

EFFICIENT METHODS FOR NANOMAGNETITE SYNTHESIS

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This paper presents two efficient methods for nanomagnetite obtaining using co-precipitation and precipitation by partial reduction. The synthesis of magnetic nanoparticles has become of great interest for both fundamental and applicative research. The iron magnetic nanoparticles (especially magnetite and maghemite) are considered materials with high adsorption capacity especially because of their large surface area. It is well known the fact that the magnetic properties of the nanoparticles depend on their size and state of aggregation. The goal of this paper is to investigate efficient and cost effective methods in order to obtain monodispersed and coated stabilized nanoparticles.

Keywords: magnetic nanoparticles, synthesis, wastewaters, heavy metals

1. Introduction

Nanotechnology is indicated by the latest literature research as a good method for resolving many of the water quality problems [1]. Among the used techniques for water treatment such as reverse osmosis, ion exchange, nanofiltration, coagulation, adsorption proved to be a superior technique especially because of its efficiency and low costs. Magnetic nanoparticles possess high adsorptive properties and may be used effectively to remove heavy metal ions from wastewaters as vehicles to capture and separate pollutants from wastewaters. By using nanomaterials in the water treatment process, their separation can become a real challenge. In general, nanoparticles are anchored into a solid matrix such as carbon, zeolite or membrane, whose main disadvantage is the manufacturing cost, regeneration and recovery being also a difficult process,

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because the used nanoparticles can subsequently transform into a form of environmental pollution [2]. Therefore, it is necessary to find new adsorbents with high specific surface area and low exploitation costs. Nanoparticles can limit the sludge production by adsorbent regeneration and may allow the development of in situ treatment of contaminated groundwater. The reactivity can be the same per surface specific unit for materials with different specific surface areas. By comparison, the adsorbed quantity on millimoles per gram of the adsorbent is increased when particle size decreases. However, when the adsorbed amount is normalized on the particles surface, it can be noticed that the particles reactivity is the same for the sizes ranging from 300-20 nm, while a significant increase of the 10 nm particle size occurs [3].

In order to obtain magnetic nanoparticles, various techniques such as precipitation, micro-emulsion, hydrolysis, sol-gel are used. One of the oldest and most conventional techniques for nanoparticles synthesis is the precipitation method [4]. In precipitation reactions, metal precursors such as chloride, oxychloride or nitrate dissolved in a common solvent such as water and a base solution such as sodium hydroxide or ammonium hydroxide solution is added to form nanoparticles [5]. The precipitation of metals from aqueous or non-aqueous solutions is generated by the chemical reduction of a metal cation. The precipitation reactions involve the simultaneous occurrence of nucleation, growth and agglomeration processes. The nucleation process is a key step of the precipitation process in that a large number of small particles will be formed.

Based on the literature information, the paper presents two efficient methods for the synthesis of iron oxide nanoparticles based on co-precipitation and partial reduction by precipitation.

2. Materials and methods

For nanomagnetite synthesis, two co-precipitation methods were used, thus: classical method Massart (1981) and the partial reduction method described by Sun et al. [6].

For the co-precipitation method, the used reagents were of Merck type, respectively: iron chloride (III) hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), iron chloride (II) tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and sodium hydroxide (NaOH). D-sorbitol was used as dispersant [7].

Another method for nanomagnetite synthesis was the partial reduction method by co-precipitation. For synthesis, 3 ml FeCl_3 , 10 ml double distilled water and 2 ml Na_2SO_3 were added by drop for 1 minute, under magnetic stirring [8].

