

Analyses of particle size and magnetisation of magnetic nanoparticles via Minitab Statistical Software

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In this work, the influence of statistically determined synthesis parameters on the properties of magnetite (Fe₃O₄) nanoparticles (MNPs) was investigated. The synthesis temperature and pH parameters generated with the help of Minitab Statistical Software v.16 were selected to examine. The effects of these parameters on MNPs produced by using co-precipitation method were presented. The average particle size and saturation magnetisation were measured, which were chosen for statistical evaluation in the software. The fit test results of Minitab show that the initial condition parameters and results of the selected measurements in correlation to fit in the normal distribution. It was also shown that the results of saturation magnetisation and particle size depend on solution pH and the temperature is compatible with several studies. Outcomes of this work indicate that this software can be used for determining a minimum number of trials needed to find the influence of synthesis parameters (temperature, pH) on the material properties and so decrease the time for synthesis of new material with desired properties.

1. Introduction: Many chemical methods have been used for the production of magnetic nanoparticles (MNPs). These methods include co-precipitation [1], microemulsions [2], sol-gel syntheses [3], sonochemical reactions [4], hydrolysis and thermolysis of precursors [5], flow injection syntheses [6] and electrospray ionic syntheses [7]. However, the most widely used and the probably simplest method to synthesise MNP is the co-precipitation method.

Magnetite (Fe₃O₄) is an MNP. The crystal structure of the magnetite has an inverse spinel and occurs two parts. These parts are tetrahedral sites and octahedral sites [8, 9]. The magnetic properties and particle size (structure) of the synthesised MNP depend on the many conditions such as temperature, pH value and type of salts (NO₃, SO₄ etc.), the molar ratio of salts and the some other experiment parameters such a stirring rate, environment conditions and washing procedure [10]. As an example the crystal structure of the MNP influenced by changing the rate of iron molarities from (Fe⁺²: Fe⁺³) 1 : 2 to 2 : 3 which affects the particle size distribution [11]. The investigation of every parameter on properties of MNPs is needed to conduct many systematically experiments. Results of these kinds of experiments were presented by several studies. It is possible to reduce the number of experiments needed to comprehend the influence of synthesis parameters on the MNPs by using statistical software. Minitab Statistical Software (MSS) was chosen for this purpose.

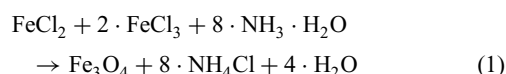
MSS provides Quantitative Data Analysis and numerous sample data sets. This statistical program is used by different disciplines such as chemistry, biology, physics, mathematics and social sciences [12]. MSS determines the number of measurements be made by describing factors that are effect input variables and provides deeper and easier analysis for initial parameters. Therefore, this program allows researchers to make a qualified experiment, i.e. eliminates unnecessary and random made testing.

In this Letter, the usage of MSS on nanoparticle material production investigated. The pH and temperature parameters determined by the software used to synthesise MNPs. Influence of these parameters on the MNP size and magnetisation presented.

2. Experiment: MNPs were synthesised by using co-precipitation method with ferric chloride hexahydrate (FeCl₃·6H₂O), ferrous chloride tetrahydrate (FeCl₂·4H₂O) and hydrochloric acid

(HCl) ACS 37%, ammonium hydroxide (NH₄OH) 28%, tetramethylammonium hydroxide and these chemicals were purchased by Sigma-Aldrich.

General chemical reaction of MNP formation is written in (1) [13]. According to the thermodynamics of this reaction, pH value should be between 8 and 14 and with a molar ratio (Fe⁺²/Fe⁺³) 1 : 2 in a non-oxidising medium



In this Letter, briefly, FeCl₃·6H₂O was dissolved in deionised water. FeCl₂·4H₂O should be only dissolved in 1 M HCl because Fe⁺² ions downgraded Fe⁺³ [14]. The iron solutions (Fe⁺²/Fe⁺³) were added into the same flask with molar ratio 1 : 2 and mixed with magnetic stirrer in air atmosphere. After this mixing procedure, ammonium hydroxide was added with peristaltic pump. The pH and mixture temperature were maintained during the synthesis. Particle aggregation after synthesising the nanoparticles is undesirable for many applications. Washing with pure water causes to decrease of the surface OH⁻ ions and also agglomeration. For this reason, the resulted particles were separated magnetically and washed several times with 5% M (NH₄OH\water) solution to prevent aggregation of the particles [15] After washing the MNPs were coated with surfactant tetramethylammonium hydroxide to prevent agglomerations. The other parameters may affect the particle's shape and size distribution were arranged to be constant such as speed of mixing [16]. Part of the products was dried in the oven at 74°C for 12 h to measure their magnetic properties. Saturation magnetisations of dried particles were measured at room temperature under applied field of 7000 Oe.

