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LEACHING TESTS FOR SYNTHESIZED MAGNETITE NANOPARTICLES USED AS ADSORBENT FOR METAL IONS FROM LIQUID SOLUTIONS

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Two different protocols for magnetite and magnetite covered with dextran are presented. These products can be used in waste water treatment, especially as adsorbents for different metal ions. The synthesis methods, characterization of the final products and leaching test at different pH media were tested. The investigation methods for the characterization of the products obtained with different methods were scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. The quantity of iron dissolved from magnetite was evaluated with flame atomic absorption spectrometry (FAAS).

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1. Introduction

The synthesized methods for the obtaining of nano-iron oxides are simple and reproducible. From all nano-iron oxides, the magnetic nanocrystals present very interesting applications. The time evolution of the physical properties of hard and soft magnetic materials is shortly reviewed [1].

These oxides can be obtained with desired size, shape and self-assembly have drawn much attention due to its unique size dependant properties such as magnetic, optical, electronic and surface reactivity [2]. In addition, these nanoparticles serve as ideal systems for fundamental studies such as superparamagnetism, magnetic dipolar interactions [3,4], to understand molecular interactions at emulsion droplet interface [2].

Ferrofluid, a stable suspension of surfactant coated magnetic nanoparticles in a non-magnetic liquid carrier, has been one of the most widely studied nanofluids due to their immense applications [2].

Magnetite is a magnetic product frequently used one because of its high saturation magnetization value.

There are various synthesis procedures of the magnetite nanoparticles, but most commonly used is the coprecipitation of Fe^{2+} and Fe^{3+} ions by an alkali, usually NH_4OH or NaOH in an aqueous solution.

Besides, coprecipitation, partial oxidation of Fe^{2+}, followed by coprecipitation is another well-known method for magnetite synthesis.

Ferrous and ferric chlorides or sulfates are usually used as the iron source [5]. Also, the magnetite nanoparticles were synthesized by partial oxidation of $FeSO_4$ with $NaNO_3$ or KNO_3 at elevated pH and temperature (60–100 ◦C) [5].

Magnetite nanoparticles were prepared via partial reduction of $FeCl_3$ with sodium sulfite [6] or hydrazine [7] as reductants.

In environmental engineering, Hu et al. [8] examined the removal efficiency of Cr^{6+} from wastewater with the magnetite nanoparticles prepared through coprecipitation.

The processes on a solid-liquid interface are of primary importance in many chemical and biological technologies.

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For example, adsorption processes are playing the fundamental role for synthesis of magnetic liquids, which are unique nanosystems combining properties of magnetic materials and liquids [9].

Good adsorption results were obtained on natural and synthetic zeolite for the drinking water treatment [10].

In this paper, two protocols are presented, regarding the obtaining of magnetite and magnetite covered with dextran and also the leaching tendency for the two products is presented.

2. Experimental

2.1. Preparation and characterization of magnetite (Fe_3O_4) nanoparticles by coprecipitation

One of the oldest and most conventional techniques for nanoparticles synthesis is the precipitation method [11, 12,13].

In general, the synthesis of monodispersed particles is performed under a kinetic control of the precipitation using very dilute solutions, the transitory precipitation of another phase or thermohydrolysis conditions [14].

This paper describes the method for preparation of magnetite nanoparticles by coprecipitation method. The synthesis of magnetite was carried out by coprecipitation of Fe (II) and (III) [15].

A volume of 5 mL solution of Fe (II) and Fe (III) chloride (molar ratio 1:2) in ultrapure water was poured slowly (dropwise) into a three-neck flask reaction vessel containing 40 mL of 0.9M NH_4OH solution.

The solution was vigorously stirred. After addition of the iron salts, stirring the mixture continued for another 30 minutes and then the precipitated magnetite was separated from the supernatant by decantation.

The solid was washed 4 times with ultrapure water and separated by decantation. Finally, the suspension was centrifuged at 4000 rpm and the solid was dried in a desiccator.

In order to obtain good information regarding the material structures a strict control of the nanostructured morphology and topology elements entering the composition of the material base is required [16].

Investigation of samples were performed by using of a Quanta INSPECT F scanning electron microscope (SEM) equipped with field emission gun (FEG) with a resolution of 1.2 nm and an energy dispersive X -ray spectrometer (EDXS) with the resolution for MnKα of 133 eV.

The structure of the Fe_3O_4 nanoparticles was characterized by X-ray powder diffraction (XRD), which was carried out in a SHIMADZU diffractometer with high-intensity Cu Kα radiation ($\lambda = 1.54065$ Å) with the 2θ range from 10^o to 90^o [11].

2.2. Preparation and characterization of magnetite nanoparticles covered with dextran (Fe_3O_4-D)

In the literature [9], the prevention of the aggregation for magnetite nanoparticles is made by adding of some surfactants, e.g. with fatty acids. Dextran as natural polysaccharide, which is widely used in the pharmaceutical field, has a good solubility in water and is inert in biological systems, not influencing cell viability [17].

