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Response surface strategy in the synthesis of Fe_3O_4 nanoparticles

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ABSTRACT

In the present study, Fe_3O_4 super paramagnetic nanoparticles were synthesized via co-precipitation of Fe^{3+} and Fe^{2+} chloride salts in the presence of ammonia Solution. The product was characterized by Fourier Transform Infrared spectroscopy (FT-IR), Transmission Electron Microscopy (TEM), and zeta–potential particle size distributing methods. The synthetic procedure of nano iron oxides were optimized using modern statistical optimization methods. A major bottleneck of common optimization protocols is the variation of just one factor at each trial. In modern optimization protocols (experimental design) a combination of factor levels is considered. In the present study, response surface method (RSM) was applied to optimize the synthetic approach towards Fe_3O_4 nanoparticles. Results indicated the importance of acidity and ferric ion amount in achieving desired Fe_3O_4 nanoparticles.

Keywords: *Synthesis; Nanoparticle; Fe_3O_4; Optimization; Experimental design.*

INTRODUCTION

Super-paramagnetic iron oxide (Magnetite; Fe_3O_4) nanoparticles have achieved much attention due to their distinctive properties and potential benefits in biomedical applications [1-3]. Ferrofluid is a form of Fe_3O_4 nanoparticles finding especial usage in many areas [4]. A colloidal suspension including appropriately coated magnetite particles in a liquid medium is called a ferrofluid. Ferrofluid possesses unique properties owing to the concurrent mechanic and magnetic effects [5].

Prominent synthesis routs towards Fe_3O_4 nanoparticles are as follows: co-precipitation [6, 7], thermal decomposition [8, 9], micro-emulsion [10], hydrothermal synthesis [11] and continuous flow technique [12]. The thing which is important is that the size and magnetic properties of obtained nanoparticles highly depend on the synthesis procedure [13, 14].

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In this regard, systematic optimization of the effective variables on the preparation of Fe_3O_4 nanoparticles may be regarded as an important strategy. This may lead to tiny particles possessing interesting characteristics.

Nowadays, optimization techniques are of significant importance for industrial planning, resource allocation, scheduling, laboratory processes, and etc. Classic optimizations can be done by varying any of the process parameters and keeping the other parameters constant. When multiple variables are involved, it becomes difficult to study the system using the common approach of varying only one factor at a time while holding the others constant. The new statistical designs consider all factors simultaneously and hence provide the possibility for evaluation of all the effects at once. Modern experimental designs have been regarded as the most favorable techniques in covering a wide area of practical statistics and obtain unambiguous results with the least expense.
Response surface method (RSM) designs help us in quantifying the relationships between one or more measured responses and the vital input factors [15]. They include a category of statistical methods for model building and exploitation. Box-Behnken design is an efficient and creative three-level composite design for fitting second-order response surfaces. It is an independent quadratic design in that it does not contain an embedded factorial or fractional factorial design. The methodology is based on the construction of balance designs which are rotatable and enable each factor level to be tested several times. For getting more details, readers are referred to previous publications on the field [15].

In continuation to our study on Fe_3O_4 nanoparticles [16], we decided to synthesize Fe_3O_4 nanoparticles and optimize the effect of various experimental factors on the size of obtained nanoparticles.

EXPERIMENTAL

Chemicals and instruments

Ferric chloride hexahydrate, ferrous chloride tetrahydrate and ammonium hydroxide (%25) were all purchased from Merck chemical company. Ultra-pure nitrogen gas (%99.99) was used to provide anaerobic condition in solution. Distilled deionized water was used to prepare all the solutions.

FT-IR spectra were recorded on a Nicolet FT-IR Magna 550 spectrophotometer. TEM images were captured by Philips apparatus while particle sizes were obtained using Horiba (Japan) particle size analyzer.

Preparation of magnetite nanoparticles

Super paramagnetic iron oxide (Fe_3O_4) nanoparticles were prepared by the co-precipitation of ferric and ferrous chloride in an anaerobic condition at room temperature. For this purpose, desired amounts of $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ were dissolved in 60 and 30 ml of distilled deionized water, respectively (formerly purged with 99.99% nitrogen gas). Two solutions were mixed with each other and subjected to N_2 purging for 15 min. In the next step, 4 ml ammonia was mixed with 6 ml of deionized water (formerly purged with N_2) and added drop by drop to the solution containing ferric and ferrous ions. The reaction was proceeded under vigorous stiration and purging of N_2 gas. Purging of N_2 was continued for another 15 min after completion of the reaction.

