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A simple way to obtain high saturation magnetization for superparamagnetic iron oxide nanoparticles synthesized in air atmosphere: Optimization by experimental design

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ABSTRACT

Orthogonal design technique was applied to obtain superparamagnetic iron oxide nanoparticles with high saturation magnetization, M_s. Synthesis of the nanoparticles were done in air atmosphere according to the orthogonal table $L_9 3^4$. Magnetic properties of the synthesized nanoparticles were measured by a vibrating sample magnetometer. Structural analysis of the nanoparticles was also carried out by X-ray diffraction technique (XRD), Fourier transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM). After the analysis of magnetic data, the optimized experimental parameters were determined as $[Fe^{+2}]/[Fe^{+3}]=6/6$, iron ion concentration = 1500 mM, base concentration = 6.7 M and reaction time = 2 min. Magnetic results showed that the synthesis carried out according to the optimized conditions gave the highest M_s of 69.83 emu/g for the nanoparticles synthesized in air atmosphere. Magnetic measurements at 10 K and 300 K showed the sample is superparamagnetic at room temperature. Structural analysis by XRD, FTIR and selected area electron diffraction showed that the sample had the inverse spinel crystal structure of iron oxide. The particle size of the optimized sample determined from the TEM image is 7.0 ± 2.2 nm. The results indicated that the M_s of superparamagnetic iron oxide nanoparticles can be optimized by experimental design with the suitable choice of the synthesis parameters.

1. Introduction

Synthesis and characterization of superparamagnetic nanoparticles have been attracted interest in recent years. They have many applications such as, ferrofluid applications [1,2], enzyme immobilization [3,4], magnetic resonance imaging [5,6], targeted drug delivery [7,8] and magnetic hyperthermia [9,10]. Iron oxide is very convenient for biomedical applications due to its high saturation magnetization, superparamagnetic behavior, small size and non-toxic character in human body [11–13]. Iron oxide (Fe_3O_4 or γ-Fe_2O_3) shows higher saturation magnetization than the other ferrites such as $NiFe_2O_4$, $MgFe_2O_4$ [11]. It also shows superparamagnetism under critical particle sizes which is an extraordinary advantage in biotechnological and biomedical applications [12]. Fe_3O_4 nanoparticles are also found to be biocompatible as compared with $ZnFe_2O_4$ and $NiFe_2O_4$ [13].

Co-precipitation is one of the most useful ways to synthesize iron oxide nanoparticles. It is a simple and easy technique with high product yield [14]. Besides, the synthesis parameters such as ion concentration [15,16], base concentration [17] and $[Fe^{+2}]/[Fe^{+3}]$ ratio [18] are very important to obtain iron oxide nanoparticles with desired properties. Synthesis parameters of co-precipitation have a strong effect on the properties of the magnetic nanoparticles. The iron ion effect was studied in [15]. According to this study, crystallinity of the nanoparticles and particle sizes increased as the iron ion concentration in the solution increased. Saturation magnetization and magnetic sizes were also increased with the increase of iron ion concentration. Similarly in the study [16] it is observed that the average size of Fe_3O_4 magnetic nanoparticles increases as concentration increases. According to the [17], there is a critical NaOH concentration to obtain iron oxide nanoparticles. It is concluded in [18] that magnetic properties of iron oxide nanoparticles changed with the change of particle size caused by the change of Fe^{+2}/Fe^{+3} ratio, and this effect reveals the particle size limit between ferrimagnetic and superparamagnetic characteristics of the samples.

To obtain the highest saturation magnetization, it is important to choose the optimum parameters of the co-precipitation of

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Table 1
Input parameters and level settings of co-precipitation of iron-oxide nanoparticles.

Level setting	Input parameters			
	$[Fe^{+2}]/[Fe^{+3}]$ ratio	Total iron ion concentration (mM)*	Base concentration (M)*	Reaction time (min.)
1	1/2	500	4.0	2
2	3/4	1500	5.3	15
3	6/6	2500	6.7	90

* Total solution is 100 ml.

superparamagnetic iron oxide nanoparticles. However, the effect of every single factor on co-precipitation is not enough to decide which parameter is optimum. Therefore, the optimum parameters should be obtained by using orthogonal design [19]. The maximum amount of information can be gained without having to perform the large number of experiments, by following the orthogonal tables [20,21].

