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Optimisation of saturation magnetisation of iron nanoparticles synthesized by hydrogen reduction: Taguchi technique, response surface method, and multiple linear and quadratic regression analyses

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ABSTRACT

In this study, Taguchi method, response surface methodology and regression analyses have been applied to assess the effects of synthesis parameters on saturation magnetisation, M_s of iron nanoparticles produced by hydrogen reduction of iron oxide nanoparticles. The M_s values were obtained from the magnetisation loops measured by a vibrating sample magnetometer. Structural characterisations of the selected samples were done by X-ray diffraction technique and transmission electron microscopy. Orthogonal array L9 with three parameters (temperature, reaction time and H_2 flow rate) at three levels (low, medium and high) was used to obtain the experimental trials. Based on the signal to noise (S/N) ratio considering the condition larger is the better approach and the mean response, the highest M_s condition has been found when the temperature is 800 °C m/min, reaction time is 60 min and H_2 flow rate is 1000 ml/min. Analysis of Variance (ANOVA) is applied to find out the F-ratio and percentage contribution of each parameter by using experimental trials and S/N ratios. It was found that the temperature was the most significant parameter on the M_s of iron nanoparticles. A confirmation experiment has been carried out by using the experimental conditions obtained from Taguchi method. The M_s of the optimum sample was found to be 217.42 emu/g which was within 95% confidence level with the predicted optimal M_s of 214.03 emu/g. The quality losses for M_s obtained at the highest combinations were 70.7%. In addition, analyses of multiple linear and quadratic regressions were employed to derive the predictive equations of the M_s achieved via experimental design. The predicted values from the developed models and experimental values are found to be very close to each other justifying the significance of the models. Besides, the quadratic interactive regression model provided the best statistical performance with high R^2 and R^2(adj) values of 100 and 100%, respectively between the experimental and predicted values of M_s. More intensive predicted values were obtained by the quadratic regression models as compared to the multiple linear regression models. Taguchi prediction method was also very successful in the optimization of synthesis parameters for the highest M_s of nanoparticles within the prescribed limit.

1. Introduction

Zero-valent α-Fe nano/microparticles are very useful due to their high adsorption and recovery capabilities [1], and they can be used in environmental remediation [2,3]. The investigations of iron particles obtained by hydrogen reduction attract interest because of the simple, useful and direct synthesis of iron. There are many studies on the reduction of iron oxide [4–6]. In [4], the effect of reduction temperature on the reduction process, specific surface area and physicochemical properties of the product was studied. In [5], a mathematical model was used to simulate the dynamic motion and progress of the reduction of magnetite particles from ore concentrate. In the study of Zhong Ma et al. [6], kinetics of sintering in the reduction and the effects of temperature and time of the reduction process of Fe_2O_3 powder were investigated. In all studies mentioned, commercially available Fe_2O_3 or ore material were used in the reduction process as precursor and only the effects of the synthesis parameters were investigated. In our study, superparamagnetic iron oxide nanoparticles with high saturation magnetisation were used as precursor [7], and the optimization process as well as regression analyses were applied to obtain high saturation magnetisation and estimated saturation magnetisation values for iron particles, respectively.

It is important to obtain the iron particles with desired properties; hence optimization of the process is eligible to find out the effects of the

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parameters on the reduction process, and to obtain particles with optimum properties. Taguchi design is a useful method in many areas to optimize the desired properties/outputs. Therefore, Taguchi method is used in many studies [8–14]. Our study presents the very first optimization of iron particles obtained by reduction of iron oxide nanoparticles under hydrogen atmosphere to our knowledge.

The purpose of this paper is to assess the effects of reduction parameters on the saturation magnetisation, M_s of the iron nanoparticles produced by hydrogen reduction. Taguchi's L9 parameter design was used to identify the highest M_s value with a particular combination of synthesis parameters. For the determination of optimal synthesis conditions (temperature, reaction time and H_2 flow rate) for the highest M_s value, Taguchi's signal-to-noise (S/N) ratio and the main response were used. A statistical Analysis of Variance (ANOVA) was also performed to see which parameters were significant. The optimal combination of process parameters were predicted by using S/N ratio, main response and also ANOVA analysis. Response surface method was applied to see the significance and interactions of the parameters. The results of the method verify the effects of the each parameter on M_s value without performing the experimental studies. Linear and quadratic regression analyses were also applied to predict the measured value of M_s. For both regressions, the equations of the M_s were generated based on the parameters (parameter regression models) and also the parameters together with their interactions (interactive parameter regression models). Finally, the reliability of developed models was tested by the confirmation experiment.

2. Experimental procedure

2.1. Synthesis and measurement techniques

Iron nanoparticles were obtained by the hydrogen reduction of superparamagnetic iron oxide nanoparticles described in [7]. Nabertherm electrical heated furnace was used for the reduction. H_2 flow rate was controlled by Agilent flowmeter. Mass of the precursor (superparamagnetic iron oxide nanoparticles) was fixed at 2.00 g. Temperature, reaction time and H_2 flow rate were selected as synthesis parameters. The synthesis conditions for each reduction experiment were decided according to the system limits and orthogonal array L9 as described in Section 2.3. Reduction was performed at desired temperatures and reaction times with certain H_2 flow rates. For safety reasons and creation of an inert atmosphere, nitrogen, N_2, was flowed in the furnace prior to the reduction process.

Magnetisation values of the samples were measured by using vibrating sample magnetometer (VSM, ADE Technologies EV9) at room temperature. A magnetic field between −20 kOe and +20 kOe was applied with 1 Oe intervals. The crystal structure of the particles was investigated with Phillips PANalytical's X'Pert PRO X-ray diffractometer (XRD) system. Samples were scanned with Cu K_α radiation (λ = 1.54 Å) between 20° and 80°. High resolution transmission electron microscope (HRTEM, FEI TECNAI G2 F30 model) was also used for the observation of the particles. Particle sizes were measured by using ImageJ. Selected areas of electron diffraction (SAED) patterns were also obtained.