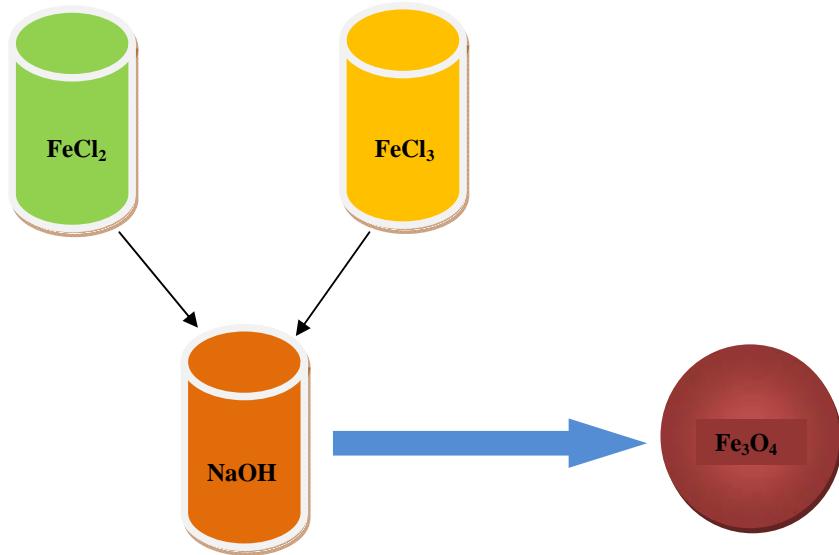


Fig. 1: Synthesis of magnetite nanoparticles

The size and the morphology of the obtained nanoparticles were then investigated by microstructural analysis using XRD (X-Ray diffraction), SEM (scanning electron microscopy) and TEM (transmission electron microscopy).

3. Results and discussions

The nanomagnetite (Magn-1) obtaining using the co-precipitation method took place by blackening of the solution. The resulting suspension was maintained in stirring for 2 hours. After stirring the solution at a high temperature for 2 hours, the stirring was continued for another 30 minutes at room temperature in order to complete the reaction. The Fe_3O_4 precipitate was washed with distilled water and alcohol. It was then dried into oven at 55 °C. For Magn-1 obtaining, the molar ratio 1:2:8 of $\text{FeCl}_3:\text{FeCl}_3:\text{NaOH}$ was used. The reaction temperature was 95 °C, while the final pH was 13. The reaction time was 1 hour, the rotation speed being 900 rpm [7, 10].

An overview of the sample can be observed in fig. 2. The image was obtained at transmission electron microscope (TEM) – Fig. 2(a) and selected area electron diffraction (SAED) – for Fig. 2(b). By indexing of electron diffraction according to the Miller index planes, it can be noticed the presence of magnetite nanoparticles, with an average size of 7 nm.

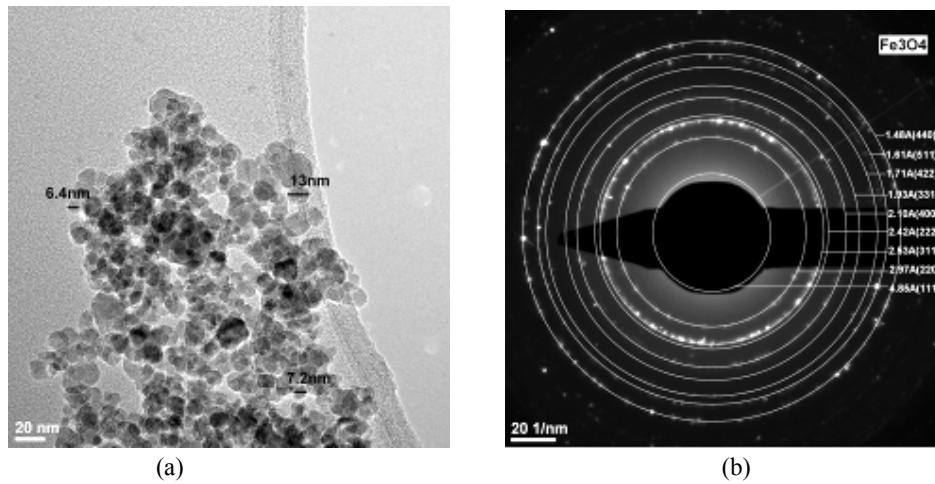


Fig. 2: (a) TEM image for Fe₃O₄ (Magn-1); (b) Electron diffraction (SAED) [9]

The SAED image confirms the crystalline structure of the nanomagnetite. The high resolution transmission electron microscopy (HRTEM) – Fig. 3 showed that the nanoparticles size can reach even 2 nm, which indicates the small sizes of the synthesized compound.