In this study, the feasibility of producing co-precipitated superparamagnetic iron oxide nanoparticles with high saturation magnetization, M_s by using orthogonal design was presented. According to the appropriate choice of input parameters and the orthogonal table, the nanoparticles were synthesized and their magnetic and structural characterization was performed. The orthogonal analysis of the magnetic data showed the optimum parameters to co-precipitate the iron oxide nanoparticles with the highest M_s. The highest M_s (69.83 emu/g) for the superparamagnetic iron oxide nanoparticles was obtained by following the optimum recipe. Crystal structure of the optimized sample was investigated by X-ray diffraction (XRD) and selected area electron diffraction techniques (SAED) and found that the sample is iron oxide. The magnetic measurements performed by physical properties measurement system (PPMS) at 10 K and 300 K showed that the optimized sample is superparamagnetic at room temperature. Particle size of the optimized sample from transmission electron (TEM) image is 7.0 ± 2.2 nm.

2. Experimental methods

2.1. Synthesis of the nanoparticles

Iron (II) chloride tetrahydrate (Merck, > 99%), iron (III) chloride hexahydrate (Merck, > 99%) and ammonium hydroxide (Merck, 25% ammonium in water) were used for the synthesis of iron oxide nanoparticles. Base concentration is the concentration of ammonium hydroxide solution after the addition to the iron salts solution. All chemicals were in analytical grade and used without further purification. To obtain iron oxide nanoparticles, base solution was added to the iron salts solution under mechanical stirring (700 rpm) in air atmosphere at 20 °C. After the reaction, the precipitate was washed several times with distilled water and dried in the oven to remove water. To obtain the magnetic fluids

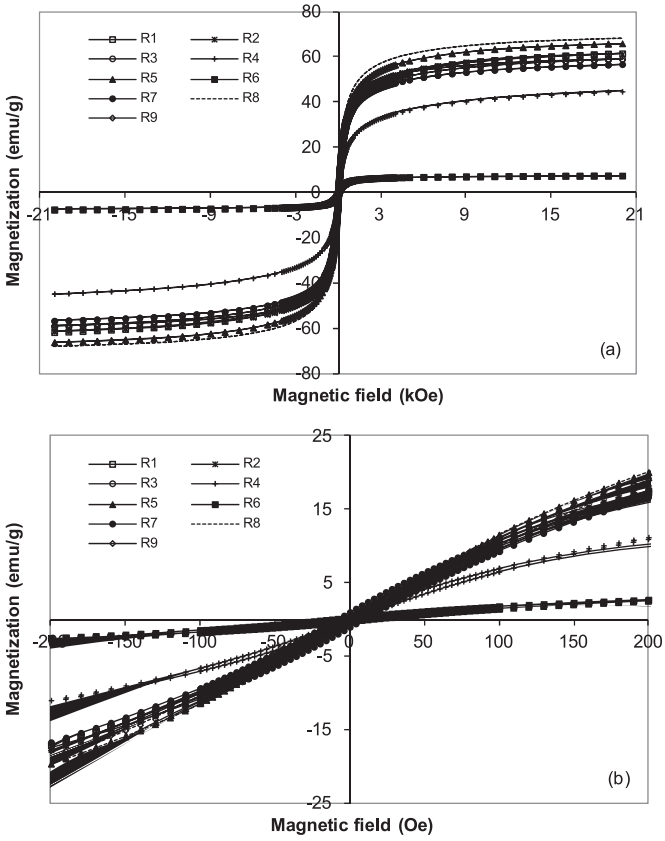

Fig. 1. Magnetization curves of the samples synthesized according to the experimental set-up (a) at ± 20 kOe, (b) at ± 200 Oe.

Table 2
Input parameters and saturation magnetization values of the samples synthesized according to the orthogonal design.

Run	Input parameters				Output function
	$[Fe^{+2}]/[Fe^{+3}]$ ratio	Total iron ion concentration (mM)	Base concentration (M)	Reaction time (min.)	Saturation magnetization (M_s) (emu/g)
R1	(1) 1/2	(1) 500	(1) 4.0	(1) 2	61.64
R2	(1) 1/2	(2) 1500	(2) 5.3	(2) 15	61.29
R3	(1) 1/2	(3) 2500	(3) 6.7	(3) 90	59.21
R4	(2) 3/4	(1) 500	(2) 5.3	(3) 90	44.74
R5	(2) 3/4	(2) 1500	(3) 6.7	(1) 2	66.08
R1′	(1) 1/2	(1) 500	(1) 4.0	(1) 2	56.73
R6	(2) 3/4	(3) 2500	(1) 4.0	(2) 15	7.52
R7	(3) 6/6	(1) 500	(3) 6.7	(2) 15	56.74
R8	(3) 6/6	(2) 1500	(1) 4.0	(3) 90	66.70
R9	(3) 6/6	(3) 2500	(2) 5.3	(1) 2	58.75
R1′′	(1) 1/2	(1) 500	(1) 4.0	(1) 2	58.62