2.2. The Taguchi design of experiments and the selection of independent parameters and orthogonal array

The Taguchi method is a simple and reliable procedure which is used to optimize process parameters by decreasing the variation time [15–18]. The arrays of Taguchi design were so designed that the number of experiments were very low compared to classical design approach. Quality loss can be approximated by Taguchi's loss function, which unites the financial loss with the function specification through a quadratic relationship [19]. The Taguchi method uses the loss function to calculate the deviation between the experimental values and the desired values. This loss function was further transferred into a (S/N) ratio (ŋ) and in other words converts the data to the S/N ratio [20]. (For further information, see Supplementary Information.) The goal of this research was to maximise the M_s thus the larger-the-better quality characteristic (Eq. (4) in Supplementary Information) was used.

Table 1
Synthesis parameters and their level settings.

Independent parameters	Parameter designation	Level 1	Level 2	Level 3
Temperature (°C)	A	300	550	800
Reaction time (min)	B	15	60	120
H_2 flow rate (ml/min)	C	125	500	1000

Compared to traditional experimental designs, the Taguchi method makes use of a special design of Orthogonal Arrays (OA) to examine the quality characteristics through a minimal number of experiments [21–23]. In the synthesis process, the effects of control parameters on the M_s values of iron nanoparticles were first investigated using the Taguchi method. Temperature, reaction time and H_2 flow rate were selected as synthesis parameters (individual parameters) with three different levels (low, medium and high) and shown in Table 1. The levels of control parameters were selected from previous experimental trials [24,25]. The first step of the Taguchi method is to select an appropriate OA for the selected parameters. The Taguchi L9 standard orthogonal array with 8°-of-freedom (DOF) was selected in this study as shown in Table 2. The parameters used for the selected OA are assigned to each column and nine combinations (9 from 3 × 3 × 3 = 27 possible combinations) of parameters were generated. The M_s values of the samples obtained from experimental design for each combination of the independent parameters were measured. Determination of the quality characteristics of the measured individual parameters are provided by the S/N ratios and the main response characteristics.

2.3. ANOVA method

ANOVA is a statistical method which is to investigate whether the effects of the experimental design parameters are significant or not [15,26]. In this study, ANOVA was used to analyse the effects of temperature, reaction time and H_2 flow rate on the M_s values of iron particles. The F ratio and the percentage contribution of the parameters for experimental trials and S/N ratios are calculated and then compared to determine the significance of each parameter with the degree of influence on the process performance.

2.4. Response surface method

Interactions of independent parameters cannot be specified using Taguchi experimental design. For this reason, response surface method was also employed to determine the interactions of the parameters. Response surface method is a mathematical model formation method which is dependent on the relation between the independent parameters (individual variables) and the dependent variable (response) [27-29]. The model is based on the examination of the response surface

Table 2
L9 standard orthogonal array.

Experimental no.	Parameter A	Parameter B	Parameter C
1	1	1	1
2	1	2	2
3	1	3	3
4	2	2	3
5	2	3	1
6	2	1	2
7	3	3	2
8	3	1	3
9	3	2	1

which is obtained from the design matrix results. These are created depending on the parameters between the highest and the lowest levels of the parameters as temperature, reaction time and H_2 flow rate. And, the significance of the each parameter on the response was obtained. In the formation of the experimental design; a Face-Central Composite Design technique was used.

2.5. Regression analysis

Regression analysis is used for the modelling and analysing of several variables where there is relationship between a dependent parameter and one or more independent parameters [30]. The predictive equations were made for multiple linear and quadratic regression models. In this study, the dependent variable is M_s whereas the independent variables are A: temperature, B: reaction time and C: H_2 flow rate. For multiple linear regression models, two types of first order analysis of the responses contain all process parameters, and the parameters and their interactions, separately. Therefore, two response equations can be obtained for M_s. For quadratic models, the first analysis of the responses obtained with the response surface method contains all process parameters with second order analysis. And also, the second analysis of the responses obtained with the response surface method contains all process parameters, which include second order analysis, and parameter interactions. Depending on the significance of the parameters, the quadratic models of the response equations can be obtained for M_s.

3. Results and discussion

3.1. Magnetic and structural characterization of the samples obtained by orthogonal array experiments

Fig. 1 presents the magnetisation loops of the samples obtained from the hydrogen reduction according to the reduction conditions of L9 orthogonal array in Table 2. And, the saturation magnetisation values obtained from the loops were given in Table 3. Structural characterisations of the selected sample were done by XRD and TEM analysis. The XRD pattern of the selected sample was given in Fig. 2. In the pattern of the sample 9, (1 1 0) and (2 0 0) peaks of α-Fe can be seen according to the JCPDS card no. 06-0696. This means that a complete reduction is obtained for sample 9. The TEM image and SAED pattern of the sample 9 are given in Fig. 3a and b, respectively. In the image, sintered iron particle which is approximately 190 nm can be seen. In the SAED pattern, (1 1 0) and (2 0 0) peaks of α-Fe are observed confirming the XRD analysis results.

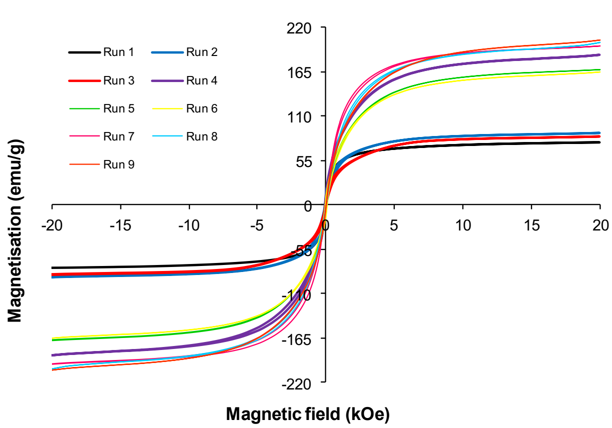

Fig. 1. Magnetization curves of the samples obtained from the orthogonal array experiments (Run 1-Run 9).