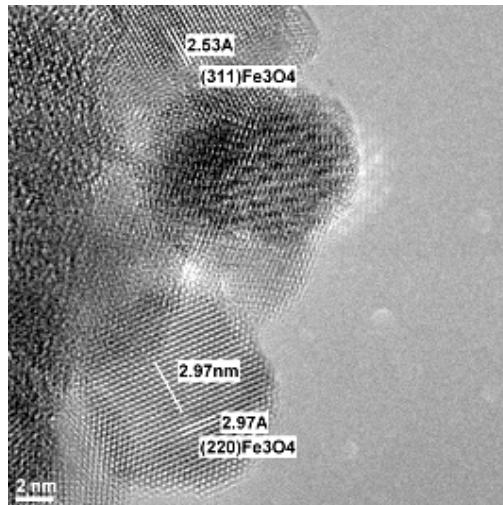


Fig. 3: (HRTEM) image for Fe₃O₄ (Magn-1)

The synthesized particles showed a good dispersion due to the use of D-sorbitol as dispersant. The nanoparticles were also analyzed by X-ray diffraction (XRD), being identified as magnetite compound, as can be noticed in Fig. 4. The

peak intensities characteristic to the magnetite indicate as single phase magnetite, without other compounds or impurities.

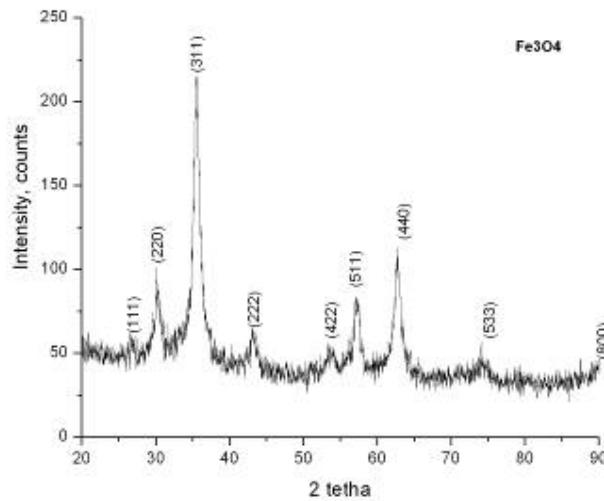


Fig. 4: X-Ray diffractogramm with single phase Fe_3O_4 (Magn-1)

The magnetite nanoparticles obtained by partial reduction by co-precipitation were characterized by transmission electron microscopy and electron diffraction.

