Preparation of Fe₃O₄ Nanoparticles and Removal of Methylene Blue through Adsorption

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Abstract. In this work, we studied the catalytic activity, structural properties, and behavior of a Fe₃O₄ magnetic system. The Fe₃O₄ nanoparticles were prepared by the thermal decomposition method. X-ray diffraction confirmed the presence of a structural Fe₃O₄ phase, where acicular shape of the grains is shown. Transmission Mössbauer spectroscopy showed a wide distribution of particle sizes at room temperature, some of these present superparamagnetic behavior and are responsible of paramagnetic sites. The hysteresis loops obtained by the use of a vibrating sample magnetometer showed that these nanoparticles exhibit superparamagnetic behavior. However, the cycles present a significant contribution from a ferrimagnetic component at 2 K, which agrees with Mössbauer results. Through scanning electron microscopy, a tendency to the agglomeration of nanoparticles was observed. Nanoparticle activity in the degradation of methylene blue (MB) was studied through fluorescence spectroscopy, finding dye adsorption properties.

1. Introduction

The magnetic properties of iron oxide nanoparticles have been widely applied in the electronics industry [1-2]; however, currently investigations are conducted in the search for pharmaceutical [3] and catalytic applications [4-6]. These magnetic properties, coupled with the surface area of the nanoparticles of magnetite, are among the major advantages at the time of studying catalytic activity, providing new analytical chemistry methods for removing metals in water [7-8] and contaminants dyes degrade in aqueous matrices [9-10]. Methylene blue dye is widely used in staining procedures; to examine DNA or RNA in microscopy studies, and as redox indicator. Despite its health benefits, in higher doses methylene blue can take electrons from complexes of the electron transport chain, becoming a health risk. In many catalytic applications, Fe3O4 nanoparticles are used as a metal complex support material or to be functionalized with other materials (gold, manganese complexes, polyethyleneimine), which enhances activity [11-13], so it is important to carry out studies with magnetite before functionalization.

In this paper, magnetite nanoparticles were obtained from ferric solutions. During characterization, a particle size distribution was observed, where some showed superparamagnetic behavior. Nanoparticle activity in the degradation over time of methylene blue was studied via fluorescence spectroscopy.
2. Experimental procedures

2.1 Synthesis of Fe$_3$O$_4$ nanoparticles

Synthesis of magnetite nanoparticles was performed as reported in the literature [14]. Iron chloride tetrahydrate [FeCl$_2$·4H$_2$O] (278.3 mg, 1.4 mmol); and sodium oleate (1851.2 mg, 5.1 mmol) were put into two-neck round bottom flask were stirred in a mixture (280 ml) of ethanol:water:hexane (4:3:7). The resulting solution was heated to 70 °C and kept at that temperature for 4 h. When the reaction was completed, the upper organic layer containing Fe$_3$O$_4$-oleate complex was washed three times with 30 ml distilled water. After washing, hexane was evaporated-off, the resulting Fe$_3$O$_4$-oleate complex was introduced into a pyrex tube and then sealed less than 40 Pa. The pyrex tube was heated to 380 °C for 4 h. The reaction mixture was cooled to room temperature, yielding a black fluid. The Fe$_3$O$_4$ nanoparticles produced dispersed in chloroform. To precipitate the particles, 20 ml of ethanol was added. The particles were isolated by centrifuge, and then dissolved in 20 ml of hexane. After adding 0.02 ml of dispersion agent, the precipitate appeared and was isolated by centrifuge. The precipitate was washed with ethanol and centrifuged to get the black solid product, which was washed again with ethanol, centrifuged, and finally re-dispersed in hexane and stored under argon.

2.2 Characterization

The sample prepared was characterized by the following techniques: X-ray diffraction, Mössbauer spectroscopy, vibrating sample magnetometer, scanning electron microscopy, and fluorescence spectrometer. The X-ray measurements were obtained at room temperature for the sample by using a PANalytical diffractometer equipped with a Cu target X-ray tube and a Ni filter to select the Cu-K$_\alpha$ radiation. The X-ray profile was collected from 20-90° in scattering angle using a 0.02° step and counting times of 2 s per point. The patterns were refined by the Rietveld method combined with Fourier analysis to describe the broadening of the lines by using the GSAS program [15]. This yielded the average values of the lattice parameter, crystallite size and the structural phase. Mössbauer measurement was performed at room temperature with transmission geometry using a 57Co(Rh) source of 25 mCi. The spectra were fitted with the MOSFIT program [16], taking an α-Fe foil as the calibration sample and using a HMFD and two paramagnetic sites. The behavior of magnetization as a function of the field was studied by using VSM and using a physical properties measurement system (PPMS) available at the Center of Excellence for Novel Materials (CENM). Surface morphology of the sample was observed by using SEM.

2.3 Adsorption studies

The degradation activity of nanoparticles was assessed for cationic (MB) dye. The temperature and shaking speed for all the adsorption experiments were kept constant at 25.0 ± 0.1 °C and 130 rpm, respectively. Typically 10 ml of dye solution with concentration of 20 mg·L$^{-1}$ MB was mechanically shaken with 0.2 g·L$^{-1}$ Fe$_3$O$_4$. The concentrations of residual MB, after magnetic separation of Fe$_3$O$_4$, were measured with the emission band at 680 nm ($\lambda_{ex}$ = 633 nm) using a fluorescence spectrometer (FP-8500, JASCO). The excitation lambda (633 nm) corresponds to the most intense band after performing the sweep from the UV region at 230 nm to the UV-Vis region at 800 nm.

