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Characterization and Synthesis of Magnetite Nanoparticles by Innovative Sonochemical Method

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Abstract

Magnetite nanoparticles are of great interest for biomedical applications such as contrast agents in MRI, drug delivery, gene therapy and tissue engineering. In this study, in order to obtain nanoparticles with narrow size distribution and united shape, reverse coprecipitation method was done under ultrasound. Structural analysis was done using XRD and FTIR. The XRD result was analyzed using Scherrer method and formation of spinel structure with $Fd\bar{3}m$ was confirmed. The crystallite size and lattice parameters were calculated 17.7nm and 8.358 Å respectively. FTIR peaks were observed in $\Delta\vee\Delta\text{ cm}^{-1}$ and $\Psi\psi\text{ cm}^{-1}$ wave number and confirms the structure. Magnetic properties of the MNPs was studied using VSM and the saturation magnetization (M_s) and the coercive field of the MNPs is 63.13emu/g and 9.10e respectively which indicates appropriate magnetic properties in biomedical applications. Transmission electron microscope (TEM) was done to observe the morphology of magnetite nanoparticles.

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Keywords: Magnetic nanoparticles; magnetite; sonochemical synthesis.

1. Introduction

During the last decade, the application of nanotechnology to medicine for diagnosis and therapy has emerged as a promising new field, often referred to as nanomedicine. A wide selection of nano-sized constructs has been developed for applications in drug delivery, imaging, and tissue engineering, Kempe et al. (2010). Among the different chemical composition nanomaterials superparamagnetic iron oxide nanoparticles are certainly the most

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promising material for medical applications such as cellular labeling, bio-assay, imaging, as drug carriers and for hyperthermia treatment. First, their tunable core sizes, ranging from a few up to tens of nanometers, allow control of the properties appropriate to the intended application. For example, extremely small sized iron oxide nanoparticles ($d < 4$ nm) can be used as T1 magnetic resonance imaging (MRI) contrast agents, whereas 10 nm iron oxide nanoparticles are more efficient T2 MRI contrast agents, de Montferrand et al. (2013) .

Magnetite nanoparticles can be synthesized using a lot of different methods such as thermal decomposition, microemulsion and coprecipitation. Among all these methods, coprecipitation is an appropriate one using aqueous solutions of Fe^{II} and Fe^{III} . This method does not produce toxic solution or medium, does not need complex precursors and is done in temperatures under $100^{\circ}C$. This method can be used in mass production. All these reasons make coprecipitation method important in industrial scale. However broad size distribution is one of the issues of this method and might be due to complex paths in the formation of magnetite particles, Ahn et al. (2012) .

Magnetite received more attention due to its potential applications in nanobiotechnology such as using both as a tag for sensing and imaging, and as an active agent for antitumor therapy. However, for high performance in biological applications, MNPs should be spherical, biocompatible, superparamagnetic and have narrow size distributions and moderate size, high crystallinity, large surface areas (for maximal protein or enzyme binding), high magnetic saturation to provide maximum signal, and good dispersion in liquid media, Guo et al. (2009). Iron oxide nanoparticles meet these requirements. The advantage they have over other magnetic nanoparticles is that they present low toxicity, since Fe exists in the human body, Filippousi et al. (2013).

By incorporation into standard scaffolds pioneering magnetic scaffolds can be produced. Under an external magnetic field, the magnetic moment of the magnetic scaffolds can be continuously controlled. This allows reloading of the scaffold from an external supervising center with MNPs that can be coupled to bioactive molecules such as tissue GFs facilitating and orchestrating the degree and type of tissue growth, Panseri et al. (2012).

The crystal structure of magnetite (Fe_3O_4) is inverse spinel and the space group is $Fd\bar{3}m$. The general formulation of inverse spinel is $(Y)[XY]O_4$ where in Fe_3O_4 , $X = Fe^{II}$ and $Y = Fe^{III}$ and the brackets and parentheses indicate octahedral and tetrahedral atomic sites respectively. 8 tetrahedral sites are distributed between Fe^{II} and Fe^{III} atoms, Kempe et al. (2010), de Montferrand et al. (2013) .

Magnetite, with an inverse spinel structure, can be synthesized by well-defined processes, such as the thermal decomposition, microemulsion, hydrothermal, and coprecipitation methods. Among the various techniques for magnetite synthesis, the coprecipitation method is a convenient way to synthesize magnetite nanoparticles from an aqueous iron salt ($Fe^{2+} + Fe^{3+}$) solution; a base is simply added under an inert atmosphere at room temperature. The coprecipitation process does not produce or use any toxic intermediates or solvents, does not require precursor complexes, and proceeds at temperatures under $100^{\circ}C$. This process has been recognized for its industrial importance because of its ability to be scaled up, its reproducibility, and its eco-friendly reaction conditions.

