process, while the selectivity of the metal ions on this material is influenced by the atomic radius of the respective elements. The maximum adsorbed amount of the heavy-metal ions reached after the first 10 minutes decreases in order Cd>Cu>Ni. After the first ten minutes, the adsorption is due to the monolayer retention of the metal ions on the cationic resin surface.

4. Conclusions

Magnetite nanoparticles with an average diameter of 10 nm were synthesized using a co-precipitation method. The iron nanoparticles were then coated with cationic resin and characterized by transmission electron microscopy, X-Ray diffraction and TEM. The removal of certain toxic metals from synthetic aqueous solutions, such as cadmium, copper and nickel with the help of magnetic nanoparticles was successfully demonstrated by atomic spectrometry. The adsorption data indicated a good and fast adsorption capacity for metal ions removal especially for cadmium in comparison with the other metal ions.

The results of this work can be used to assess the efficiency of these types of nanomaterials in environmental applications, especially for water treatments, where these compounds can be used as adsorbents for toxic metal ions. The use of magnetic nanoparticles as adsorbents is justified by high surface area and reactivity, while their magnetic properties confer high and rapid collection and removal of toxic material.

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