3.2. Analysis of the S/N ratio and the main response characteristics

The M_s value was obtained from hysteresis loops of the iron nanoparticles, using the same operating condition. Conventionally, data from design of experiments were used to study the main objective function. The S/N ratios were also calculated using the condition as larger-is-the better for each of the nine experimental combinations which are reported in Table 3. From the table, initial experimental highest recipe was A3B2C1. And, the Ms_{ini} was 204.40 emu/g and its S/N ratio was 46.21 dB. Also, the $\underline{Y}_{Ms}$-total mean value of the M_s is calculated as 152.51 emu/g and the $Y_{Ms-S/N}$-total mean of S/N ratio of M_s is 43.09 dB.

As the experimental design was orthogonal, the effects of independent parameters were separated out in terms of the S/N ratio as well as the mean response characteristics. The highest levels of the S/N ratio means and the mean response of the M_s values at all parameters and levels are given in Table 4 and Table 5, respectively and highest experimental conditions as depicted in bold with "*". In tables, the Δ is the difference between the maximum and the minimum value of each level settings. The highest S/N ratio specified for each parameter provides the best experimental result, namely the experimental result of the lowest M_s value error. Also, the highest mean value of each parameters supply the best experimental finding. The average S/N ratios corresponding to each level of independent parameters for M_s values are given in Fig. 4. In the figure, the levels corresponding to the highest S/N ratio values were chosen for each parameter. The optimum conditions to reach the maximisation of M_s value was found out to be as follows: the highest level for parameter A, Temperature (800 °C), the medium level for parameter B, Reaction time (60 min) and the highest level for parameter C, H_2 flow rate (1000 ml/min). In addition to the S/N analysis, main effects of the process parameters on the mean response were also analysed. The mean response referred to the average value of quality characteristics for each parameter at different levels. Thus the average values of the M_s for each parameter at three levels had been calculated and plotted in Fig. 5. The figure also indicates the same optimum experimental conditions as obtained in S/N ratio analysis.

3.3. Analysis of ANOVA results

ANOVA method was used to analyse the independent parameters of temperature, reaction time and H_2 flow rate for experimental trial and S/N ratio on M_s. F ratio and the percentage contribution are calculated to show by what amount the test results are affected by the individual parameters. Table 6 and 7 show the computed results of the ANOVA with 95% confidence. According to Table 6, all three parameters i.e. (temperature, reaction time and H_2 flow rate) have effects on M_s value. The F ratio for temperature (parameter A) has the most significant contribution of 1327.37, and the reaction time (parameter B) and the H_2 flow rate (parameter C) are 17.92 and 7.50, respectively. For the synthesis process, the most effective parameter on M_s was temperature with percentage contribution of 97.88%. After temperature, the percentage contributions were in the order of 1.25% for reaction time and 0.48% for H_2 flow rate.

In Table 7, the F ratio for temperature has the most significant contribution of 1620.66, and the contributions of reaction time and H_2 flow rate are in the order of 20.16 and 7.54, respectively. It was observed that temperature was found to be the major factor (with contribution rate of 98.20%). This parameter is followed by reaction time with a ratio of 1.16%. H_2 flow rate is the least effective one with the contribution rate of 0.40%. The error ratio (0.24%) obtained according to S/N ratios is smaller than other ratios, thus the effect of reaction parameters are more effective than the uncounted parameters which are not included in the experimental set-up e.g. environmental conditions. ANOVA analyses of the experimental trials and the S/N ratios of M_s were parallel.

Table 3
The results of experiments and S/N ratios.

Experiment no.	Independent parameters			Experimental results	
	A: Temperature (°C)	B: Reaction time (min)	C: H_2 flow rate (ml/min)	M_s (emu/g)	S/N ratio for M_s (dB)
1	300	15	125	77.74	37.81
2	300	60	500	89.97	39.08
3	300	120	1000	85.77	38.67
4	550	60	1000	186.80	45.43
5	550	120	125	167.65	44.49
6	550	15	500	162.00	44.19
7	800	120	500	197.51	45.91
8	800	15	1000	200.74	46.05
9	**800**	**60**	**125**	**204.40**	**46.21**

Initial Combination = $\mathbf{A_3B_2C_1}$.
$\bar{Y}_{Ms}$ (Saturation magnetisation total mean value) = 152.51 emu/g.
$\bar{Y}_{Ms-S/N}$ (Saturation manetisation S/N ratio total mean value) = 43.09 dB.

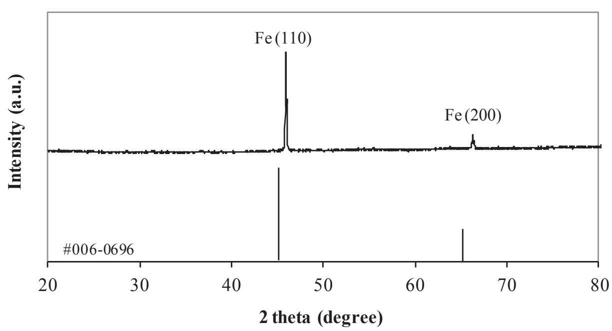

Fig. 2. XRD pattern of the sample 9.

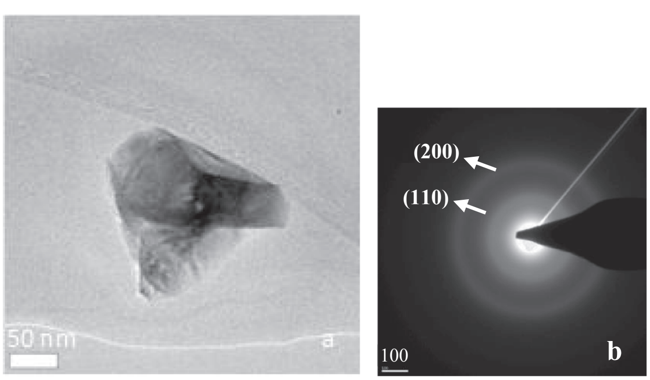

Fig. 3. a) TEM image and b) SAED pattern of the sample 9.

Table 4
Mean S/N ratios (dB) of independent parameters (A, B and C).