It is known the use magnetic maghemite nanoparticles of prepared by a chemical co-precipitation method and their suspension into dextran as the surfactant [18].

For this work, the iron salt solution was added into 50% (w/v) solution of dextran. The mixture was adjusted to pH 11 with a drop of NaOH solution. The carboxyl group of dextran binds to the iron atom at pH 11 [19]. The value of pH decreased to 7 by HCl and then the mixture was refluxed for 1 h at 100 ºC.

After cooling to room temperature, methanol was added in order to precipitate the dextran particles. After centrifugation for 15 min, the precipitate was kept overnight. After this the obtained solution was adjusted to pH 8 with a drop of NaOH solution and was then concentrated in Fe base using an evaporator.

The size and morphology of the nanoparticles were analyzed by the same methods as magnetite nanoparticles, namely, SEM and XRD, respectively.

2.3. Leaching test

In order to evaluate the stability of nanoparticles under different pH values, the hydrochloric acid (HCl 0.1 M) and sodium hydroxide (NaOH 0.1M) were added into nano-magnetite (Fe_3O_4 and Fe_3O_4-D) suspensions.

The pH media were 2.5, 6.5 and 8.5, respectively. After stirring, suspensions were isolated by centrifugation with an iron hallow cathode lamp (HCL).

Determinations were made at 248.3 nm with an flame atomic absorption spectrometer (FAAS) GBC 932 AB Plus, lamp current 12.5 mA, spectral bandwidth of 0.2 nm.

The samples were magnetically separated and the supernatant was analyzed by FAAS in order to establish the leached quantity of total iron resulted by dissolution under different media.

3. Results

3.1. Characterization of magnetite (Fe_3O_4) nanoparticles and magnetite covered by dextran (Fe_3O_4-D) by X-ray diffraction (XRD)

The X-ray diffraction pattern for the two nanomaterials is presented in the Figure 1 show differences between the two diffractograms.

The two diffractograms indicate the presence of the synthesized compounds. In case of Fe_3O_4, the indexed peaks from XRD diffractogram correspond to the Fe_3O_4 with crystal system orthorhombic, according to ASTM reference code 01-075-1609.

Also, the quantify diagram for Fe_3O_4 indicate the presence of the maghemite (γ-Fe_2O_3) as secondary phase as it is shown in the Figure 2.

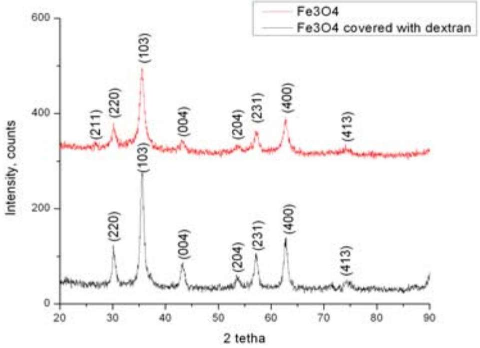

Fig. 1. XRD diffractograms for Fe_3O_4 and Fe_3O_4-D

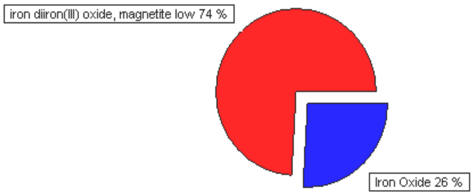

Fig. 2. Quantify diagram for the synthesized Fe_3O_4

3.2. Characterization of magnetite (Fe_3O_4) nanoparticles and magnetite covered by + dextran (Fe_3O_4-D) by scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) was made for the two compounds at different magnifications up to 400000x orders.

The images obtained at magnification of 100 000x are presented in the Figure 3 (a) for Fe_3O_4 and (b) for Fe_3O_4-D.

