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Synthesis of Pure Magnetite Nanoparticles Using Microwave Hydrothermal and Sonication

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Relatively pure Fe_3O_4 nanoparticles was synthesized by microwave hydrothermal (MWH) and sonication-assisted co-precipitation. The precipitating agent was 0.5 % hexamine in 10 % ammonia solution. This was added to 100 mL of 0.01 M HCl containing stoichiometric amount of stable salt of Fe^{3+} and Fe^{2+} ions. The formaldehyde produced from hydrolysis of hexamine prevents partial oxidation of Fe^{2+} during the precipitation process. For stabilization of colloidal suspension a small amount of a bifunctional fatty acid was used to coat the Fe_3O_4 nanoparticles and make them hydrophobic. The extraction of Fe_3O_4 nanoparticles from aqueous phase into chloroform gave a stable magnetite suspension which was attracted by a magnet. The product was analyzed by XRD, LLS, EDX and quantities chemical analysis of iron content in magnetite. The average diameter of nanoparticles was found to be about 6.2 nm. The order of main factors according to their effectiveness on the yield of product was determined using a factorial design and ANOVA.

Key Words: Magnetite, Nanoparticles, Hexamine, Microwave, Sonication, Factorial design.

INTRODUCTION

The preparation and study of nanometric magnetite has attracted great attention in recent years. Because of the importance of current and future applications, there is a good deal of interest in investing of new synthetic methods, for controlling the particle size and purity of this compound[1-3]. Some of the important applications of magnetite nanoparticles in engineering and technologies are transportation, jet ink printing catalysis, black pigment, sealing of rotating shafts, *etc.*[4,5]. In medicinal application it is possible to attach drugs to the surface of magnetite particles and use magnetic field to transfer the drug at the site needed[6,7]. The magnetite ferrofluid has been used in the separation of some metals from ores based on the density change in this fluid under the application of magnetic field[6].

In this work a relatively pure nanosize Fe_3O_4 powder and its aqueous suspension are prepared using combined microwave and ulterasonication. The formaldehyde produced from hydrolysis of hexamine deoxygenates the reaction medium. A bifunctional organic acid (adipic acid) was used as capping agent to stabilize the magnetite suspension and its function was compared with a monofunctional acid (capric acid) using the experimental design.

EXPERIMENTAL

All chemicals used were of reagent grade obtained from sigma-Aldrich. The equipments used were (i) X-ray diffraction (XRD) shumadzu XD3A, (ii) Atomic absorption spectrophotometer, Philips model Pu 9100, (iii) Laser light scattering (LLS) SEMATECH (230 V, 50 Hz), (iv) Sumsung microwave generator 300 GHz, 900 W, (v) Ultrasonication processor UP 200H (200W, 24 KHz), (vi) Energy Dispersive X-ray (EDX).LEO-144 Vp.

Preparation of samples: The reactor used was a three necked flask equipped with reflux condenser, nitrogen, ultrasonic processor and a digital thermometer. 0.01 mol (3.92 g) ammonium iron(II) sulfate hexahydrate 0.02 mol (6.64 g) ammonium iron(III)-sulphate $NH_4SO_4{\cdot}Fe(SO_4)_3{\cdot}12H_2O$ and 0.002 mol (0.3 g) adipic acid were dissolved in 100 mL 0.01 M HCl. Then the precipitating agent (0.5 %) hexamine in 10 % aqueous ammonia was added to the solution at slow rate.

The solution was irradiated by microwave at 300 GHz for 10 min under reflux with ultrasound stirring (20 KHz). The pH range of precipitation was 2.5-10.5. The balanced equation for the formation of Fe_3O_4 is shown in the following equations.

$$2(CH_2)_6N_4 + 12H_2O \xrightarrow{\text{MWH+Sonication}} 8NH_3 + 12HCHO$$

$$HCHO + \frac{1}{2}O_2 \longrightarrow HCOOH$$

$$2Fe^{3+} + Fe^{2+} + 8NH_3 + 4H_2O \xrightarrow[\text{MWH + Sonication}]{\text{Adipic acid}} Fe_3O_4 + 8NH_4^+$$

To extract the product into organic phase 100 mL chloroform was added to the flask and the sonication continued for 1 min. The chloroform phase containing the dispersed magnetite particles was separated using a separating funnel.