	A	B	C
Level 1	38.52	42.69	42.84
Level 2	44.70	**43.57***	43.06
Level 3	**46.06***	43.02	**43.38***
Δ	7.54	0.89	0.55

3.4. Interactions of independent parameters with response surface method

Variations of the M_s values obtained from the experimental study against synthesis parameters are shown in Fig. 6(a)–(c). Depending on the difference of the temperature, there was significant change in the M_s values. 800 °C showed a better performance than temperature 550 °C and 300 °C in terms of M_s values (Fig. 6(a) and (b)). Therefore, the M_s values significantly increased with increasing temperature. This is

Table 5
Mean response of M_s table of independent parameters (A, B and C).

	A	B	C
Level 1	84.49	146.83	149.93
Level 2	172.15	**160.39***	149.83
Level 3	**200.88***	150.31	**157.77***
Δ	116.39	13.56	7.94

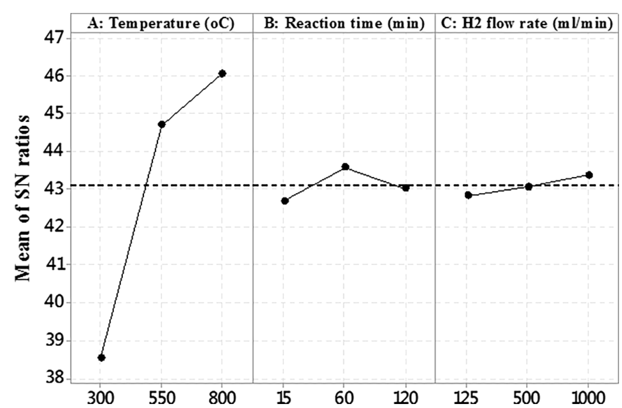

Fig. 4. Effect of independent parameters on average S/N ratios.

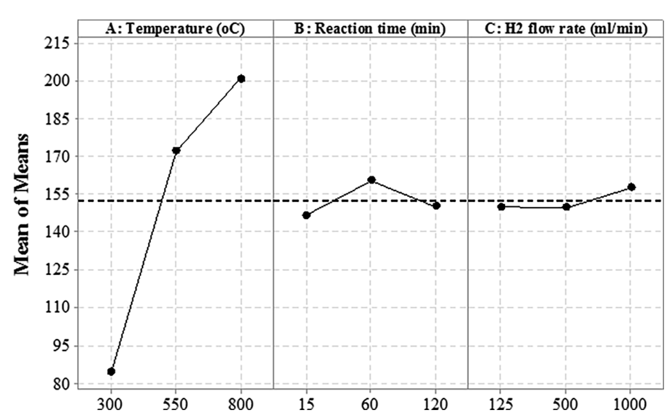

Fig. 5. Effect of independent parameters on mean response characteristics.

followed by the reaction time and the H_2 flow rate with small amount of changes with the change of levels. At 60 min. the highest M_s values were obtained (Fig. 6(a) and (c)). And, for the H_2 flow rate, the highest M_s value was obtained at 1000 ml/min (Fig. 6(b) and (c)).

Table 6
Results of ANOVA of experimental trials for M_s.

Variance source	Degree of freedom (DOF)	Sum of squares (SS)	Mean square (MS)	F-ratio	Contribution rate (%)
A	**2**	**22055.9**	**11028.0**	**1327.37**	**97.98**
B	2	297.7	148.9	17.92	1.25
C	2	124.6	62.3	7.50	0.48
Error	2	16.6	8.3	–	0.29
Total	8	22494.8	–	–	100

The selected important values are depicted in bold.

Table 7
Results of ANOVA of S/N ratios for M_s.

Variance source	Degree of freedom (DOF)	Sum of squares (SS)	Mean square (MS)	F-ratio	Contribution rate (%)
A	**2**	**96.8633**	**48.4316**	**1620.66**	**98.20**
B	2	1.2050	0.6025	20.16	1.16
C	2	0.4509	0.2255	7.54	0.40
Error	2	0.0598	0.0299	–	0.24
Total	8	98.5790	–	–	100

The selected important values are depicted in bold.

The results derived by the response surface model can be used to precisely estimate the Ms without performing the experimental studies. The figures verify the effects of the each independent parameter on the Ms values obtained with Taguchi Method (Table 4 and Fig. 4), main response characteristics (Table 5 and Fig. 5) and significance of each parameters on Ms values with ANOVA (Tables 6 and 7).

3.5. Taguchi confirmation experiment

For validation of the optimized result, the replication experiment has been conducted using the optimal setting of the process parameters as the temperature at 800 °C, reaction time at 60 min. and H2 flow rate at 1000 ml/min. For validation of the Taguchi optimised result, the three replication experiments has been conducted using the optimal setting of the process parameters i.e. for the highest Msexp (A3B2C3) value was calculated as 217.42 emu/g and its S/N ratio was 46.75 dB. The Msexp value of the optimized sample obtained from this experiment is represented in Fig. 7. Thus, the system optimization for Ms was achieved using the Taguchi method at the predicted 95% confidence interval. It is seen that the Taguchi results are consistent with the experimental results.

3.6. Estimation of the highest M_s

From the S/N analysis, mean response characteristics and response surface model, the highest levels of independent parameters were calculated as 800 °C, 60 min and 1000 mg/min H_2 flow rate. In the estimation of the highest M_s (Ms_{opt}), Eq. (5) in the Supplementary Information was used. The mean highest value of the M_s has been predicted as Ms_{opt} = 214.03emu/g.