Fe_3O_4 nanoparticles were separated using a super magnet while rinsed with deoxygenated deionized water. The characterization of Nano Fe_3O_4 particles was performed via TEM (Figure 1a), FTIR (Figure 1b) and particle size analyzer (Figure 2).

Experimental design

All statistical analysis, modeling and numerical optimization was performed using Design-Expert software-v.7 (State-Ease, Corp., Minnesota). Box-Behnken design was used as an optimization method in our synthetic procedure.

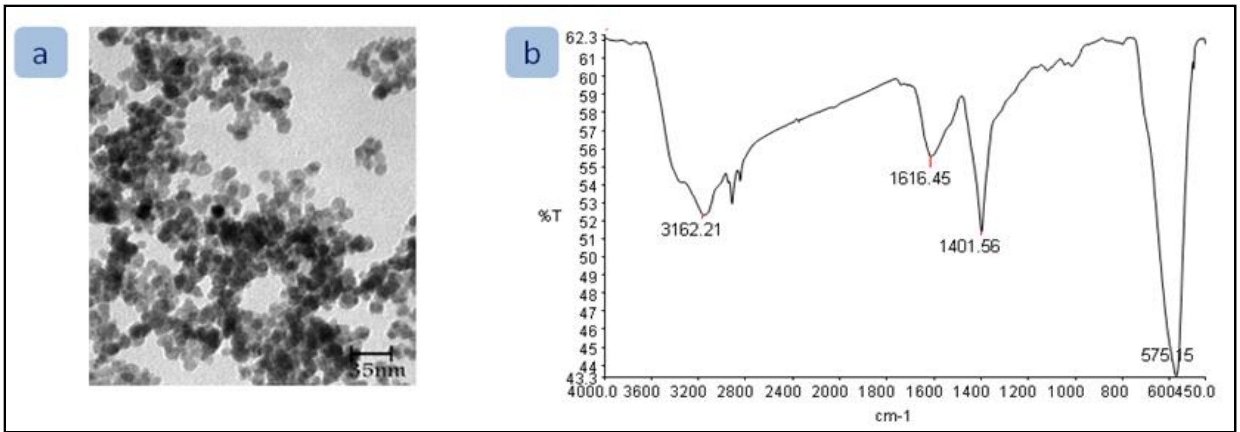
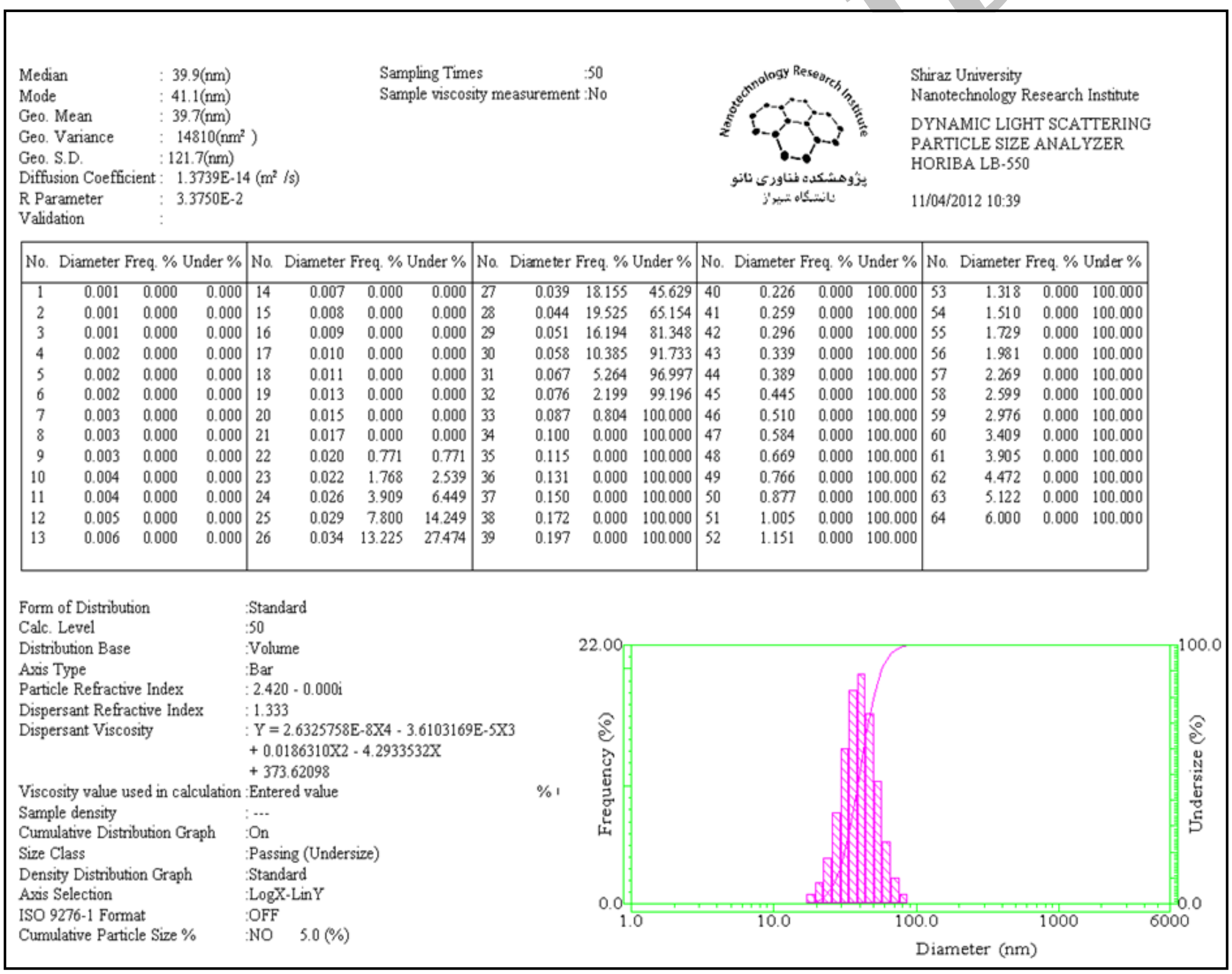