Product recovery: In the recommended procedure after completion of reaction, the solvent was removed by a rotary evaporator. To collect the product particles a strong magnet was located underneath of the flask. The product was washed several times with water and alcohol filterd and dried in an electric oven (120 ºC). The small amount of dried precipitate (0.5 g)

was dissolved in aqua regia after appropriate dilution. The iron content was determined by atomic absorption spectrometry.

RESULTS AND DISCUSSION

Several methods have been reported for the preparation of magnetite nanoparticles without the report of yield[8-10]. In this work the value of yield was found by chemical analysis to be 97.4 %[11,12]. The possible oxidation of Fe^{2+} during the reaction time is prevented by the generation of formaldehyde from hexamine which acts as oxygen scavenger in the reaction medium. The specific gravity of the chloroform suspension was measured with a picnometer and was found to be 2.12 g/cm^3 at room temperature.

Fig. 1 represents the X-ray diffraction pattern for the prepared magnetite. All peaks positions are consistent with the standard data for Fe_3O_4 according to JCPDS card file No. 3-863. The per cent of iron in magnetite was found by duplicate measurements (using AAS) to be 72.05 % (theoretical value is 72.35 %), *i.e.* the prepared sample has high purity. To identify the elemental composition of purified product its EDX spectrum was recorded (Fig. 3). The result indicates that there is no appreciable impurity in the synthesized magnetite. The average particle size determined from XRD spectrum by Scherrer's equation to be 6.1 nm.

$$t = (0.9\ \lambda)/(B \cos \theta_B)$$

In this equation, t is the average particle diameter in Å, λ is the wavelength of the X-ray radiation in Å, θ_B is the peak width at the maximum peak intensity in radian.

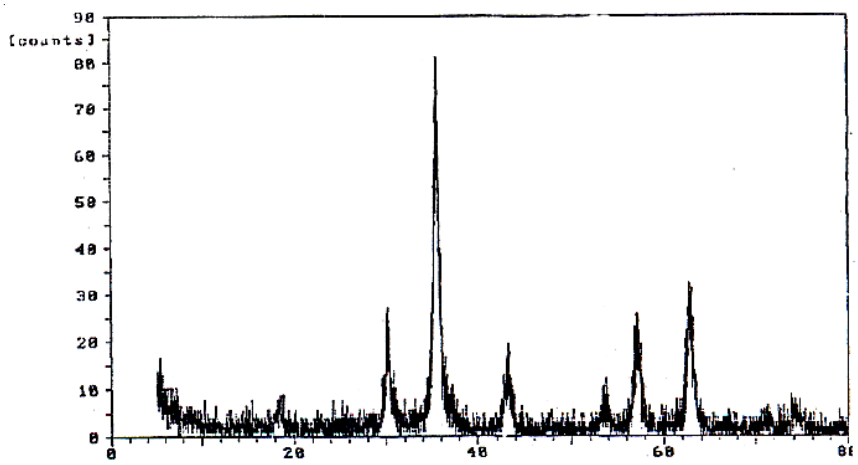

Fig. 1. X-Ray diffraction pattern of synthesized Fe_3O_4

Fig. 2 shows the size distribution of nanoparticles of magnetite sample obtained by LLS method. The magnetite nanoparticles have diameters ranging between 1.5-11.5 nm. The mean diameter of particles was obtained from size distribution curve using RTG correlator software to be 6.3 nm (the result calculated from XRD curve is 6.1 nm. The mean of these results is 6.2 nm which considered as the average particle size). To study the effects of three main factors: A (time), B (Type of capping agent) and C (reaction temperature) on the yield of nanosize magnetite an experimental design was arranged for three factors at two levels (high level and low level) (Table-1). The factor effects were determined according to the 23 factorial design (Table-1).