In Taguchi optimization technique confirmation experiment was required to be conducted for validating of the optimized condition [31]. If the reliability of the condition is assumed to be 95%, then the confidence interval (CI) can be calculated [20]. By using the Eqs. (6) and (7) in the Supplementary Information, the confidence intervals were calculated as N_{eff} = 1.29 and CI = ± 13.06. The estimated average highest M_s from Eq. (8) in Supplementary Information with the confidence interval at 95% confidence is:

$$[214.03 - 13.06] < [217.42] < [214.03 + 13.06]$$
$$= 200.97 < 217.42 < 227.09$$

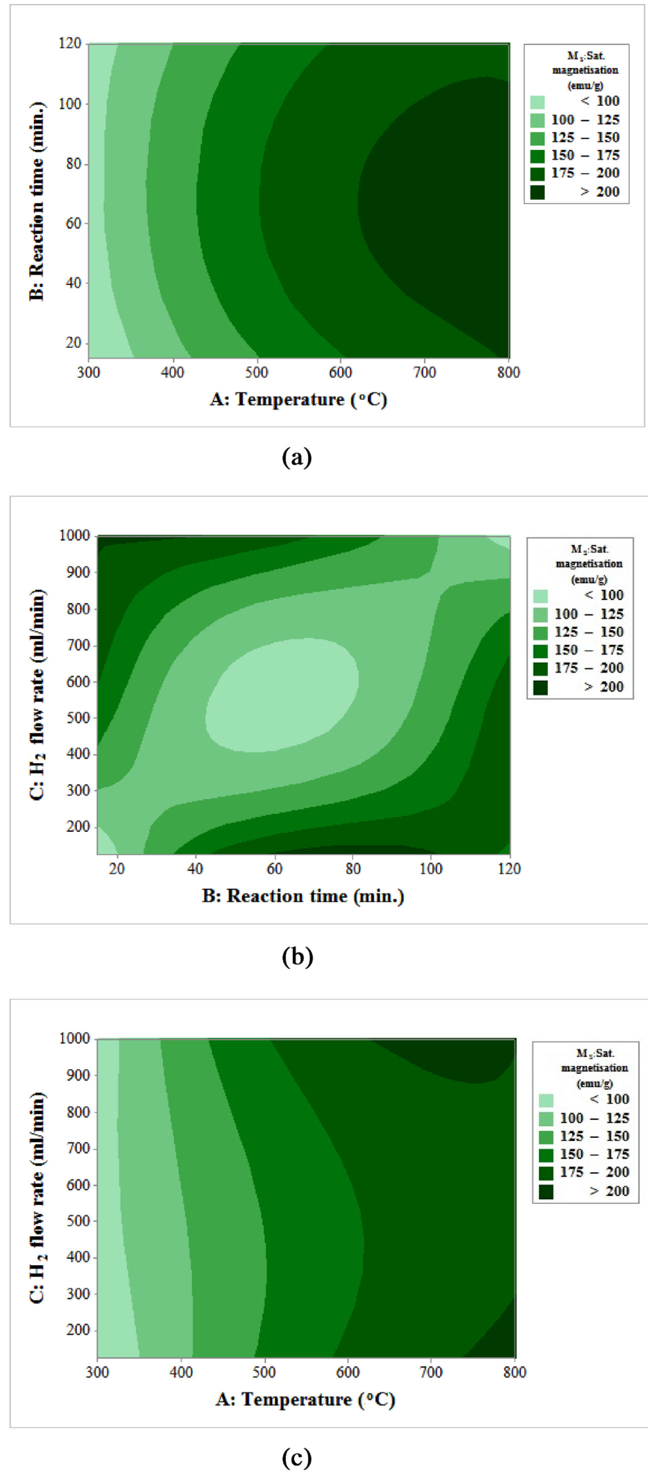

Fig. 6. Response counter plots showing the effects of two variables on M_s value a) effects of temperature and reaction time, b) effects of temperature and H_2 flow rate and c) effects of reaction time and H_2 flow rate.

3.7. Magnetic and structural characterization of the Taguchi optimum sample

Magnetization curve of iron particles obtained under optimum synthesis conditions is given in Fig. 7. The M_s value of the optimized sample is 217.42 emu/g. Structural characterizations were also conducted. According to the XRD pattern given in Fig. 8(a), the optimum

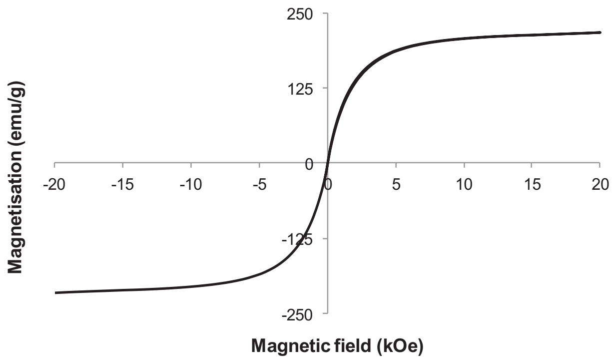

Fig. 7. Magnetization curve of the optimum sample.

Table 8
Comparison of Taguchi results and quality loss.

	Levels		
	Initial experiment Temperature: 800 °C Reaction time: 60 min. H_2 flow rate: 125 ml/min.	Experimental highest Temperature: 800 °C Reaction time: 60 min. H_2 flow rate: 1000 ml/min.	Predicted highest Temperature: 800 °C Reaction time: 60 min. H_2 flow rate: 1000 ml/min.
M_s (emu/g)	204.40	217.42	214.03 (± 13.06)
S/N ratio (dB)	46.21	46.75	–
Quality loss	–	70.7%	–

sample has the characteristic (1 1 0) and (2 0 0) peaks of Fe (JCPDS no. 06-0696) at 2θ ≈ 45° and 65°, respectively, which means that the precursor is completely reduced to iron since there are only iron peaks in the pattern. TEM image of the optimum iron particles were also given in Fig. 8(b). According to the TEM image, the optimum sample has a smaller particles besides the sintered 50–100 nm particles of iron.

3.8. Quality loss

The comparisons of the M_s values according to the initial test (Temperature is 800 °C, Reaction time is 60 min. and H_2 flow rate is 125 ml/min.), the predicted combination and the experimental combination (Temperature is 800 °C, Reaction time is 60 min. and H_2 flow rate is 1000 ml/min.), selected from 9 initial trials are given in Table 8. According to these comparisons, the M_s values were increased from 204.40 to 217.42 emu/g. The improved accuracy because of the optimal combination was increased by up to 5.99% ((217.42–204.40)/217.42). To compare the quality characteristics of the initial and optimal conditions, S/N ratios in Table 8 were used. In practice, the quality losses between initial and highest combinations for the M_s are calculated as in [32] (see Eq. (9) in Supplementary Information). The quality loss of surface roughness was calculated as 0.707. Thereby, the quality loss at the optimal combination becomes only 70.7% of initial combination. When these results were evaluated, the quality losses for the M_s were lowered as 29.3% using the Taguchi method.