Fig. 1. Characterization of prepared nano-Fe_3O_4 nano particles by a) TEM and b) FTIR



Median : 39.9(nm)
Mode : 41.1(nm)
Geo. Mean : 39.7(nm)
Geo. Variance : 14810(nm²)
Geo. S.D. : 121.7(nm)
Diffusion Coefficient : 1.3739E-14 (m²/s)
R Parameter : 3.3750E-2
Validation :

Sampling Times :50
Sample viscosity measurement :No

Shiraz University
Nanotechnology Research Institute
DYNAMIC LIGHT SCATTERING
PARTICLE SIZE ANALYZER
HORIBA LB-550

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No.	Diameter	Freq. %	Under %	No.	Diameter	Freq. %	Under %	No.	Diameter	Freq. %	Under %	No.	Diameter	Freq. %	Under %	No.	Diameter	Freq. %	Under %
1	0.001	0.000	0.000	14	0.007	0.000	0.000	27	0.039	18.155	45.629	40	0.226	0.000	100.000	53	1.318	0.000	100.000
2	0.001	0.000	0.000	15	0.008	0.000	0.000	28	0.044	19.525	65.154	41	0.259	0.000	100.000	54	1.510	0.000	100.000
3	0.001	0.000	0.000	16	0.009	0.000	0.000	29	0.051	16.194	81.348	42	0.296	0.000	100.000	55	1.729	0.000	100.000
4	0.002	0.000	0.000	17	0.010	0.000	0.000	30	0.058	10.385	91.733	43	0.339	0.000	100.000	56	1.981	0.000	100.000
5	0.002	0.000	0.000	18	0.011	0.000	0.000	31	0.067	5.264	96.997	44	0.389	0.000	100.000	57	2.269	0.000	100.000
6	0.002	0.000	0.000	19	0.013	0.000	0.000	32	0.076	2.199	99.196	45	0.445	0.000	100.000	58	2.599	0.000	100.000
7	0.003	0.000	0.000	20	0.015	0.000	0.000	33	0.087	0.804	100.000	46	0.510	0.000	100.000	59	2.976	0.000	100.000
8	0.003	0.000	0.000	21	0.017	0.000	0.000	34	0.100	0.000	100.000	47	0.584	0.000	100.000	60	3.409	0.000	100.000
9	0.003	0.000	0.000	22	0.020	0.771	0.771	35	0.115	0.000	100.000	48	0.669	0.000	100.000	61	3.905	0.000	100.000
10	0.004	0.000	0.000	23	0.022	1.768	2.539	36	0.131	0.000	100.000	49	0.766	0.000	100.000	62	4.472	0.000	100.000
11	0.004	0.000	0.000	24	0.026	3.909	6.449	37	0.150	0.000	100.000	50	0.877	0.000	100.000	63	5.122	0.000	100.000
12	0.005	0.000	0.000	25	0.029	7.800	14.249	38	0.172	0.000	100.000	51	1.005	0.000	100.000	64	6.000	0.000	100.000
13	0.006	0.000	0.000	26	0.034	13.225	27.474	39	0.197	0.000	100.000	52	1.151	0.000	100.000				

Form of Distribution :Standard
Calc. Level :50
Distribution Base :Volume
Axis Type :Bar
Particle Refractive Index : 2.420 - 0.000i
Dispersant Refractive Index : 1.333
Dispersant Viscosity : Y = 2.6325758E-8X4 - 3.6103169E-5X3 + 0.0186310X2 - 4.2933532X + 373.62098
Viscosity value used in calculation :Entered value
Sample density : ---
Cumulative Distribution Graph :On
Size Class :Passing (Undersize)
Density Distribution Graph :Standard
Axis Selection :LogX-LinY
ISO 9276-1 Format :OFF
Cumulative Particle Size % :NO 5.0 (%)

Fig. 2. Characterization of prepared nano-Fe_3O_4 nano particles by particle size analyzing method

RESULTS AND DISCUSSION

In order to run the systematic optimization method, five experimental factors were chosen. Stirration rate (rpm), Solvent type (NH_3:H_2O), pH, ferric ion amount and ferrous ion amount were the designated factors each evaluated under three distinct levels (Table 1).

Table 1. Levels of experimental factors used for synthesis of Fe_3O_4 super paramagnetic nanoparticles

Factors	Low level (-1)	Medium level (0)	High level (+1)
Fe(II) (g) (A)	0.5	1.00	1.62
Fe(III) (g) (B)	0.1	0.3	0.6
pH (C)	2.25	3	4
Solvent (NH_3:H_2O) (D)	4:6	6:4	8:2
Stirration rate (rpm) (E)	500	1000	2000

Experimental factors were selected as they were considered to have the most significant effect on the efficiency of the method. Factor levels were chosen on the basis of previous experimental trials. The factors along with their assigned levels were defined as input data for Box-Behnken method in DOE program.

To construct a model that can capture interactions between design variables, a Box-Behnken design matrix was planned to investigate all possible combinations of factors. In our design strategy, Box-Behnken matrix contained 46 solutions (Table 2). It should be noted that Fe_3O_4 particle size (nm) was considered as response in each run.

Box-Behnken design provided fewer runs while similar 3-level full factorial design for five factors included 243 experiments. A comparison between these two statistical methods reveals the Box-Behnken method to be more economic, efficient and time fluent [17]. With the Box-Behnken design methodology, major and interaction effects can be easily evaluated. The factor effect refers to the effect caused by the varied factor, while the interaction effect is related to the case in which the effect of one factor is dependent on the value of another [18]. Analysis of variance (ANOVA) was applied to realize the significant factors in the regression model. Analysis of variance for response surface quadratic model is shown in Table 3.

On the basis of obtained results, the effect of different factors on the size of produced Fe_3O_4 particles can be depicted as follows: pH > Fe(III) > Solvent > Fe (II) > rpm. P-values less than 0.05 indicated that the effect of the factor on response is determinant. In our experimental condition, acidity of the solution is the most determinant factor.

