Characterization and Comparison of Magnetite Nanoparticles Prepared by Coprecipitation and Autocombustion Techniques

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Abstract

From the need to produce nanoparticles (NPs) with effective crystallite size that are required for many applications as waste water purification, magnetite nanoparticles (Fe3O4) were prepared by coprecipitation (sample M1) and sol-gel autocombustion (sample M2) techniques. The samples were characterized and M1 and M2 showed close lattice constants (8.35, 8.37Å), and close densities (5.27, 5.23) (g/cm3), respectively. Both samples exhibited nanosized particles, where M1 showed relatively higher average crystallite size (32.09 nm) than M2 (42.2 nm), while M2 showed higher crystallinity. By SEM results M1 showed sphere-like particles of homogenous distribution, while M2 showed agglomerations due to the highly magnetic nature of the sample NPs. Coprecipitation technique produced NPs with possible good ability to adsorb heavy metal ions from aqueous solutions

Keywords*:* Magnetite; Coprecipitation; Sol-gel; Nanoparticles

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1. Introduction

New and cost-effective nanomaterials development for pollution detection, environmental remediation and other applications has attracted much attention. Advanced studies concluded that the solution for many issues including water quality was the use of nanoparticles, nanofiltration or other products resulting from the nanotechnology development [1]. Recently, the investigation of the preparation and application of iron oxides specially of magnetite nanoparticles (NPs) for removal of metals has been widely used owing to their nano size, ease of synthesis, magnetic separation, coating and modification [2]. The development of magnetite NPs synthesis has been intensively achieved not only for its crucial scientific benefit, but also for plenty of technological applications: including magnetic resonance imaging, magnetic targeted drug delivery, ferrofluids for audio speakers, and magnetic recording media [3]. It is interesting to note that only magnetite particles having size near 30 nm have a large surface area and show super paramagnetism that make them affected by magnetic fields and they do not keep magnetism without support of an external magnetic field [17]. These properties are highly valuable in the development of new separation processes [4]. Iron oxide nanoparticles among superparamagnetic nanoparticles, such as magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3, magnetite oxidized form) are by far the most feasible for biomedical applications, because they are proved to be biocompatible to living organisms [5].

The late years have seen the development of nanoscale fabrication techniques in a broad variety to reach the high anticipations related to nanofabrication and nanotechnology. Various methods have been emerged for the magnetic nanoparticles synthesis. These nanofabrication techniques are [6]: co-precipitation, sonochemical processing, flow injection, supercritical fluid techniques, hydrothermal routes, spray pyrolysis, flame spray pyrolysis, sol-gel, etc.

The use of co-precipitation method for the synthesis of magnetite NPs is the most suitable, time-providing, and economic method. This technique offers mass production at higher levels, and is usually used among the rest of other techniques to get particles with uniform sizes [7].

Sol-gel autocombustion technique includes redox reaction of anion of xerogel which is exothermic and self-dependent thermal inducer, achieved from chosen organic complexant as reductant and salts of metal as oxidizer aqueous solutions. The advantages of sol–gel synthesis include its mono dispersity, good control of the particle size, control of the microstructure, desirable shapes and lengths of the products, its high purity, and good crystallinity of the products [8].

2. Methodology

Magnetite (Fe_3O_4) NPs sample prepared by coprecipitation technique will be symbolled by M1, the method includes dissolving 0.12M of $FeSO_4.7H_2O$ in 50 ml of deionized water. KNO_3

solution (KNO_3 is used as an oxidant) 1.01 g dissolved in 10 ml of deionized water added to the $FeSO_4.7H_2O$ solution and stirred for 30 min. KOH solution is used as a base to precipitate the magnetite NPs, is prepared by dissolving 1.402 g of KOH in 10 ml of deionized water was slowly added to the last solution mixture. As the reaction needs, the temperature of the final solution was raised up to 100°C then was left at this temperature for 2 hours. Finally, a black precipitate was obtained (see Fig. 1), then cooled down to room temperature and washed with deionized water for several times and dried overnight at 50°C. Figure (1) shows the prepared magnetite NPs being attracted to a magnet [9]. Figure (2) includes the flow chart of the process.