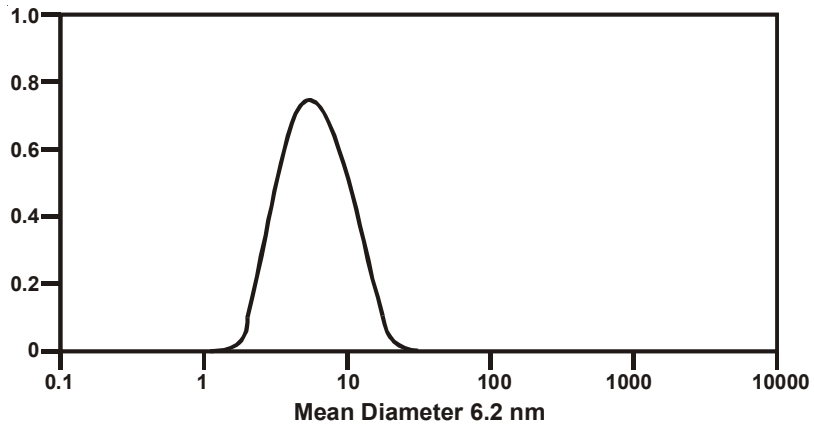

Fig. 2. LLS particle distribution of magnetite

TABLE-1
PLUS AND MINUS SIGNS FOR THE 2^3 DESIGN

Treatment combination	A	B	AB	C	AC	BC	ABC
(1)	-	-	+	-	+	+	-
a	+	-	-	-	-	+	+
b	-	+	-	-	+	-	+
c	+	+	+	-	-	-	-
ab	-	-	+	+	-	-	+
ac	+	-	-	+	+	-	-
bc	-	+	-	+	-	+	-
abc	+	+	+	+	+	+	+

The estimation of factors effect and their interactions are given in Table-3. The main effects B and C are significant, the AB interaction is insignificant, the effects of A, AC, BC and ABC are low. The empirical model relating the response to A, B and C is:

$$R = b_o + b_aA^* + b_bB^* + b_cC^* + b_{ab}A^*B^* + b_{ac}A^*C^* + b_{abc}A^*B^*C^* \quad (4)$$

The constants of empirical models are:

$b_o = 73.86$; $b_a = 1.54$; $b_b = 10.06$; $b_c = 6.69$; $b_{ab} = 0.038$; $b_{ac} = 1.71$; $b_{bc} = 1.84$; $b_{abc} = 1.66$.

The coded empirical model is:

$$R = 73.86 + 1.54A^* + 10.06B^* + 6.69C^* + 0.038A^*B^* + 1.71A^*C^* + 1.84B^*C^* + 1.66A^*B^*C^*$$

TABLE-2
EXPERIMENTAL DESIGN DATA

Run	Treatment combination	Time of MWH and sonication (min)	Type of capping	Temperature (ºC)	Yield (%)
		A	B	C	
1	(1)	5	Capric	90	57.5
2	a	10	Capric	90	60.4
3	b	5	Adipic	90	77.2
4	ab	10	Adipic	90	73.6
5	c	5	Capric	100	67.1
6	ac	10	Capric	100	70.2
7	bc	5	Adipic	100	87.5
8	abc	10	Adipic	100	97.4

TABLE-3
EFFECT OF FACTORS

Factors and possible interactions	A	B	C	AB	AC	BC	ABC
Effect	1.54	10.06	6.69	0.038	1.71	1.84	1.66

To control the magnitude of effects the analysis of variance for the factor effects was performed (Table-4). The results confirm that B and C are the main factors. The graphical design is given in Fig. 4. Analysis of data in (Fig. 5a and b) shows that increasing A factor causes increase in yield of product.

From ANOVA table it can be concluded that AB interaction is not significant. AC, BC, ABC interactions and factor A have moderate effect on the yield of process. Results are in agreement with the values calculated for factor effects.