However, it yields particles with a broad size distribution, probably because of the complicated sets of pathways that lead to the formation of magnetite, Ahn et al. (2012).

In this study magnetite nanoparticles were synthesized by coprecipitation method under ultrasonic condition to obtain uniform and narrow sized magnetite nanoparticles and overcome the most important issue using coprecipitation method.

2. Experimental

2.1. Synthesis of magnetite nanoparticles

$FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ were dissolved in 60ml of HCl (0.167M). The solution was then added to a 100ml NaOH(1M) dropwise, under mechanical stirring(1000rpm) and in an ultrasonic bath. The black magnetite precipitate was obtained and remained under mechanical stirring and in an ultrasonic bath for 30 minutes. The precipitate was then separated by a permanent magnet and washed with distilled water.

2.2. Characterization

The obtained magnetite nanoparticles were characterized by X-ray diffraction (XRD) (Philips-PW3710) using Co K α radiation ($\lambda = 1.788\text{\AA}$). For Fourier Transform Infrared spectrum (FTIR) (Bruker-Dector33) measurement, the samples were blended with KBr and the wave number range was $400\text{--}4000\text{cm}^{-1}$. The magnetic measurement was carried out using a vibrating sample magnetometer (VSM) (Meghnatis Daghigh Kavir, MDK6). Transmission electron microscope (TEM) (Zeiss - EM 900) was done to observe the morphology of magnetite nanoparticles.

3. Result and discussion

3.1. X-ray diffraction (XRD)

X-ray diffraction (XRD) pattern of the MNPs is shown in Fig. 1.

According to Scherrer, if the crystallites in a powder are sufficiently small, the maxima of diffraction pattern are broadened by an amount inversely proportional to the crystallite size, and measurement of additional broadening thus gives a means of estimating the size through the formula, J. I. and Wilson (1978)

$$\varepsilon = \frac{k\lambda}{b \cos\theta}$$

where ε is the apparent crystallite size, λ is the wavelength of the radiation, b is the additional broadening (in radius), and θ is the Bragg angle, J. I. and Wilson (1978).

The calculated crystallite size using Scherrer formula of the synthesized MNPs is approximately 16nm.

The diffraction peaks were seen at $2\theta = 21^\circ, 35^\circ, 41^\circ, 50^\circ, 63^\circ, 67^\circ, 75^\circ$ which can be indexed to (111), (220), (311), (400), (422), (511), (440). The diffraction peaks confirm the spinel structure of the synthesized MNPs

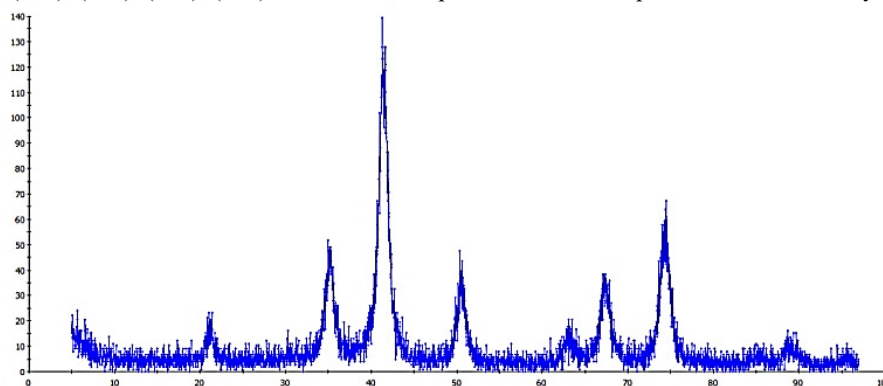


Fig. 1. X-ray diffraction pattern and reitveld refined pattern of MNPs.

3.2. Fourier transform infrared spectrum (FTIR)

Fourier transform infrared spectrum (FTIR) is done to determine the structural characterization of the MNPs. Figure 2 shows the FTIR spectra of the MNPs in wave number range of $400 - 4000\text{cm}^{-1}$. According to Waldron, Waldron (1955) ferrites can be considered as crystals with continuous bonds; i.e. the atoms are bonded together with an equal force (ionic, covalent or van der vaes force). Under 1000cm^{-1} , normally there are 2 peaks in ferrites, which indicate the internal bonds of ferrites. 441 and 557cm^{-1} are related to Fe-O bonds and are attributed to octahedral and tetrahedral sites respectively. The reason of witnessing 2 peaks for one bond (Fe-O) is attributed to the difference in the bond length of the atoms in two different atomic sites. The two peaks confirm the spinel

structure of the MNPs and validate the XRD result. The 3371cm^{-1} peak is attributed to O-H bond and is most likely because of the presence of water.