3.9. Regression analysis (multiple linear and quadratic regression models) of saturation magnetisation

In obtaining predictive equations for the M_s, multiple linear regression analyses were used. The first analysis of the responds contains all process parameters. The comparison of experimental results and predicted values, which were obtained by the multiple linear parameter model, are given in Fig. 9a. The R^2 and R^2(adj) values of the equations (see Eq. (10) in Supplementary Information) obtained by the parameter regression model for M_s was found to be 90.82 and 89.50%, respectively. As seen from the figure, there is a good relation between predicted values and experimental results.

On the other hand, the second predictive equation contains the control parameters and their interactions by the multiple linear interactive model for the M_s value. Fig. 9b shows the experimental results versus the predicted values which were obtained by the multiple linear interaction regression model. The R^2 and R^2(adj) values of the equation which was obtained by multiple linear interactive model for M_s were found to be 96.31 and 85.25%, respectively (see Eq. (11) in Supplementary Information). As it is observed in the figure, there is a good relation between predicted values and experimental results.

The predictive equations were also made for quadratic regression models. The first analysis of the response obtained by the response surface model contains all process parameters. The quadratic parameter model derived by the response surface model can be used to estimate the M_s without performing the experimental studies. The differences between the real responses which were measured after the experiments and the estimated responses that were calculated (see Eq. (12) in see Supplementary Information) were given in Fig. 9c. The figure shows the relationships between experimental and predicted response values for M_s. The presented quadratic parameter regression model provided a very good statistical performance with high R^2 and R^2(adj) values of 99.98 and 99.82%, respectively between the experimental and predicted values of M_s. Therefore, quadratic parameter regression equations can be much more successfully applied to obtain the predicted values of M_s. Hence, more intensive predicted values were obtained by the quadratic parameter regression model as compared to the multiple linear regression model. As a result, the quadratic parameter regression model was shown to be more successful for the estimation of M_s.

The second predictive equation was also made for quadratic interactive regression model. The first analysis of the response obtained with the response surface model contains all process parameters and their interactions. Depending on the significance of the individual parameters, the quadratic model of the predictive equation was obtained

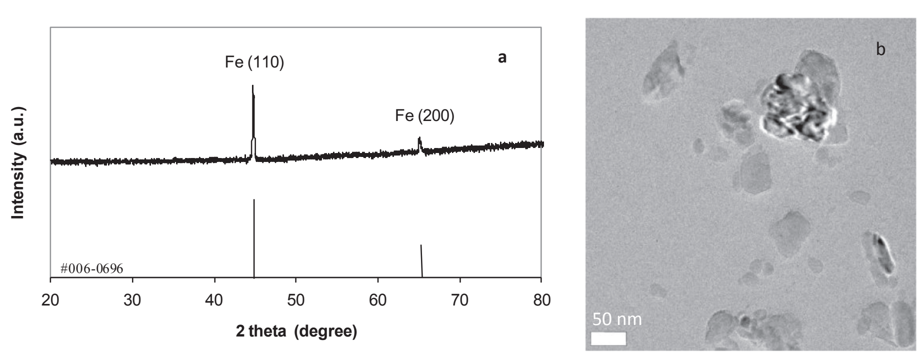

Fig. 8. a) XRD pattern and b) TEM image of the optimum sample.

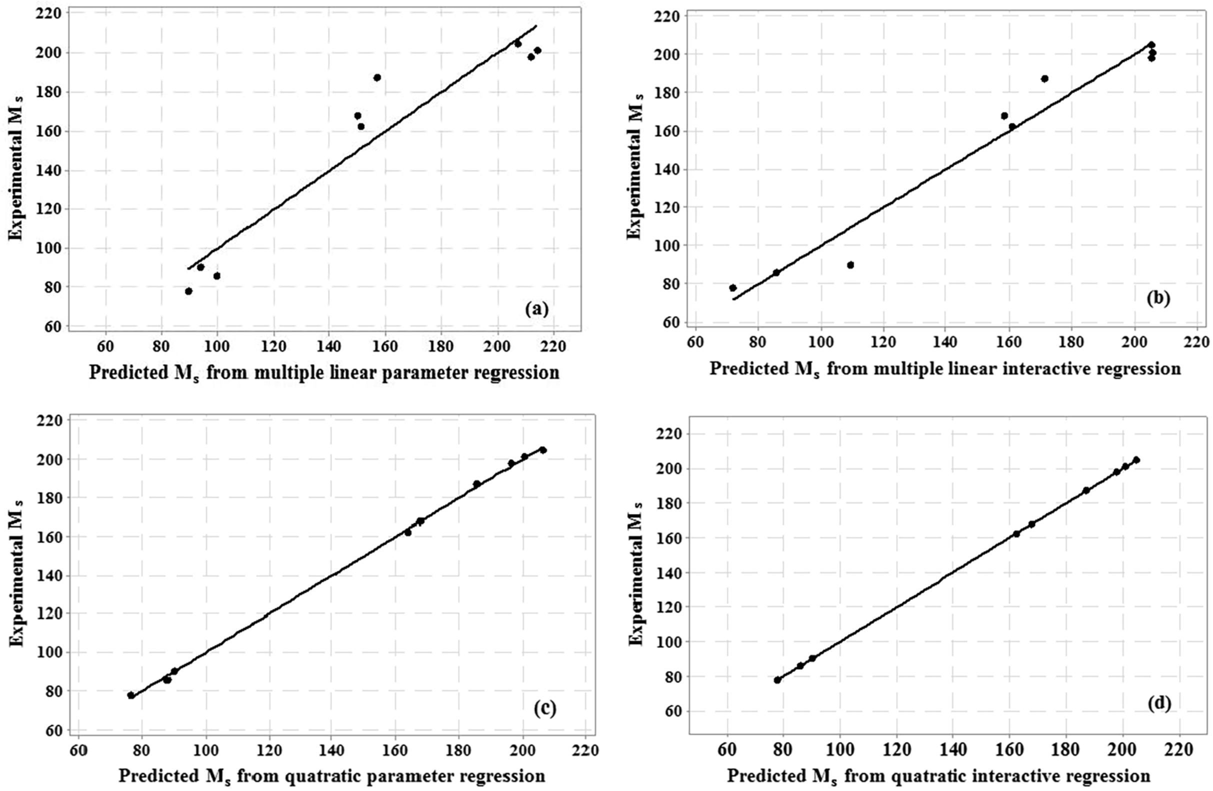

Fig. 9. Relationships between a) multiple linear parameter regression model and experimental results for M_s, b) linear interactive regression model and experimental results for M_s, c) quadratic parameter regression model and experimental results for M_s and d) quadratic interactive regression model and experimental results for M_s.