In contrast, P-values more than 0.1 indicated that the factor may not have any significant effect on response. Owing to the ANOVA results and with the aim of qualification, model reduction was performed via removal of two factors, i.e. stiration rate and Fe (II) amount.

Classification and ANOVA of selected factors

Considering the obtained sizes of Fe_3O_4 particles (Table 2), a combination of factor levels leading to the particles with less than 200 nm diameters were selected and applied in the modeling process. In this step, a statistical design was done by RSM technique and three important factors, namely pH, Fe(III) amount and solvent type (Table 4) were considered. The related ANOVA is summarized in Table 5.

F-value of 4.49 showed that the model was significant for applied data. The estimated F-value could be related to noise with the only probability of 3.97%. The lack of fit parameter of the proposed model was found to be 0.33 which indicated its insignificance when compared to pure error. The proposed model in this method is linear:

$$\textit{Particle diameter} = +127.12 - 91.30A + 1.48B + 36.46AB \quad (R^2=0.727)$$

Table 2. Box-Behnken design with actual and coded factor levels in synthetic approach to Fe_3O_4 nanoparticles

Run	Fe(II) (g)	Fe(III) (g)	pH (C)	Solvent (NH_3:H_2O) (D)	Stirration rate (rpm) (E)	Size of Fe_3O_4 particles
1	0	0	-1	-1	0	151.8
2	0	0	0	1	1	98.3
3	0	1	1	0	0	107.5
4	-1	0	-1	1	0	754.1
5	1	0	0	0	0	631.9
6	-1	0	0	0	-1	837.4
7	0	0	0	0	-1	2207.6
8	-1	-1	0	-1	0	160.8
9	0	0	0	1	0	5541.1
10	-1	-1	0	0	0	1380.6
11	0	1	0	1	0	5540.7
12	1	0	1	0	0	5540.4
13	0	-1	0	1	0	3121.6
14	1	1	0	1	-1	2390.6
15	0	0	1	0	-1	2579.4
16	0	0	0	0	0	1422.3
17	-1	0	1	0	0	5212.2
18	0	-1	0	-1	0	3701.0
19	0	-1	0	-1	1	3122.7
20	1	1	0	0	1	5541.4
21	0	0	0	0	-1	5539.0
22	0	1	0	0	-1	5541.1
23	1	0	0	1	0	5540.5
24	0	1	0	0	0	4788.8
25	0	1	0	-1	1	718.4
26	0	0	1	0	1	5539.2
27	-1	0	0	-1	0	5540.6
28	0	-1	0	0	0	5490.9
29	-1	0	0	0	0	5254.7
30	0	0	-1	0	-1	1245.6
31	0	0	-1	0	0	5528.8
32	0	-1	-1	0	1	2275.2
33	0	-1	1	1	0	1428.0
34	1	0	0	0	0	1421.4
35	0	0	-1	-1	0	2078.6
36	0	0	1	0	0	2490.2
37	0	0	1	0	0	2432.4
38	0	-1	0	0	0	5468.7
39	1	0	-1	1	0	861.4
40	-1	0	0	0	1	5539.5
41	0	0	-1	-1	0	113.9
42	0	0	-1	0	1	172.4
43	1	0	0	-1	0	131.2
44	0	1	-1	0	0	104.6
45	0	0	-1	-1	0	145.9
46	0	0	0	-1	-1	112.6

Table 3. ANOVA for RSM quadratic model in synthesis of Fe_3O_4 nanoparticles

Source	Sum of Squares	Degrees of freedom (DF)	Mean Square	F Value	p-value Prob > F
A	0.022	1	0.022	1.35	0.2720
B	0.034	1	0.034	4.01	0.0319
C	0.073	1	0.073	9.15	0.0048
D	0.016	1	0.016	2.05	0.1618
E	8.775E-003	1	8.775E-003	0.55	0.5839

Table 4. A combination of experiments for the optimizing the synthesis of Fe_3O_4 nanoparticles

Run	Fe(III) Amount (g)	pH	Solvent type	Particle size (nm)
1	0	-1	-1	151.8
2	0	0	1	98.3
3	1	1	0	107.5
4	0	0	-1	160.8
5	0	0	0	113.9
6	0	-1	0	172.4
7	0	0	-1	131.2
8	1	1	0	104.6
9	0	0	0	145.9
10	0	0	-1	112.6
11	1	-1	0	37.0
12	1	1	0	40.0

