Mercury removal in wastewater by iron oxide nanoparticles

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Abstract. Mercury is one of the persistent pollutants in wastewater; it is becoming a severe environmental and public health problem, this is why nowadays its removal is an obligation. Iron oxide nanoparticles are receiving much attention due to their properties, such as: great biocompatibility, ease of separation, high relation of surface-area to volume, surface modifiability, reusability, excellent magnetic properties and relative low cost. In this experiment, Fe3O4 and γ-Fe2O3 nanoparticles were synthesized using iron salts and NaOH as precipitation agents, and Aloe Vera as stabilizing agent; then these nanoparticles were characterized by three different measurements: first, using a Zetasizer Nano ZS for their size estimation, secondly UV−visible spectroscopy which showed the existence of resonance of plasmon at λmax~360 nm, and lastly by Scanning Electron Microscopy (SEM) to determine nanoparticles form. The results of this characterization showed that the obtained Iron oxides nanoparticles have a narrow size distribution (∼100nm). Mercury removal of 70% approximately was confirmed by atomic absorption spectroscopy measurements.

1. Introduction
The toxicity and persistence in environment of heavy metals released by industrial effluents have generated a significant threat to public health; these effluents have been treated through various conventional techniques (precipitation, electrochemical processes and/or membrane processes) [1]. Mercury is one of these persistent pollutants in wastewater and its removal has become a necessity. It shows its most toxic form as the highly reactive mercury (II) salts [2], which are often converted by bacteria into a neurotoxic substance, methylmercury, which increases the health risk for humans and wildlife through the aquatic food chain [3,4]. Nanomaterials such as iron oxide nanoparticles (IONPs) are efficient adsorbents because they combine magnetic separation with ionic exchange capacity for heavy metals removal [5,6]. Also, magnetic properties of iron oxide nanoparticles allow, for simple dispersion, the removal from an aqueous system [5-7]. Specifically the magnetite (Fe3O4) and maghemite (γ-Fe2O3) nanoparticles have been used in the adsorption of arsenic and chromium due to their surface properties [8], in this research we used it for mercury removal. In the present work, we report an efficient removal of Hg (II) ions from polluted water by using IONPs. The nanoparticles were synthesized by co-precipitation method, and characterized using different techniques to verify nanoparticles size and form.

2. Experiment
γ-Fe2O3 nanoparticles (IONPs) were prepared by co-precipitating Fe2+ and Fe3+ ions (in a molar ratio 1:2) in aqueous medium. Chemical precipitation was achieved at room temperature under vigorous
stirring while adding NaOH solution (1.5M), Aloe Vera solution (6.25mL) was used as stabilizing agent [9], and in this step a black precipitate is formed. During the reaction process, the pH was maintained at about 11-12. The precipitate was isolated after decanting the solution, then washed with deoxygenated water and finally centrifuged at 4000rpm (this process was done three times). Lastly, 0.01M solution of HCl is added to neutralize the ionic charges of nanoparticles. Cationic colloidal nanoparticles are then separated by centrifugation at 4000rpm, resulting in a translucent colloidal solution. Synthesized samples were characterized by using dynamic light scattering measurements (for this purpose we use both: a Nanozeta S - Malvern device), UV–vis absorption spectroscopy (UV-Visible Cary-100 VARIAN) in the wavelength range from 200 to 900nm, was also used to identify the presence of metal nanoparticles, these small particles exhibit an absorption of visible electromagnetic waves by the collective oscillation of the electrons in the conduction band at the surface (this is known as the surface plasmon resonance effect) [10]. The absorption bands for iron oxide nanoparticles have been reported to be in the range between 330–450nm [11,12]. The size and morphology of iron oxide nanoparticles were observed by Scanning Electron Microscopy (SEM) from JEOL JSM-6490LV equipment. Samples for SEM measurements were suspended in ethanol and ultrasonically dispersed. The Atomic Absorption Spectroscopy (AAS) measurements were carried out by a Thermo CientificTM iCE 3000.