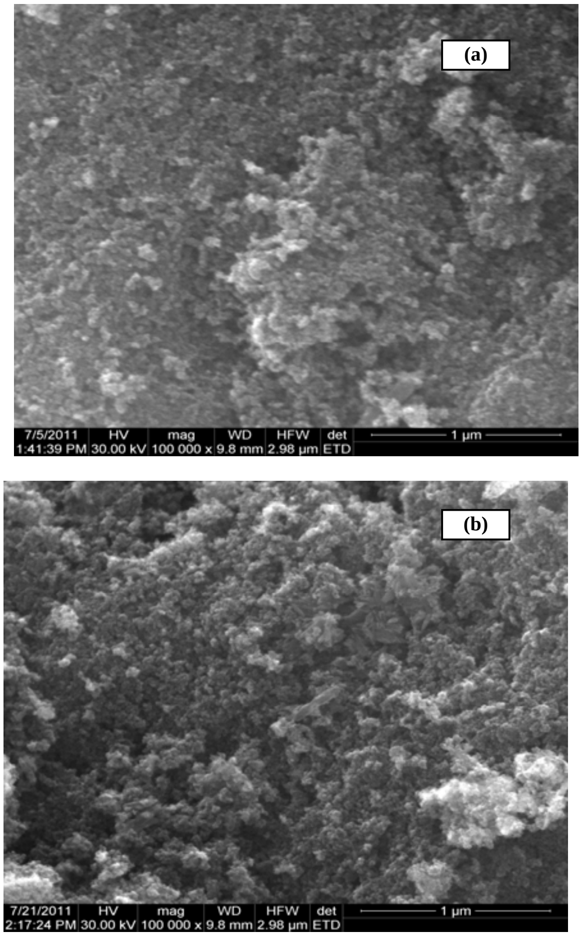

Fig. 3. SEM images for Fe_3O_4 (a) and for Fe_3O_4-D (b) at 100 000x

As it can be seen from Figure 3, the SEM images of magnetite and magnetite modified with dextran at 100 000x, the tendency of the aggregation remains even after the coating of the dextran. The same tendency can be observed in case of 400 000x magnification from Figure 4 (a) for Fe_3O_4 and (b) for Fe_3O_4-D.

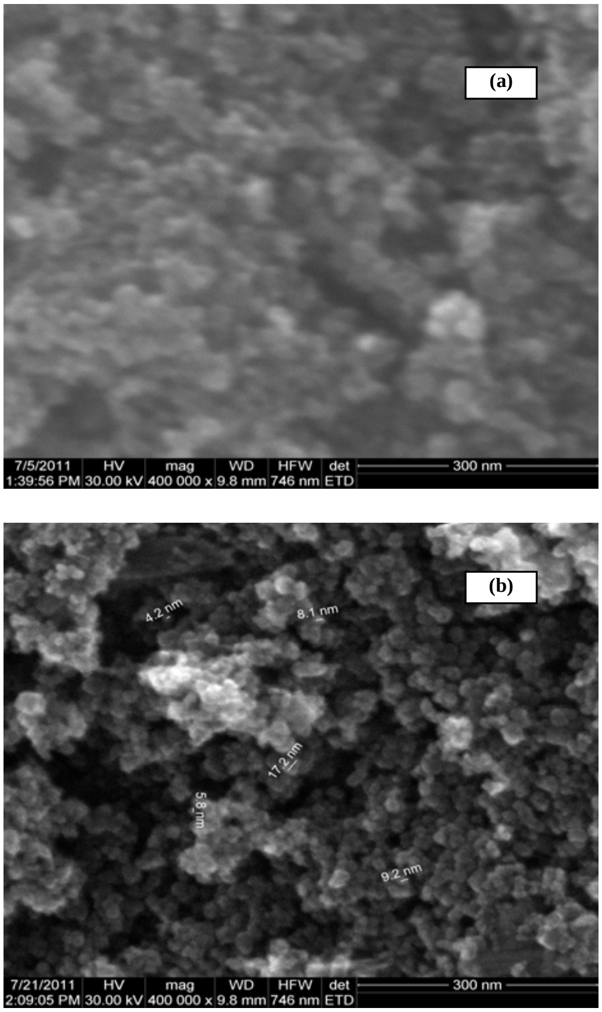

Fig. 4. SEM images for Fe_3O_4 (a) and for Fe_3O_4-D (b) at 400 000x

Some of the nanospheres of Fe_3O_4 and Fe_3O_4-D have different shapes but the size of them is mostly lower than 100 nm. Besides, most of the nanospheres have a bright shell.

3.3. Leaching test

The total dissolved iron content was measured at pH 2.5, 6.5 and 8.5. The tested products were Fe_3O_4 and Fe_3O_4-D.

The initial quantity from each nanomaterial was 1 g which was added at 100 mL HCl and NaOH, respectively. The contact time was 24 hours. The total dissolved iron content, expressed as mg/g was measured with flame atomic absorption spectrometer (FAAS) and the results obtained are shown in Figure 5. It can be observed that the most total dissolved iron concentration was obtained under acidic conditions (pH 2.5) for Fe_3O_4, which had the lowest stability.

The concentrations were detected for 10 samples from each solution and the presented resulted represent average values.