Table 5. ANOVA Table of factor effect estimation in prepared Fe_3O_4 nanoparticles

Source	Sum of squares	DF	Mean square	F value	Probe>F P-value
Model	12626.77	3	4208.99	4.49	0.0397 / significant
Fe(III) (A)	8335.69	1	8335.69	8.90	0.0175
pH (B)	8.70	1	8.70	9.289E-003	0.9256
AB	1450.05	1	1450.05	1.55	0.2487
Residual	7495.05	8	936.88		
Lack of fit	1238.26	3	412.75	0.33	0.8049 / not significant
Pure error	6256.79	5	1251.36		
Cor total	20121.83	11			

The above equation is represented in terms of coded factor levels (-1, 0, +1). Following points may be extracted from the obtained model:

The model offers relatively good predictability (R^2=0.727). The plot of predicted *vs* actual size of Fe_3O_4 particles is shown in Figure 3.

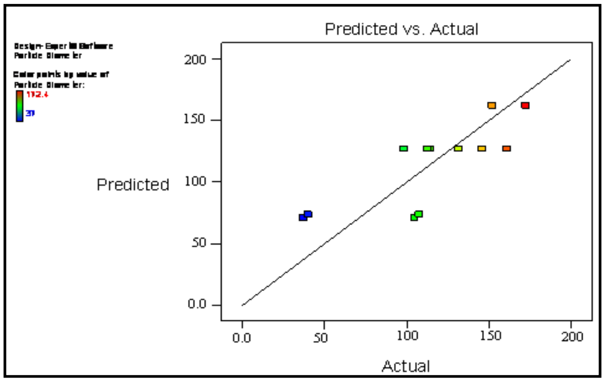

Fig. 3. The predictability of RSM linear model in Fe_3O_4 nanoparticle size

Factor A (amount of Fe^{3+}) possessed the highest coefficient in the obtained model (highest effect on response). This showed that the control of Fe^{3+} amount should be done with care in order to achieve desired Fe_3O_4 nanoparticles.

The interaction between factor A (amount of Fe^{3+}) and B (pH) was significant. This factor interference demonstrated that prediction of response with only considering the dependent variation of each factor would be meaningless. Factor B (pH) had an inverse effect on the size of Fe_3O_4 nanoparticles (Figure 4), therefore decrease in acidity of the medium might reduce nano particle sizes.

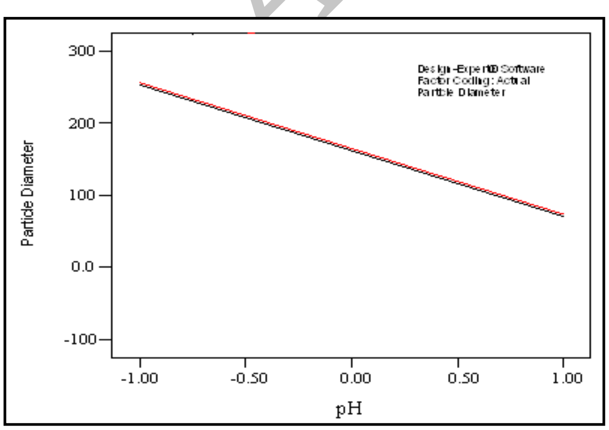

Fig. 4. Effect of pH on the size of Fe_3O_4 nanoparticles

Factor A (amount of Fe^{3+}) had a direct effect on response (Figure 5). This showed that with the increase in amount of Fe^{3+} from 0.1 to 0.6 g, a decrease in the size of nano particles would be expected.