3. Results and discussion

3.1. Synthesis and characterization
To identify the presence of iron oxide nanoparticles (IONPs) we used UV–visible spectrometer, and the Figure 1 represents the UV-vis spectra, which shows a broad absorption peak at ~360nm, due to the absorption and scattering of light by IONPs, indicating nanoparticles presence. The Figure 2 shows the size distribution versus intensity of the synthesized IONPs, which were mono-disperse with a diameter of ~99.56nm.

![Figure 1. UV-vis spectra of IONPs.](image)

In this work, we used Aloe Vera as stabilizing agent because of its low cost, and non-toxicity. 6.25mL of solution of Aloe Vera was used to obtain the size and shape of synthesized nanoparticles [9]. The usage of surfactant is necessary to avoid nuclei aggregation, in order to decrease the total surface energy. This aggregation, which can be a consequence of electrical charges in the surface (produced by dipolar moment) between atoms of the crystals, should be inhibited or limited to restrict the final particle size at the nanometric scale. One way to prevent nanoparticles from aggregation is by using substances that lead to steric repulsion between individuals [13]. The shape and size distribution of
IONPs were characterized by SEM and is shown in Figure 3, here the presence of nanoparticles with a size approximately 100nm is confirmed, as well as the presence of particles of greater size, but in minimum quantities.

![Size Distribution by Intensity](image1)

**Figure 2.** Particle size distribution analysis of IONPs.

![Micrograph SEM of IONPs with Aloe Vera](image2)

**Figure 3.** Micrograph SEM of IONPs with Aloe Vera.

### 3.2. Mercury removal

In order to evaluate the mercury removal capacity, the IOPNs synthesized in this study were used. A series of dilutions of nanoparticles in an Agar Plate Count matrix were prepared, on which a fixed volume of IOPNs solution was incorporated. When each system has been solidified, 5mL of standard solution Hg (II) is added to each different concentrations (4, 6, 8, 10, 25, 50mg/L). The experiment was performed in triplicate, and was left in contact by 24 h. The quantification of Hg (II) in the solution was carried out by atomic absorption spectroscopy measurements, complexed with NH₄Br. To evaluate the efficiency of IOPNs for Hg (II) removal, a removal percentage (%) is calculated. Figure 4 shows the effect of initial Hg (II) concentration on the removal efficiency of Hg (II) using IONPs.

A maximum removal percentage of about 87% was observed from an initial Hg (II) concentration of 8mg/L; for concentrations of 6mg/L and 4mg/L the removal percentages (%) have values close to 73 % and 68% respectively. At 10mg/L and 25mg/L, removal percentages (%) decreased with the
increase of initial Hg (II) concentration, this is because the IOPNs sites would eventually become saturated with adsorbed Hg (II), at this point further addition of Hg (II) to the solution hardly increase the amount of adsorbed Hg (II). At 50mg/L, removal percentage (%) was below 50% and its value is not reported in Figure 4(a). Keeping the highest Hg (II) concentration of 8mg/L with the same contact time, different concentrations of IONPs was applied to explore the removal percentage of Hg (II), Figure 4(b). It is observed that at any concentration value of IONPs the removal percentage of Hg (II) is above 60%, therefore it is not necessary to use high concentrations of nanoparticles for effective removal of mercury.

![Figure 4](image)

**Figure 4.** Hg (II) removal percentage (a) from Hg (II) solutions of different concentrations, [IOPNs]=100%. (b) With different concentration of IONPs, [Hg (II)]=8mg/L. Adsorption time of 24h.

### 4. Conclusions

In this paper the synthesis and characterizations of Iron Oxides Nanoparticles, stabilized with Aloe Vera was carried out. The nanoparticles showed a monodisperse behaviour, with an average size ~100nm, which was corroborated by UV-Vis, DLS and SEM measurements. Mercury removal more than 85% was achieved (70% average), using low concentrations of IOPNs solution; therefore these can be used as an alternative for treating wastewater.

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