(see Eq. (13) in Supplementary Information). The quadratic interactive model derived by the response surface model can be used to precisely estimate the M_s without performing the experimental studies. The differences between the real responses which were measured after the experiments and the estimated responses that were calculated with the above equation are given in Fig. 9d. Figure shows the relationship between experimental and predicted response values for M_s. Presented quadratic interactive regression model provided a very good statistical analysis between the experimental and predicted values of M_s with high R^2 and R^2(adj) values of 100 and 100%, respectively. More intensive predicted values were obtained by the quadratic regression models as compared to multiple linear regression models, hence quadratic regression equations can be much more successfully applied to obtain the predicted values of M_s. The quadratic interactive regression model contains the interactions between the parameters that are not available in quadratic parameter regression model, therefore it gives better fitting result than the latter model.

3.10. Comparison of experimental and predicted values

Predicted values and confirmation test results from Taguchi method and regression equations at initial and highest levels are presented in Table 9. The experimental values and the predicted values are very close to each other. For reliable statistical analyses, error values must be less than 20% [20]. Thus, the error percentages calculated in the M_s are well within the acceptable limits. Therefore, the results obtained from the confirmation tests reflect successful optimization. The error percentages of quadratic regression equations were the smallest ones (interactive model; 0.06 and 0.12%, and parameter model; 1.65 and 0.85%). This is followed by the Taguchi Method (1.56 and 0.87%) and then linear regression equations (parameter model; 6.82 and 6.44%, and interactive model; 11.34 and 5.64%). It is seen that quadratic

Table 9
Error percentage of Taguchi experiments and the predicted results according to Taguchi method, linear and quadratic regression equations.

	M_s (emu/g)										
	Taguchi *Exp. Results	Taguchi prediction		Multi regression equations				Quadratic regression equations			
				Parameter model		Interactive model		Parameter model		Interactive model	
Levels		**Pred.	Error (%)	**Pred.	Error (%)	**Pred.	Error (%)	**Pred.	Error (%)	**Pred.	Error (%)
$A_3B_2C_1$ (Initial combination)	**204.40**	206.19	0.87	219.37	6.82	181.22	11.34	206.16	0.85	204.65	0.12
$A_3B_2C_3$ (highest confirmation)	**217.42**	214.03	1.56	227.51	4.44	205.16	5.64	213.83	1.65	217.29	0.06

The selected important values are depicted in bold.
* Exp. = Experimental.
** Pred. = Prediction.

regression equations can be much more successfully applied to obtain the predicted values of M_s.

4. Conclusions

In this article, Taguchi method with mean response and response surface methodology was applied to obtain optimal synthesis parameters for high M_s of iron nanoparticles obtained by hydrogen reduction method. The Taguchi L9 orthogonal array was applied, S/N ratio was calculated and ANOVA technique was adopted for finding the better control parameters including A: Temperature, B: Reaction time and C: H_2 flow rate. In the performed experimental trials using Taguchi orthogonal arrays, the most significant parameter for M_s was found to be temperature which had a contribution of 97.98%, this is followed by the reaction time which had almost 1.25% contribution and lastly H_2 flow rate that had a very nominal 0.48% contribution on the M_s. Based on the S/N ratio using larger is the better approach, the best optimal M_s condition is observed at $A_3B_2C_3$ i.e. A3: Temperature at 800 °C, B_2: Reaction time at 60 min and C_3: H_2 flow rate at 1000 ml/min. Using the optimal combinations of the individual parameters, predicted optimal M_s value was calculated as 214.03 emu/g and its S/N ratio was 46.83 dB. By using the optimum experimental conditions obtained, confirmation experiment was made and the M_s of this sample was measured to be 217.42 emu/g. An optimized value of M_s with 95% confidence level has been predicted. Thus, it can be concluded that Taguchi's technique holds good for the estimation of the M_s of iron nanoparticles reduced by hydrogen. Linear and quadratic regression analyses were also applied to predict the outcomes of the experiments. Predicted values of M_s using multiple linear regression analyses were very close to the experimental values. Furthermore, the quadratic models gave better results than the multiple models. The quadratic interactive regression models demonstrated the best relationship with high confidence intervals ($R^2 = 100$ and $R^2(\text{adj}) = 100\%$) between the measured and quadratic interactive predicted values for M_s. Error percentages of quadratic regression equation was the smallest one. This is followed by the Taguchi method and then the linear regression equations. It is seen that quadratic regression equations can be quite successfully applied to obtain the predicted values of M_s.

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Appendix A. Supplementary data