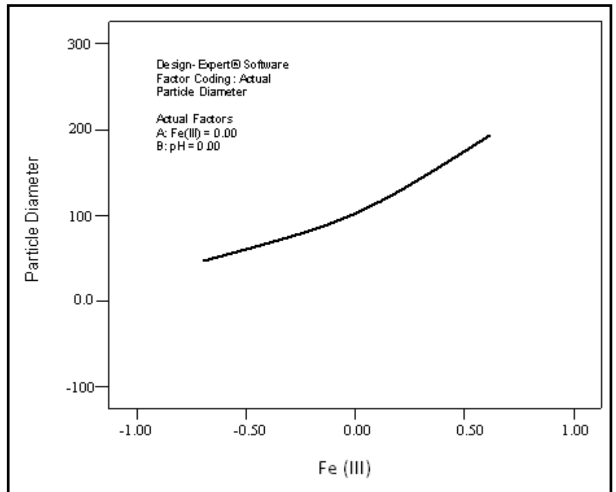

Fig. 5. Effect of Fe^{3+} amount on the size of Fe_3O_4 nanoparticles

The effect of different factors and their interactions could also be depicted via contour diagrams (Figure 6). The effect of important factors in the medium level of factor D (solvent type) is depicted in the following diagram.

As could be easily understood from the diagram contours, size of Fe_3O_4 nanoparticles was more sensitive to the variation of Fe^{3+} amounts. In the above diagram, curved lines known as contours represented a points in which the size of Fe_3O_4 nanoparticles were unvaried.

Another thing to be noticed is that for achieving tiny Fe_3O_4 nanoparticles (50nm >), 0.6 g of Fe^{3+} in acidic media with the solvent ratio of 6:4 / NH_3:H_2O might be the best solution.

We have also shown factor effects on the size of Fe_3O_4 nanoparticles using three dimensional (3D) response surface diagrams (Figure 7). In this case, the whole points of the response represent a surface known as response surface. Z-axis indicated size of Fe_3O_4 nanoparticles (response) while X and Y-axis were indicative of factor A and B, respectively.

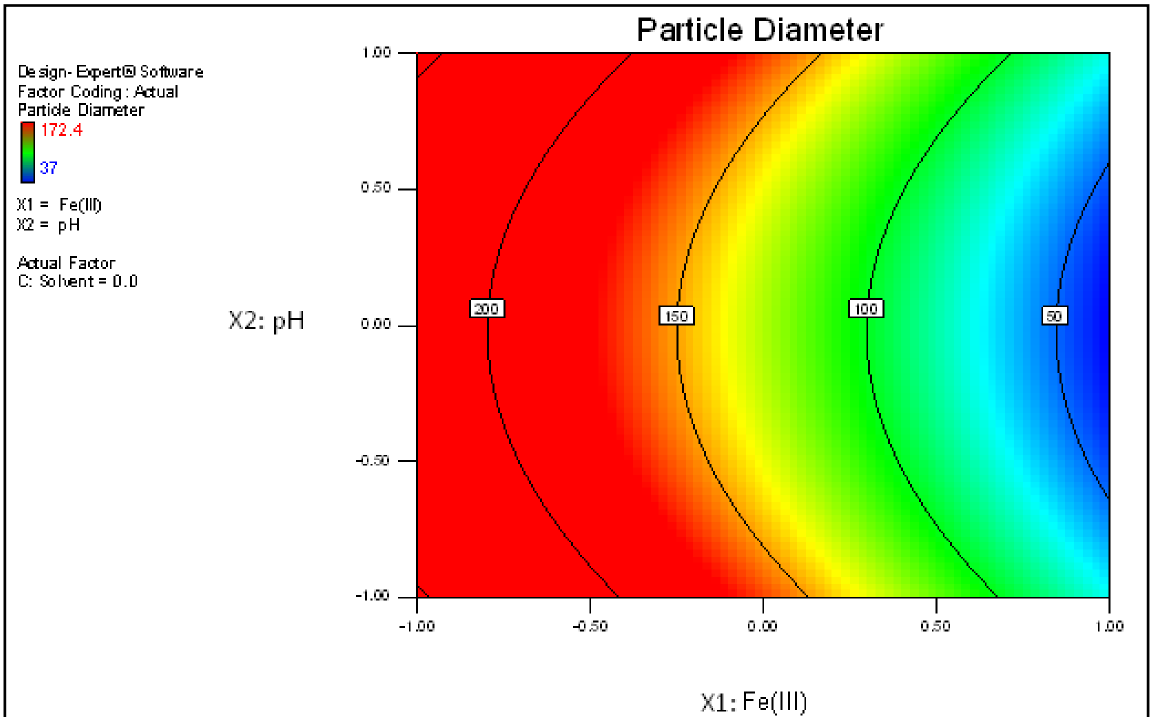

Fig. 6. Contour diagram of the pH and Fe^{3+} amount effects on the particle size of Fe_3O_4 (Solvent type has been adjusted in its medium level; 6:4 / NH_3:H_2O)