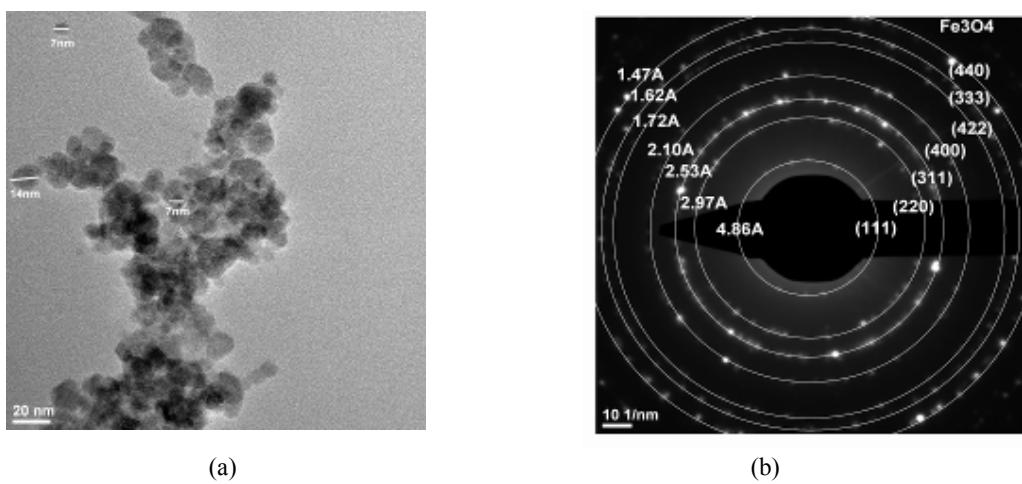


Fig. 5: (a) TEM image for Fe_3O_4 (Magn-2); (b) SAED image associated to (a) image [9]

The TEM image – Fig. 5a indicates average sizes of 7 nm for the obtained nanoparticles and the electron image (SAED) – Fig. 5b confirms the magnetite presence based on the associated Miller index planes.

The energy dispersive spectra (EDS) – Fig. 6 confirms the presence of iron and oxygen elements in the sample, the presence of copper being due to the grid on which the sample was disposed.

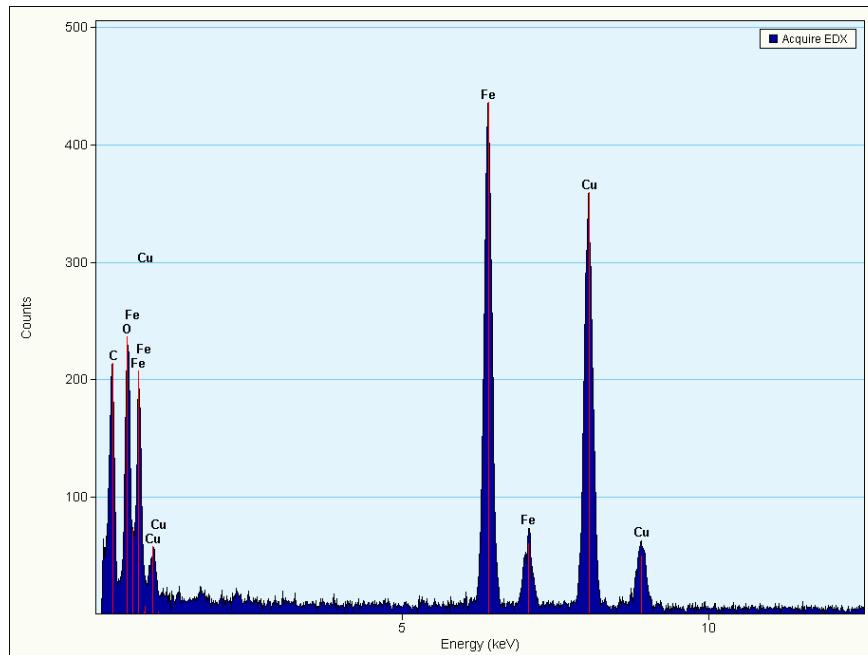


Fig. 6: EDX spectra for Fe_3O_4 (Magn-2) [9]

4 Conclusions

This paper described two methods for nanomagnetite synthesis, thus coprecipitation and partial reduction by co-precipitation. The average size of the obtained nanoparticles was under 10 nm, the samples having a good homogeneity. The control of the size and the poly-dispersion of nanoparticles is critical because the properties of the nanocrystals depend strongly on the dimension of nanoparticles [12, 13]. It was observed that magnetite particles with size of less than 30 nm have a large surface area and exhibit super paramagnetic properties that make them prone to magnetic fields and they do not

become permanently magnetized without an external magnetic field to support them [7].

The development of novel separation processes are based on these kind of size-dependent properties [14]. Since the reactivity increases with the decrease of the particle size, our objective is the controlled synthesis process to obtain particles with dimensions smaller than 30 nm, and thus to increase the removal efficiency. The adsorption capacity of magnetic iron oxide nanoparticles can be proved by their efficiency of removing various pollutants from aqueous solutions.

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