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Magnetite nanoparticle for arsenic remotion.

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Abstract. Inorganic As (V) and As (III) species are commonly found in groundwater in many countries around the world. It is known that arsenic is highly toxic and carcinogenic, at present exist reports of diverse countries with arsenic concentrations in drinking water higher than those proposed by the World Health Organization (10 µg/L). It has been reported that adsorption strategies using magnetic nanoparticles as magnetite (<20 nm) proved to be very efficient for the removal of arsenic in drinking water. Magnetic nanoparticles (magnetite) were prepared using a co-precipitation method with FeCl₃ and FeCl₂ as metal source and NaOH aqueous solution as precipitating agent. Magnetite nanoparticles synthesized were put in contact with As₂O₃ and As₂O₅ solutions at room temperature to pH 4 and 7. The nanoparticles were characterized by FT-IR, DRX, UV-vis, and XRF. The results showed that synthesized magnetite had an average diameter of 11 nm and a narrow size distribution. The presence of arsenic on magnetite nanoparticles surface was confirmed, which is more remarkable when As (V) is employed. Besides, it is possible to observe that no significant changes in the band gap values after adsorption of arsenic in the nanoparticles.

1. Introduction

Arsenic poisoning has become one of the major environmental worries worldwide, as millions of people, which have been exposed to high arsenic concentrations (through contaminated drinking water), developed severe health problems [1]. Besides, it ranks twentieth in abundance in the earth's crust, fourteenth in seawater and twelfth in the human body [2]. Both organic and inorganic arsenic exist in natural waters but organic arsenic is of less environmental concern as it undergoes biotransformation and detoxification through methylation. Evidence of chronic arsenicosis has been observed in populations ingesting arsenic contaminated drinking water in many parts of the world [1, 2]. Different reports described that major sources of arsenic are geologic formations such as soil and bedrocks, weathering of rocks, mine tailings, industrial wastes discharge, fertilizers, agricultural use of pesticides, smelting of metals, and burning of fossil fuels [3, 4]. Chronic exposure to arsenic from groundwater has been recognized to cause the largest environmental health disaster in the world, putting more than 100 million people at risk of cancer and other arsenic-related diseases [5].

Varieties of methods have been developed for the removal of arsenic compounds from drinking water including precipitation, adsorption, ion exchange and nanofiltration [6-8]. However, nanomaterials and the nanotechnologies inspire new potential solutions to major environmental issues in actuality; the



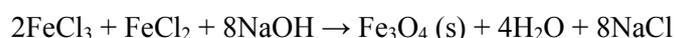
removal of arsenic by nanoparticles of iron oxide has shown promising results due to their small particle size and large surface area [9, 10]. Oxide mixtures, which employ magnetite nanoparticles, have allowed to remove arsenic species from aqueous medium [9]. It is expected that the use of pure magnetite nanoparticles (< 20 nm), allow such removal and also, it makes possible the study of a possible mechanisms of interaction between arsenic species and the surface of the nanoparticles.

Adsorption experiments were conducted using magnetite synthesized, with an average diameter of 11 nm. The overall purpose of this study is to corroborate that magnetite with naked surface can remove arsenic species from water. In this sense, our attempts are primarily based on the results of FT-IR spectroscopy, although other complementary techniques were also used (mainly UV-vis spectroscopy and XRF). The developed methodology could be implemented in the water treatment industries, reducing the costs of the processes and making them more environmental friendly.

2. Experimental

2.1 Chemicals and materials. The chemicals used in this study were mostly reagent with high analytical grade and used as received (Sigma-Aldrich) without further treatment. FeCl₃.6H₂O (>97%), FeCl₂.4H₂O (≥99 %), NaOH (>98%), As₂O₃.xH₂O (≥99 %) and As₂O₅ (≥99.99 %). All chemical solutions were prepared with deionized water. The As (III) and As (V) stock solutions were prepared by dissolving arsenic oxides (As₂O₃ and As₂O₅) powder in de-ionized water, using 4 g/L NaOH since both oxides have enhanced solubility in NaOH solution.

2.2 Synthesis of magnetite nanoparticles. Fe₃O₄ was synthesized from co-precipitation method which involves the simultaneous precipitation of ions Fe²⁺ and Fe³⁺ in a molar ratio of 1:2 respectively. The precipitation was performed by addition of base (NaOH) at room temperature. The reaction is shown in the following equation:



To the reaction was used FeCl₂.4H₂O (0.01 mol) and FeCl₃.6H₂O (0.02 mol) dissolved in 100 mL of distilled H₂O. While stirring mixture vigorously was passed a stream of N₂ at a constant flow to prevent oxidative atmosphere. NaOH (0.09 M) aqueous solution was added drop wise, as precipitant agent. After 3 hours of reaction, a black precipitate was observed, which was separated magnetically from the supernatant. Black solid was washed three times with nitric acid (HNO₃) and dried under vacuum for 24 h at 80 °C.