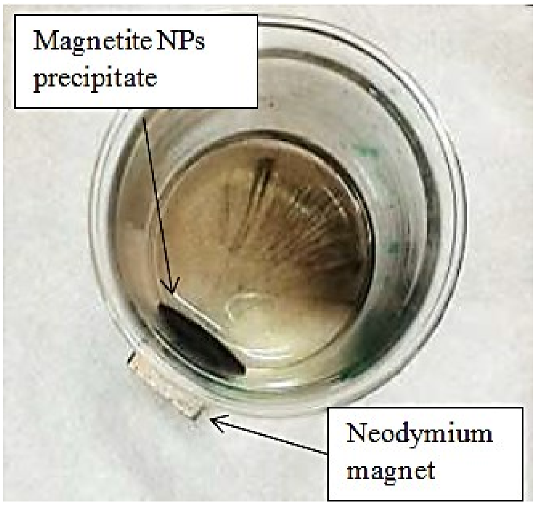


Fig. (1) Fe_3O_4 NPs prepared by coprecipitation method

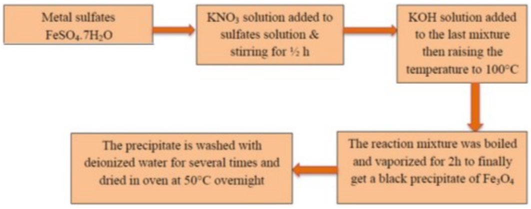


Fig. (2) The flow chart of the coprecipitation technique

This technique was used as illustrated by Al-Saadi et al. [10], using $Fe(NO_3)_2.9H_2O$ with citric acid, taking the ratio 1:1. Firstly, 3M of $Fe(NO_3)_2.9H_2O$ was dissolved in 30 ml of deionized water. 3M of citric acid was also dissolved in 30 ml of deionized water. Then the citric acid solution was slowly added to the nitrates solution. Then, to get a basal solution ammonia (NH_3) was added and the pH test of the solution was maintained until pH=7 is attained. At last, solution temperature was raised to 100°C, to boil and vaporize. The reaction took 1h to complete from the moment of boil, getting an ash-like material with gray color of magnetite NPs (see Fig. 3). The prepared NPs is calcined at 600ºC for 2 hours. to remove the non-desirable impurities. The sample prepared by this method is symbolled by M2. Figure (4) includes the flow chart of this process.

Fig. (3) Magnetite NPs final product prepared by sol-gel auto combustion

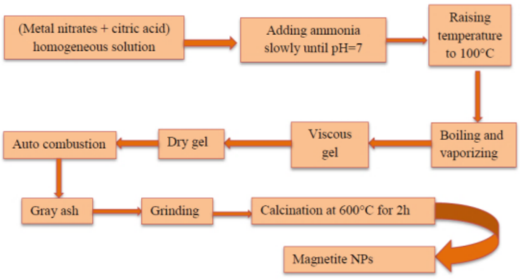


Fig. (4) Flow chart of sol-gel technique

3. Results and Discussion

Figure (5) shows x-ray diffraction patterns of the prepared magnetite NPs samples M1 and M2 prepared by co-precipitation and sol-gel autocombustion methods respectively. The main characteristic peaks were noticed at the diffraction angles, 30°, 35°, 43°, 54°, 57°, and 62° (with few shifting). These angles correspond to the Miller indices of the cubic inverse spinel iron oxide (Fe_3O_4) planes, (220), (311), (400), (422), (511), and (440); that matches the standard pattern JCPDS No. (19-0629) of iron oxide (Fe_3O_4) [10].

Table (1) shows a slight difference in the lattice constant of the two samples, may be attributed to the nanoparticles small size, the existence of strain, and when the composition is varied, these all cause the shifting of the diffraction peaks [11].

The average crystallite size (D_{ave}) was calculated by using Scherrer's equation, by calculating the crystallite size for the six main peaks of each sample then an average was taken. As seen by table (1), D_{ave} of the sample M1 is 32.09 nm where it is 42.2 nm for M2 that makes them effective magnetic nanoparticles in the field of water purification, especially for the sample M1 that has smaller crystallite size. That means coprecipitation technique is more efficient for producing magnetite nanoparticles with small sizes [12].