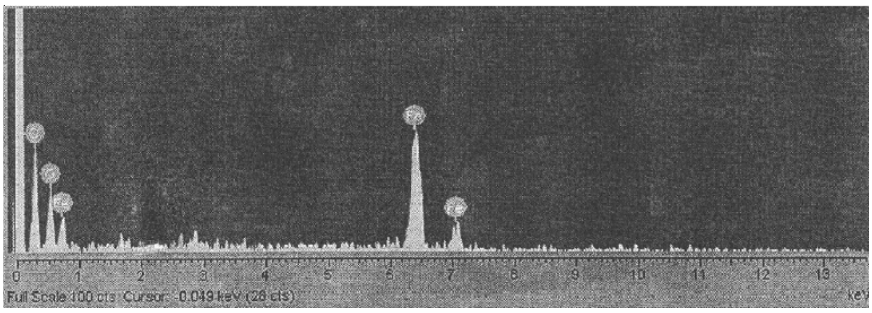

Fig. 3. EDX Spectrum of synthesized magnetite

TABLE-4
ANALYSIS OF VARIANCE (ANOVA)

Source of variance	Sum of squares	Degree of freedom	Mean square
Model	1259.320	7	179.810
A-Time of MWH and sonication	18.910	1	18.910
B-Type of capping	810.030	1	810.030
C-Temperature	357.780	1	357.780
AB	0.011	1	0.011
AC	23.460	1	23.460
BC	27.010	1	27.010
ABC	22.110	1	22.110
Pure Error	0.000	0	–
Cor Total	1259.320	7	–