3. Results and Discussion

3.1 X-ray diffraction, morphology and size distribution results

Figure 1 shows XRD patterns indicating the position and intensities corresponding to the spinel structure of the (Fe3O4) magnetite peaks (JCPDS 01-11111 data) [10, 17]. From the refinement of the diffractogram of Fe3O4 nanoparticles it was obtained that: crystallite size parallel and perpendicular equal to 79.5 ± 1 Å and 137.2 ± 2 Å, respectively, indicating that the crystallites have acicular shape; and lattice parameters of this structure are: a, b, c = 8.379 Å. According to the micrograph obtained via SEM, and shown in Figure 2, it can be noted that the particles present an agglomeration tendency. Z potential measurements showed particle sizes between 15 and 100 nm, with an average 42 nm particle size.

3.2 Mössbauer and magnetic results

The Mössbauer spectrum (Figure 3) was fitted with two sextets, one doublet, one singlet and a hyperfine field distribution due to the distribution of particle sizes [17]. This is caused by the presence
of various types of crystallographic environment of iron atoms (Fe$^{2+}$ and Fe$^{3+}$) into the spinel structure of the magnetite, where the Fe$^{2+}$ and Fe$^{3+}$ ions are located in different crystallographic positions (octahedral and tetrahedral) [17]. The ionic state of the Fe$^{2+}$ and Fe$^{3+}$ atoms cannot be distinguished at room temperature as a result of fast electron hopping [17]; this suggests that the presence of components with lower hyperfine field is due to reduced particle size. The central part of the spectrum is a consequence of particle size distribution; this suggests that refined particle sizes gives a superparamagnetic behavior and large particle sizes gives ferrimagnetic behavior. Table 1 shows the Mössbauer parameters obtained. Through magnetization it was observed that the Fe$_3$O$_4$ magnetite sample at room temperature presents a superparamagnetic behavior and at low temperatures 2 K it shows a widening of the hysteresis loop, presenting ferrimagnetic behavior with coercive field of 613.2 Oe and a saturation magnetization of 50.3 emu/g (Figure 4). The low value of magnetization with respect to the value of the bulk (92 emu/g) is probably due to the mass of the surfactant (sodium oleate), given the existence of a surface layer of the surfactant in the particles decreases the value of the magnetization because this can make a diamagnetic contribution [17]. The different behaviors shown by Mossbauer (superparamagnetic-ferrimagnetic) and hysteresis loops (superparamagnetic) are a consequence of the different measurement times of both techniques.

![Figure 1. XRD patterns of Fe$_3$O$_4$](image1)

![Figure 2. SEM micrographs of Fe$_3$O$_4$](image2)

![Figure 3. Mössbauer of Fe$_3$O$_4$](image3)

1.3. Adsorption studies

Adsorptive removal activity of the sample prepared was evaluated by measuring the degradation rate of MB in the presence of magnetite nanoparticles. It was found that the MB concentration remained stable after 1 h of stirring in the presence of the powder obtained. The results of MB degradation at different adsorption times of Fe$_3$O$_4$ are shown in Figure 5. Emission spectra obtained after exciting at 633 nm; showed a decrease in the intensity of the emission band observed at 680 nm, indicating that the MB concentration decreases with nanoparticle adsorption, finding particular properties in the degradation of this cationic dye. The activity may increase if photocatalytic studies are conducted by using UV irradiation in the presence of the nanoparticles, as has been done in similar studies [9-10].

Conclusions

In this study, magnetite particles with an average 42 nm diameter were prepared by thermal decomposition. According to magnetization and Mössbauer spectroscopy data for Fe$_3$O$_4$ particles, this indicates that the particles have superparamagnetic properties that disappear when the temperature drops. The transformation has been observed to the ferrimagnetic state in the range of 2 K, which can be explained by increased dipole-dipole interactions between the magnetic particles. The Mössbauer spectroscopy data for magnetite particles do not show a stable superparamagnetic fraction, and hyperfine magnetic structure appeared in the absence of $H_{ext}$. The study of the magnetite activity in the degradation of methylene blue shows that the nanoparticles obtained have adsorbent properties for the cationic dye over time; this is evidenced by a decrease in intensity of the emission band obtained by fluorescence. This study could be applied in wastewater decontamination.

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Table 1. Hyperfine parameter: isomer shift (IS), mean hyperfine field $<B_{hf}>$, quadrupole splitting (QS), line width (GA) and percentage of area of the Fe$_3$O$_4$ nanoparticles.

| Component     | $<B_{hf}>$ ± 0.2 [T] | QS ± 0.05 [mm/s] | IS ± 0.05 [mm/s] | GA ± 0.05 [mm/s] | Area [%] |
|---------------|-----------------------|------------------|------------------|------------------|---------|
| Sextet 1      | 39.2                  | 0.50             | 0.41             | 0.30             | 4.88    |
| Sextet 2      | 47.4                  | -0.01            | -0.23            | 0.30             | 13.14   |
| Distribution  | 39.1                  | -0.01            | -0.22            | 0.30             | 52.37   |
| Doublet       | ---                   | 0.70             | -0.19            | 0.40             | 9.08    |
| Singlet       | ---                   | 0.00             | -0.13            | 1.00             | 20.53   |

Figure 4. Hysteresis loop of Fe$_3$O$_4$

Figure 5. Emission spectra of MB vs. degradation time in the presence of Fe$_3$O$_4$

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