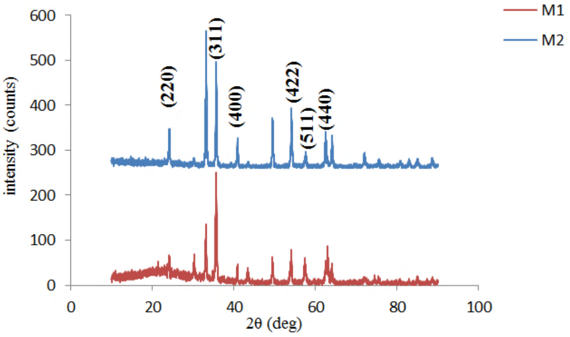


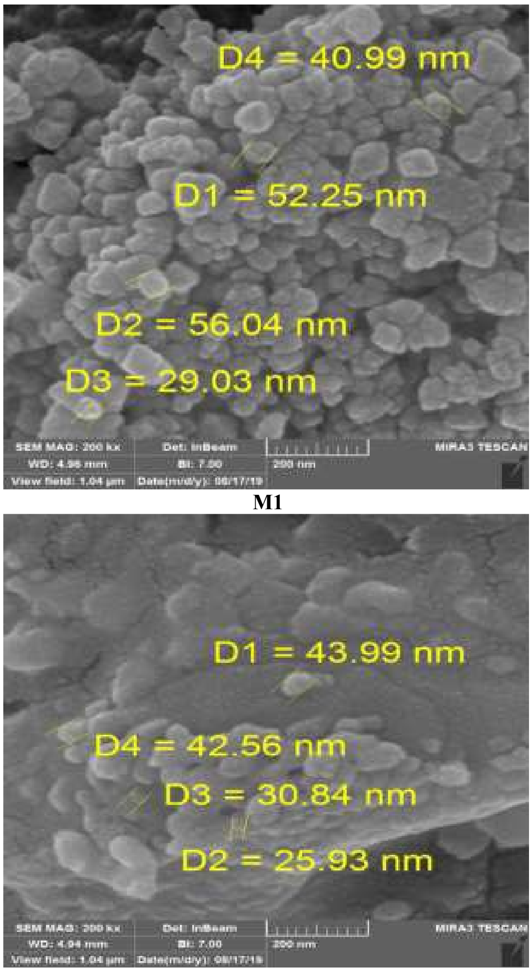
Fig. (5) X-ray diffraction patterns of the samples M1 and M2

In Fig. (3), the x-ray pattern of the sample M1 shows intensities which are not originated to the magnetite phase, whereas preparing a sample by the coprecipitation process can cause that due to multiple factors as forming intermediate phases throughout the reaction, non-equilibrium conditions, and different solubility of the reaction components. This result is expected when using different ions or complex systems [13]. The sample M2 shows higher intensities than of M1, since the method of sol-gel produces higher crystallinity and relatively larger crystallites than by coprecipitation, which returns to this technique reaction nature that is more homogenous and controlled [14], this is compatible with the result calculated using x-ray data showed in table (1). Finally, the samples showing high close densities with small difference due to the difference in the preparation method and so the crystallite structure will be influenced, which is a density of benefit in many applications as dense media separation.

Table (1) Lattice constant, average crystallite size (D_{ave}), and density ρ of the samples M1 and M2

Sample	a (Å)	Dave (nm)	ρ (g/cm³)
M1	8.35	32.09	5.27
M2	8.37	42.2	5.23

SEM images of the prepared samples were represented in Fig. (6). A magnification of 200kx was reached for these images. Using image analysis software, the particle size was measured for some particles included in the image. Both of samples show particles of nanosized; where M1 shows a sphere-like particles with uniform and homogenous distribution that makes it suitable for adsorbing the heavy metal ions from the aqueous medium, while M2 shows high agglomeration. The last result is typical since magnetite NPs prepared by sol-gel technique often display aggregation in SEM images due to their inherent magnetic properties and high surface energy. These characteristics lead to attractive forces between the particles, causing them to clump together and form larger aggregates rather than remaining dispersed [15].



M1

M2

Fig. (6) SEM images of samples M1 and M2

4. Conclusion

Magnetite nanoparticles were successfully prepared by two chemical techniques which are coprecipitation and sol-gel autocombustion. XRD data and SEM image evidenced the nanosized of the prepared samples. By XRD, sol-gel technique produces magnetite NPs with high crystallinity than coprecipitation. By SEM, sol-gel technique produce magnetite NPs with high surface energy and high magnetism than those prepared by coprecipitation. By XRD and SEM results it have been proven that M1 is the suitable choice for the application of water purification.

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