2.3 Characterization.

Fourier transformed infrared spectroscopy (FT-IR) was employed to analyse the structural characteristic of particles. IR spectra were recorded in transmission mode after making pellets with KBr powder with a Perkin Elmer Spectrum One FT-IR spectrometer in transmission mode with 16 scans at a resolution of 2 cm⁻¹ in the range of 400–4000 cm⁻¹.

X-ray diffraction (XRD) powder pattern of Fe₃O₄ nanoparticles was recorded with a Bruker D8 Advance Diffractometer and CuK_α radiation (1.54183 Å). The average crystallite size was estimated from the integral intensity of the X-ray diffraction peak maximum using the Scherer equation (1):

$$D_c = \frac{k * \lambda}{\beta * \cos \theta} \quad (1)$$

where k is the shape factor, λ is the X-ray wavelength (0.15418 nm), β is the full width at half-maximum expresses in unit of 2, and θ is the Bragg angle (°).

The optical properties of these samples were studied using UV-visible spectroscopy technique, the UV-vis spectra were recorded on a BDA 950 UV/Vis/NIR spectrophotometer, and the software computed the Kubelka-Munk function, the range of a wavelength of work was 800 – 200 nm.

The elemental composition of samples were developed by X-ray Fluorescence (XRF) and employing Bruker AXS brand equipment S2Ranger model. In this study aluminium filter was employed.

2.4 Adsorption of As (III) and As (V) by naked Fe₃O₄ nanoparticles. (Batch adsorption experiment).

As (III) and As (V) stock solutions were prepared to concentrations of 500 ppm and 300 ppm respectively, at pH=7. Adsorption studies were performed to pH=4 and pH=7. The pH values were adjusted with acid (2M HCl) and basic (1 M NaOH). Then 15 ml of arsenic aqueous solution was added to 15 mg of nanoparticles under stirring and at room temperature, 25 °C. After a specific time elapsed (12 h), the solid was separated from the liquid by magnetic field action or centrifugation. Nanoparticles are washed three times with deionized water and ethanol, and then it were dried at room temperature for further studies.

3. Results and Discussion.

3.1 Structural characterization of Fe₃O₄.

FT-IR spectroscopy was used to characterize the as-prepared magnetite nanoparticles. **Figure 1** shows the spectra of magnetite. The spectrum of pure magnetite (**Figure 1**) presents a wide band at 3432 cm⁻¹ and a small in 1622 cm⁻¹, which can be attributed to vibrations $\nu_{s(OH)}$ and dubbing in the plane $\delta_{(H-O-H)}$, respectively, by water molecules adsorbed onto the surface [12, 13]. Beside, one peak is observed at 570 cm⁻¹, which can be assigned to the stretching mode of Fe–O in Fe₃O₄ [12]. The bands at 1384 and 1230 cm⁻¹ correspond to stretching vibrations ($\nu_{(NO_3^-)}$ and $\nu_{(ON)}$) due to NO₃⁻ ions adsorbed on the surface of the nanoparticles, because the final wash is performed with nitric acid [13].