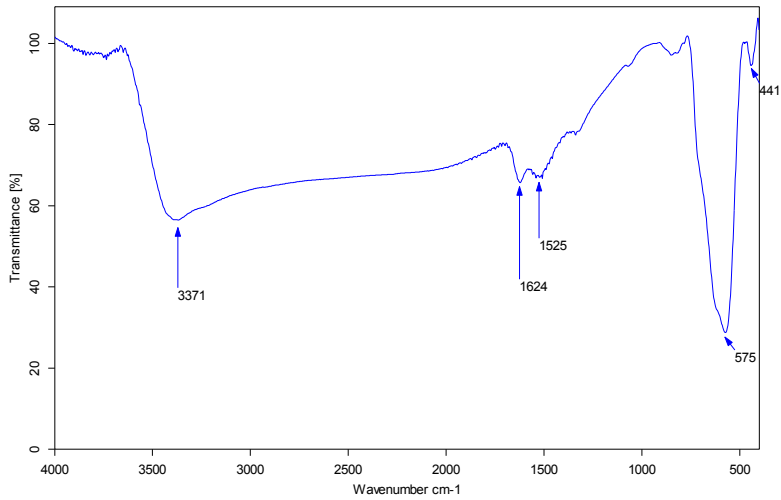


Fig. 2. FTIR spectra of the synthesised MNPs.

3.3. Magnetic characterization

The hysteresis loop of the MNPs is shown in fig. 3, and is done using a vibrating sample magnetometer (VSM). The saturation magnetization (M_s) and the coercive field of the MNPs is 63.13emu/g and 9.10e , indicating high saturation magnetization and superparamagnetic behavior.

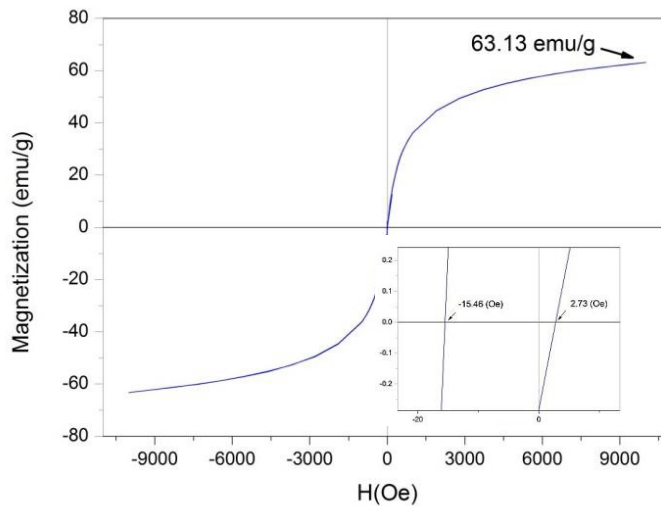


Fig. 3. Magnetic hysteresis loop of synthesized MNPs.

3.4. Transmission electron microscope (TEM)

As indicated in Fig. 4, the particles are spherical and the size of the MNPs is approximately 10-12nm with a narrow size distribution.

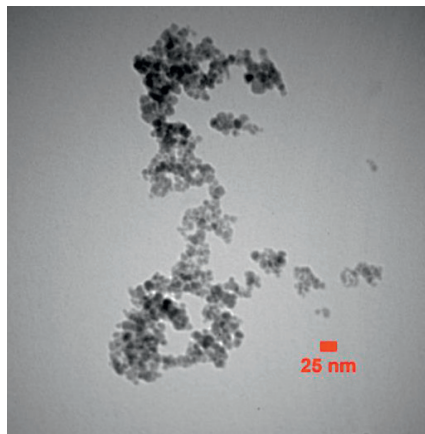


Fig. 4. TEM image of the synthesised magnetite.

4. Conclusion

In this study, MNPs were synthesized by sonochemical coprecipitation method. XRD and FTIR analysis confirmed the formation of spinel structure. Magnetic behavior of the MNPs was studied using VSM and confirmed the superparamagnetic behavior of these MNPs.

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