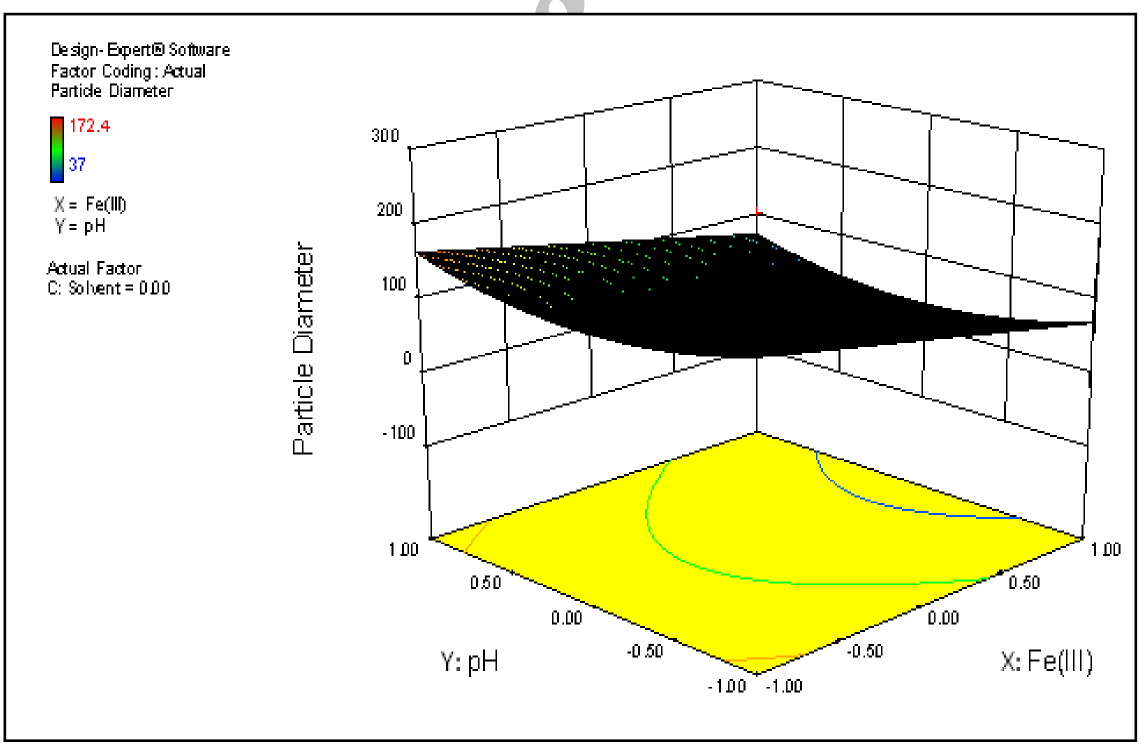

Fig. 7. 3D response plot of Fe^{3+} and pH effects on the size of Fe_3O_4 nanoparticles

In the above 3D response surface plot, minima points referred to optimized conditions (smaller Fe_3O_4 particles). The optimum solution of experimental factors may be found via imaging the points onto the abscissa.

CONCLUSIONS

When multiple factors are involved in a typical synthetic technique, common optimization of the system (varying only one factor and maintaining other variables at constant level) might not determine the real order of factor effects on response. Moreover; combined interaction effects would not be identified. Such optimization protocols would be time consuming and non-economic. In the present study, Box-Behnken method could be successfully applied to optimize a synthetic approach into Fe_3O_4 super magnetic nanoparticles while considering all of the evaluated variables and their interactions simultaneously. The optimized condition revealed that the Fe^{3+} amount and pH were the critical factors which should be controlled carefully in order to obtain desired Fe_3O_4 nanoparticles.

ACKNOWLEDGMENTS

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