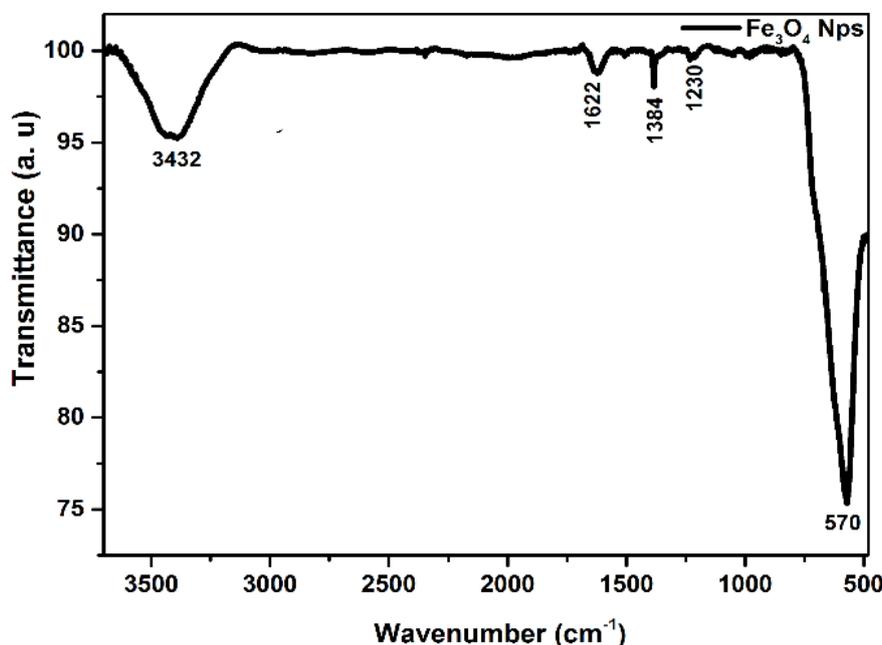


Figure 1. FT-IR spectrum of magnetite nanoparticles.

Diffraction pattern of the dried powder of magnetite nanoparticles are shown in **Figure 2**. It can be seen that, the sites and intensity of the diffraction peaks are consistent with the standard patterns for Fe₃O₄ (ICSD No. 08-4611). Cubic single phases for Fe₃O₄ powders have been obtained, which is well

consistent with the FT-IR results. Moreover, the shape of the peaks in the diffractogram and the good definition it can say that the sample is crystalline. In addition, according to Debye-Scherrer equation the average particle diameter of magnetite was calculated to be 11.3 nm.

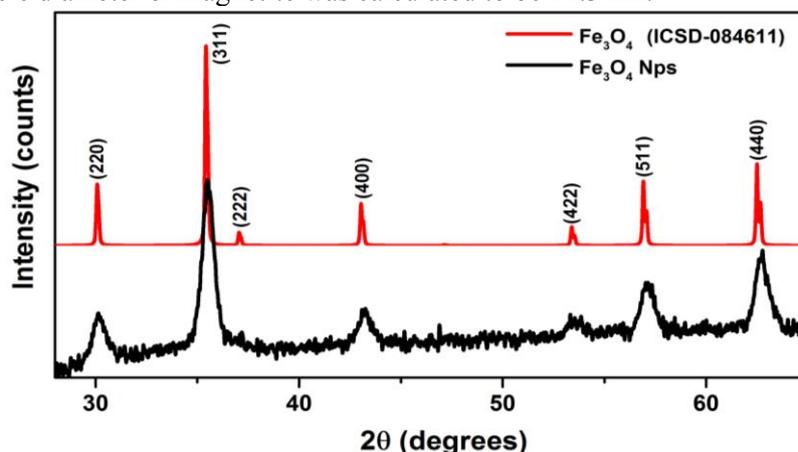


Figure 2. XRD pattern for magnetite nanoparticles.

3.1 Optic properties (UV-vis).

Figure 3 shows the measurements of absorbance in function of wavelength for magnetite nanoparticles in UV-vis zone. It is possible to observe an adsorption band at 300 nm, which is characteristic of this material, corresponding to transitions of crystalline field; in this cause due to transitions from t_{2g} to e_g orbitals (in octahedral positions) and from e_g to e_g orbitals (for tetrahedral positions) in Fe^{2+} y Fe^{3+} cations [12].

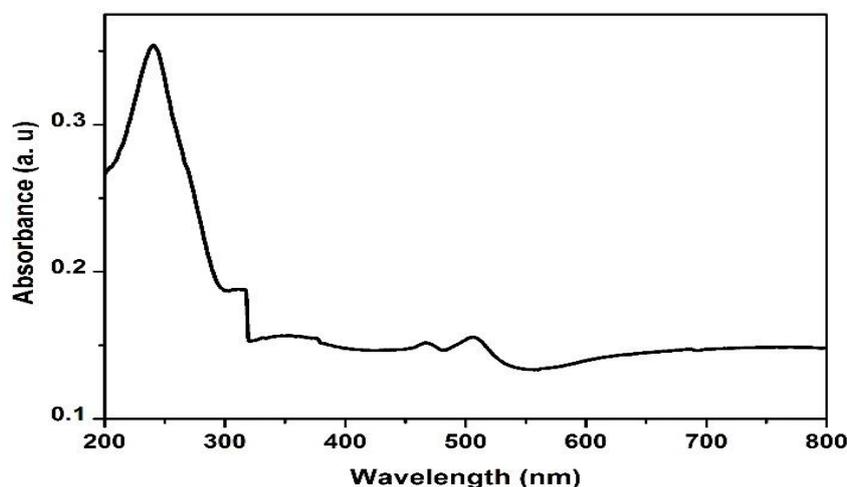


Figure 3. Absorbance in function of wavelength of pure magnetite nanoparticles.