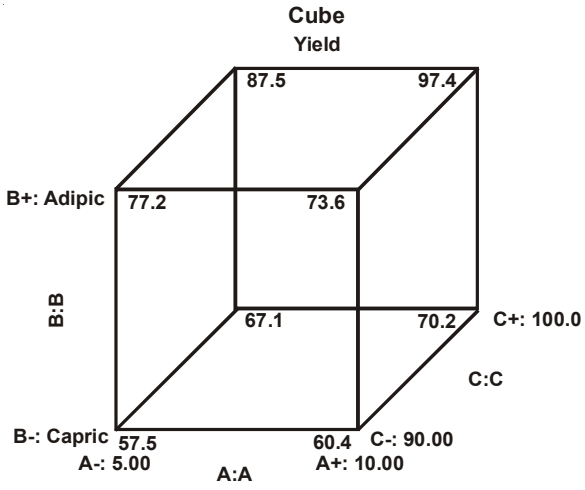

Fig. 4. The graphical 2^3 design for Table-2

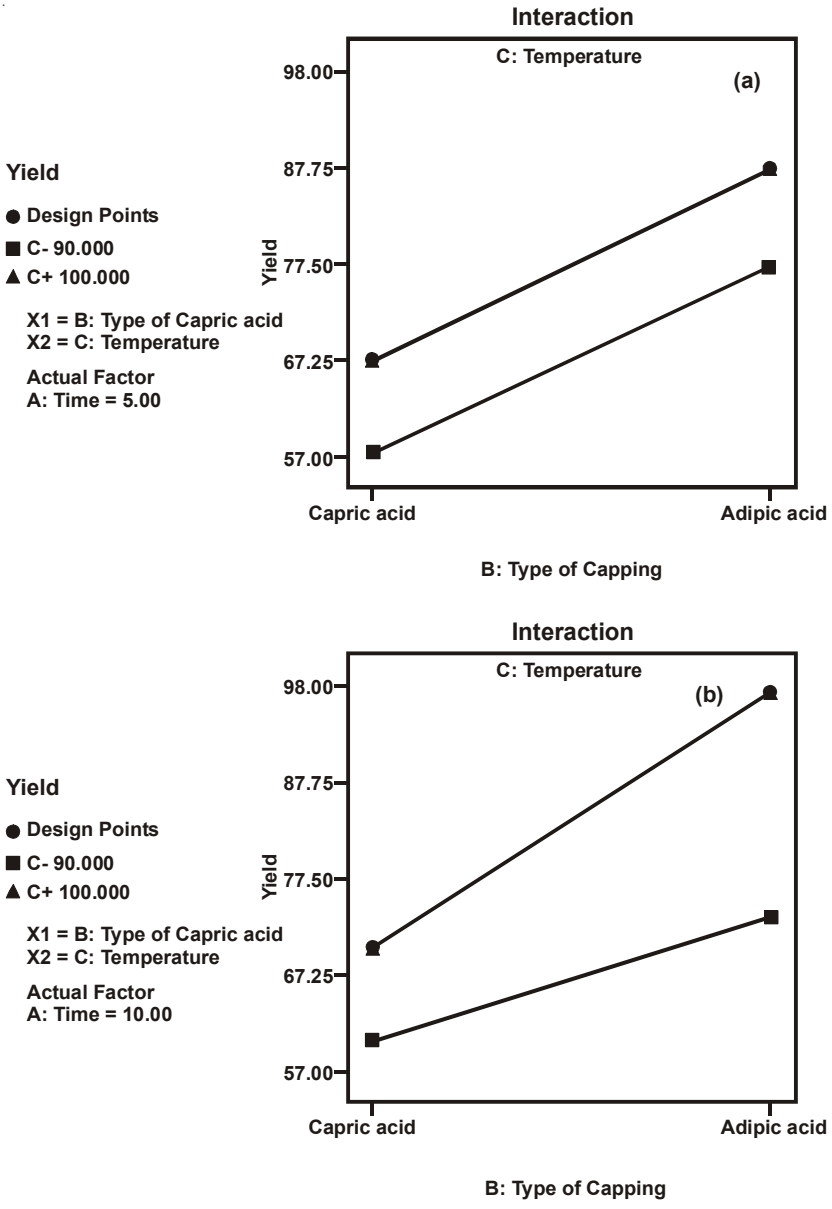

Fig. 5. Yield (BC) interaction graph

Fig.6 is the three dimensional response surface plots for the yield as function of A and C factors based on empirical model. It is clear that the yield increases as the time and temperature increase.

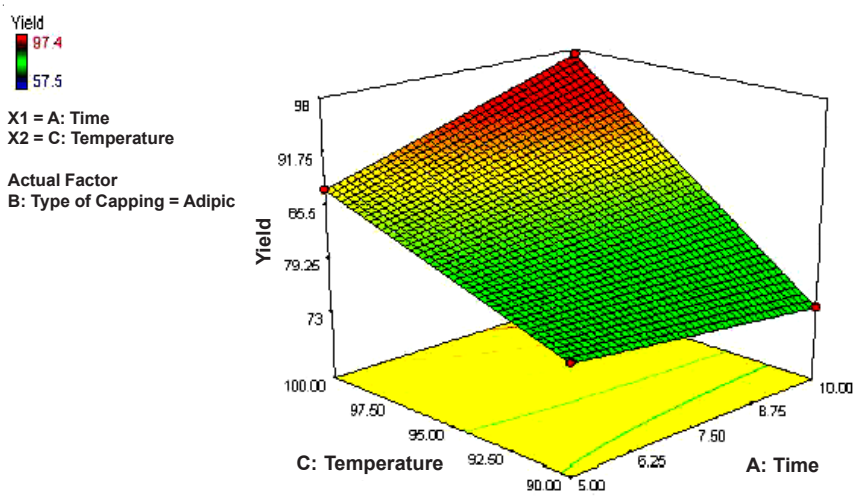

Fig. 6. Surface of magnetite yield response

The optimum condition and the highest response belong to row eight of Table-2. The conformational tests for the yield of reaction according to optimum condition had the mean of 97.2 ± 0.3 %.

Conclusion

In this work the problem of impurity of magnetite produced by partial oxidation of iron(II)[13-15] was avoided by using stable salts of Fe^{2+} and Fe^{3+} ions and generation of an oxygen scavenger during coprecipitation process. In comparison with monofunctional fatty acids used in previous works[15,16]. Bifunctional adipic acid can produce more attachment to the surface of magnetite particles giving letter capping ability.

The aqueous and organic suspensions and high purty powder of nanoparticle magnetite were prepared from stoichiometric ratio of Fe^{2+} and Fe^{3+} in the presence of small amounts of hexamine and adipic acid. The iron hydroxides were precipitated by using 0.5 % hexamine in 10 % ammonia solution. The HCHO produced by the hydrolysis of hexamine acts as oxygen scavenger and prevents Fe^{2+} from partial oxidation. The product particles have a narrow distribution with the mean diameter of about 6.2 nm which is smaller than (36 and 14 nm) reported recently[15,16]. The yield is high (97.4 %). The order of main effective factors[17] on the yield of reaction is B > C > A.

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