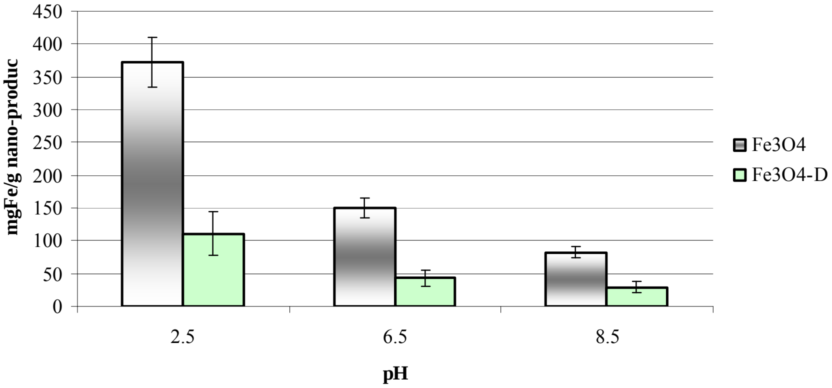

Fig. 5. The FAAS measurements of the total dissolved iron concentrations, mg/g

4. Discussions

4.1. Characterization of Fe_3O_4 and Fe_3O_4-D by XRD

The XRD is an effective characterization to confirm the crystal structure of magnetite nanoparticles. The XRD diffractograms reveal the presence of maghemite (γ-Fe_2O_3) in tetragonal crystal system together with magnetite (Fe_3O_4) in orthorhombic crystal system. The 2θ peaks at 35.48°, 43.17°, 53.50°, 56.16°, 62.69°, 74.29° are attributed to the crystal planes of magnetite at (220), (103), (004), (204), (231), (401) and (413), respectively.

The maximum intensity for the analyzed sample is at 35.48° which correspond at (103), the peak being characteristic for Fe_3O_4 according to the ASTM reference code 01-075-1609. Another characteristic peak to the ASTM sheet appears at 62.69° corresponding with (400).

We conclude that the product is magnetite particles with orthorhombic crystal system. Also, the presence at 26.24° of crystal plane at (211) indicates the presence of maghemite according to ASTM reference code 03-065-0390. Since the magnetite nanoparticles is not stable in oxygen due to the Fe^{2+} ions which are oxidized to ferric ions, the maghemite formation is obviously.

Regarding the Fe_3O_4-D diffractogram it can be observed the missing of (211) crystal plane.

The intensities of Fe_3O_4-D peaks are higher indicating the presence of some particles with possible higher diameters due the covering with dextran of magnetite nanoparticles.

The SEM images confirm the nanosize dimension of the analyzed particles.

4.2. Characterization of Fe_3O_4 and Fe_3O_4-D by SEM

Comparing the SEM images of the two compounds, it can be observed that the tendency of agglomeration is higher for Fe_3O_4 nanoparticles in comparison with Fe_3O_4-D nanoparticles.

The formed nanoparticles have oval or spherical shapes. As it can be seen from Figure 4 at 400 000x magnification, the dimension of particles is under 100 nm. Several of them adhere to each other to form conglomerates as seen in Figure 4.

The reason can be the viscosity of the dextran.

The high magnification used for the morphological characterization suggests that analyzed samples have nano- dimension that can be detected with further investigations by transmission electron microscopy.

4.3. Leaching test

The application of leaching test, well-known for environmental application, demonstrates the stability of the compounds in case of their use into different liquid media. Because the final application of these compounds is waste water treatment, the stability was tested under acidic, neutral and basic conditions. The results were monitored after 24 hours and the iron content for samples from each media was detected by atomic absorption spectrometry. The analysis method was validated under SR ISO CEI 17025/2005 requirements. Based on uncertainty estimation, the results presented were value average for 10 samples for each media.

It can be observed that tendency of iron dissolution is higher for acidic conditions in comparison with neutral or basic media. Also, the dissolved quantity of iron is higher in case of Fe_3O_4 (almost 400 mg/g) in comparison with Fe_3O_4-D (almost 150 mg/g), if we refer at acidica conditions (pH 2.5). Almost the same tendency is observed for neutral (pH 6.5) and basic conditions (pH 8.5).

5. Conclusions

Two magnetic nanoparticles (Fe_3O_4 and Fe_3O_4-D) with diameter size lower than 100 nm were synthesized using as methods coprecipitation for Fe_3O_4 and the adding of dextran solution at iron salt solution under basic conditions, followed by dextran precipitation.

The morphology studies confirmed the obtaining of Fe_3O_4 (with γ-Fe_2O_3 as secondary phase) nanoparticles and Fe_3O_4-D nanoparticles with a slightly agglomeration tendency. Also, the orthorhombic crystalline structure for Fe_3O_4 was confirmed.

The stability for these nanomaterials was demonstrated by leaching test application, under different media.

The highest stability was confirmed for Fe_3O_4 nanoparticles covered with dextran (Fe_3O_4-D), especially under basic conditions, at pH 8.5.

The acidic conditions, with pH 2.5, demonstrated a high dissolution tendency, especially for Fe_3O_4.

The results of this work are used for assessment the efficiency of these types of nanomaterials in environmental applications, especially for water treatment when these compounds can be used as adsorbents for toxic metal ions, their use as adsorbents being justified by high surface area and reactivity.

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