The results of calculations for optic energy of band gap are shown in **Figure 4**, for direct and indirect transitions were, 1.5 and 0.8 eV, respectively. Both band gap values, for powder are high for this material when are compared with the value for bulk [14, 15]. This widening of the band gap is a quantum confinement effect that has been observed in many semiconductor materials having delocalized electron states near the Fermi level [15]. These results for the band gap energy of both

direct and indirect transitions for magnetite nanoparticles, can permit classify this sample as a semiconductor, since it has a band gap energy between 0-3 eV [16].

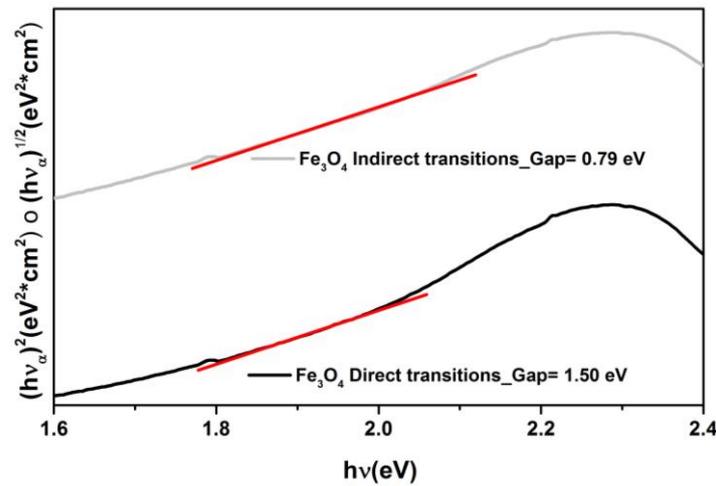


Figure 4. Determination of optic energy of band gap, for direct (E_{g1}^{opt}) and indirect (E_{g2}^{opt}) transitions.

3.2 X-Ray Fluorescence.

By XRF analysis is possible evidence the arsenic presence onto nanoparticles surface. **Table 1** show the semiquantitative estimation of arsenic after adsorption experiments, for both pH in study. From the analysis it was evidenced that in the sample there is a significant percent of arsenic, which corroborates the presence of this element in all materials. In this case, the adsorption of As (III) is favored at pH = 7, probably because in these conditions neutral species of As (III) (H_3AsO_3) are formed, while the surface of the nanoparticles is negatively charged, because at pH above the isoelectric point materials exhibit this behavior, being the case of magnetite as this pH is 6.5 [17]. Moreover, in the case of As (V), the adsorption is higher at pH = 4; in these conditions the surface of the nanoparticles is positively charged and prevail neutral species of As (V) ($H_2AsO_4^-$), which will be attracted to the oxide surface more easily, because by possessing different charges favors attraction between the species and the area. In both cases the content of Arsenic is close to 9 %.

Table 1. Semiquantitative estimation of Arsenic onto magnetite nanoparticles.

Nanoparticles	Weight (%)
Fe ₃ O ₄	As3d
Fe ₃ O ₄ + As(III) pH= 4	6,0
Fe ₃ O ₄ + As(III) pH= 7	9,9
Fe ₃ O ₄ + As(V) pH= 4	7,8
Fe ₃ O ₄ + As(V) pH= 7	5,2

3.3 Study of optic properties for magnetite nanoparticles with Arsenic onto surface.

Table 2 shows the results of band gap for direct and indirect transitions in magnetite sample at different conditions of study. As expected, no significant changes are observed in the band gap values

after adsorption of arsenic in the nanoparticles, because a simple adsorption of arsenic cannot produce changes in the optical energy of the material. Therefore, it is confirmed that adsorption of arsenic species on the nanoparticles is accomplished by forming new surface species.

Tabla 2. Band gap values for direct and indirect transition in magnetite nanoparticles with and without arsenic onto surface.

Materials	Band Gap (Direct transitions) (eV)	Band Gap (Indirect transitions) (eV)
Magnetite	1.5 ± 0.1	0.8 ± 0.1
Magnetite + As(III) pH= 4	1.4 ± 0.1	0.7 ± 0.1
Magnetite + As(III) pH= 7	1.3 ± 0.1	0.6 ± 0.1
Magnetite + As(V) pH=4	1.3 ± 0.1	0.7 ± 0.1
Magnetite + As(V) pH= 7	1.2 ± 0.1	0.6 ± 0.1

Conclusion

Magnetite nanoparticles with a spherical morphology were obtained, with a diameter of 11 nm, and it was confirmed that this nanoparticles can remove arsenic species from aqueous medium. Beside, was evidenced that arsenic onto nanoparticles surface cannot changes the values of optic energy (band gap).

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Acknowledgments

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