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References

[1] J. Wang, X. Shao, G. Tian, Z. Li, W. Bao, Preparation and properties of α-Fe microparticles with high stability, Mater. Lett. 192 (2017) 36–39.
[2] Q. Huang, X. Shi, R.A. Pinto, E.J. Petersen, W.J. Weber Jr., Tuneable synthesis and immobilization of zero-valent iron nanoparticles for environmental applications, Environ. Sci. Technol. 42 (23) (2008) 8884–8889.
[3] X. Li, D.W. Elliott, W. Zhang, Zero-valent iron nanoparticles for abatement of environmental pollutants: materials and engineering aspects, Crit. Rev. Solid State Mater. Sci. 31 (2006) 111–122.
[4] T.S.T. Saharuddin, A. Samsuri, F. Salleh, R. Othaman, Kassim M. Bin, M.W.M. Hisham, M.A. Yarmo, Studies on reduction of chromium doped iron oxide catalyst using hydrogen and various concentration of carbon monoxide, Int. J. Hydrogen Energy 42 (2017) 9077–9086.
[5] B. Abolpour, M.M. Afsahi, A.S. Goharrizi, M. Azizkarimi, Investigation of in-flight reduction of magnetite concentrate by hydrogen, Ironmaking Steelmaking (2017), https://doi.org/10.1080/03019233.2017.1405146.
[6] Z. Ma, R. Xiao, L. Chen, Kinetics of sintering induced surface area decay of iron oxide in the reduction process of chemical looping combustion, Fuel Process. Technol. 168 (2017) 20–26.
[7] O. Karaagac, H. Kockar, A simple way to obtain high saturation magnetization for superparamagnetic iron oxide nanoparticles synthesized in air atmosphere: optimization by experimental design, J. Magn. Magn. Mater. 409 (2016) 116–123.
[8] H.-C. Liu, Y.-M. Wang, C.-C. Hsieh, Optimized synthesis of Cu-doped $LiFePO_4$/C cathode material by an ethylene glycol assisted co-precipitation method, Ceram. Int. 43 (2017) 3196–3201.
[9] B.N. Akhgar, M. Pazouki, M. Ranjbar, A. Hosseinnia, R. Salarian, Application of Taguchi method for optimization of synthetic rutile nano powder preparation from ilmenite concentrate, Chem. Eng. Res. Des. 90 (2012) 220–228.
[10] V. Panchal, G. Lahoti, U. Bhandarkar, M.T. Neerga, The effects of process parameters on yield and properties of iron nanoparticles from ferrocene in a low-pressure plasma, J. Phys. D Appl. Phys. 44 (2011) 9 345205.
[11] A. Biabani, M. Rezaei, Z. Fattah, Optimization of preparation conditions of Fe-Co nanoparticles in low-temperature CO oxidation reaction by Taguchi design method, J. Nat. Gas Chem. 21 (2012) 415–420.
[12] S.M. Mousavi, S. Yaghmaei, A. Jafari, M. Vossoughi, Z. Ghobadi, Optimization of ferrous biooxidation rate in a packed bed bioreactor using Taguchi approach, Chem. Eng. Process. 46 (2007) 935–940.
[13] Hosseinabadi H. Arabian, M. Edrissi, Novel method for the synthesis of $CoFe_2O_4$ magnetic nanofluid and its application for the size-based separation of BSA and *E. coli* mixture, Synth. React. Inorg., Met.-Org., Nano-Met. Chem. 45 (2015) 1889–1896.
[14] Z. Es'haghi, T. Heidari, E. Mazloomi, In situ pre-concentration and voltammetric determination of trace lead and cadmium by a novel ionic liquid mediated hollow fibber-graphite electrode and design of experiments via Taguchi method, Electrochim. Acta 147 (2014) 279–287.
[15] P.J. Ross, Taguchi Techniques for Quality Engineering Loss Function, Orthogonal Experiments Parameter and Tolerance Design, McGraw-Hill International Book Company, New York, 1989.
[16] G. Taguchi, Introduction to Quality Engineering, Asian Productivity Organization (APO), Tokyo, Japan, 1990.
[17] D. Fratila, C. Caizar, Application of Taguchi method to selection of optimal lubrication and cutting conditions in face milling of AlMg, J. Cleaner Prod. 19 (2011) 640–645.
[18] T.V. Sibalija, V.D. Majstorovic, An integrated approach to optimise parameter design of multi-response processes based on Taguchi method and artificial intelligence, J. Intell. Manuf. 23 (2012) 1511–1528.
[19] S.H. Park, Robust Design and Analysis for Quality Engineering, Chapman & Hall, London, 1996.
[20] N. Mandal, B. Doloi, B. Mondal, R. Das, Optimization of flank wear using zirconia toughened alumina (ZTA) cutting tool: Taguchi method and regression analysis, Measurement 44 (2011) 2149–2155.
[21] I. Asilturk, S. Neseli, Multi response optimisation of CNC turning parameters via Taguchi method-based response surface analysis, Measurement 45 (2012) 785–794.
[22] P.J. Ross, Taguchi Techniques for Quality Engineering, second ed., McGraw-Hill, New York, 1996.
[23] J. Antony, D. Preece, Understanding, Managing and Implementing Quality, Frameworks Techniques and Cases, Routledge, London, 2002.
[24] O. Karaagac, Characterizations of iron particles reduced from iron oxide nanoparticles under hydrogen atmosphere, J. Supercond. Novel Magn. 26 (2013) 1707–1711.
[25] O. Karaagac, H. Kockar, B. Ebin, S. Gurmen, Reduction and characterization of iron particles: influence of reduction parameters, J. Mater. Sci.: Mater. Electron. 24 (2013) 2602–2609.
[26] Ranjit K. Roy, A Primer on Taguchi Method, Van Nostrad Reinhold, New York, 1990.
[27] J. Grum, J.M. Slabe, The use of factorial design and response surface methodology for fast determination of optimal heat treatment conditions of different Ni–Co–Mo surfaced layers, J. Mater. Process. Technol. 155 (2006) 2026–2032.
[28] V.I. Vitanov, N. Javaid, D.J. Stephenson, Application of response surface methodology for the optimisation of micro friction surfacing process, Surf. Coat. Technol. 204 (2010) 3501–3508.
[29] B. Bhattacharya, S.K. Sorkhel, Investigation for controlled electrochemical machining through response surface methodology based approach, J. Mater. Process. Technol. 86 (1999) 200–207.
[30] M.H. Cetin, B. Ozcelik, E. Kuram, E. Demirbas, Evaluation of vegetable based cutting fluids with extreme pressure and cutting parameters in turning of AISI 304L by Taguchi method, J. Cleaner Prod. 19 (2011) 2049–2056.
[31] T. Ozel, Y. Karpat, Predictive modeling of surface roughness and tool wear in hard turning using regression and neural networks, Int. J. Mach. Tools Manuf. 45 (2005) 467–479.
[32] Y.T. Liu, W.C. Chang, Y.A. Yamagata, A study on optimal compensation cutting for an aspheric surface using the Taguchi method, CIRP J. Manuf. Sci. Technol. 3 (2010) 40–48.