Temperature range between 20 and 80°C and pH range between 10 and 12 were selected in MSS. So the program gave randomly 13 sample data sets for these parameters to conduct experiments.

Dynamic Light Scattering (DLS:Malvern ZS-Nanosizer) and Vibrating Sample Magnetometer (VSM: Digital Measurement System JDM-13) were used for identifying the average particle size and magnetic properties of MNPs, respectively.

3. Results and discussion: The MNPs were produced by using initial parameters determined from MSS data sets. The result of particle size analyses (DLS) and magnetic properties (VSM analyses) were given in Table 1. The average particle size and the saturation magnetisation of particles were analysed with MSS program. The data given in the Table 1 were processed in the MSS to approximate the normal distribution as shown in Figs. 1a and 2a. The normal probability plots shown in Figs. 1b and 2b form a nearly linear pattern, which indicates that the normal distribution is a suitable model for these data sets.

Although the results of the DLS analysis do not represent accurate particle size, DLS analysis provides a comparison of the sizes of the particles. As it is seen in Table 1, the obtained particle sizes are

Table 1 According to Minitab program, initial conditions for preparation Fe_3O_4

No.	Temperature, °C	pH	Average particle size, nm	Saturation magnetisation, emu/g
1	50	11	184.1	49.3
2	50	10	44.6	60.1
3	50	11	115.5	59.3
4	50	11	74.1	60.6
5	80	10	57.5	55
6	80	11	64	50.7
7	20	10	49.4	62.3
8	80	12	46.9	60
9	20	12	41.5	58
10	50	12	79.8	57.8
11	50	11	135.5	57
12	20	11	68.4	61
13	50	11	80.1	64.2

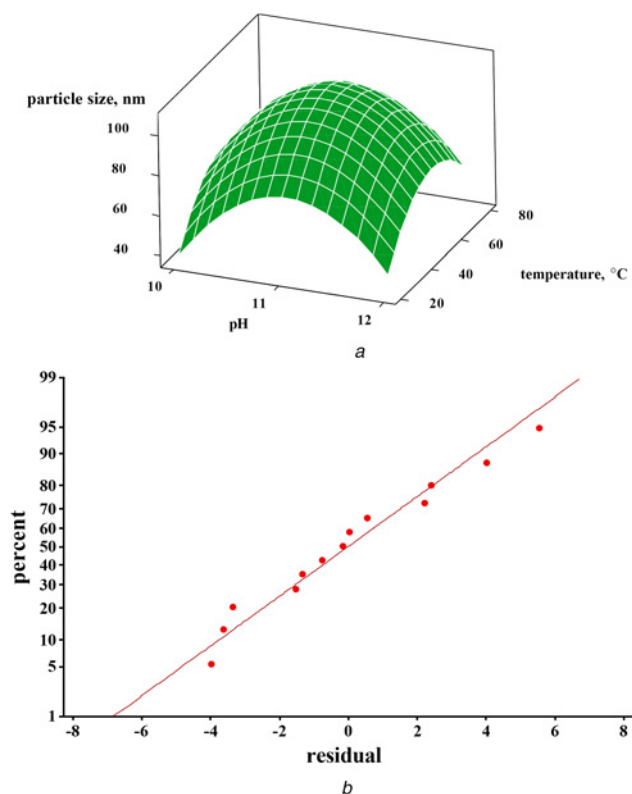


Fig. 1 Effect of initial conditions on
a Particle size
b Normal probability graph of and average particle size of MNP

larger in comparison to the particles presented in other studies [6, 17]. Main reasons of relatively larger size can be explained by the effect of the experimental conditions like amount of used water, magnetic stirring and air environment. Our results show that how the size of the particles grows in the air environment. Large particle size of particles produced [18] in air environment can be explained by the amount of oxygen in solutions which expands the unit cell volume of the magnetite [19].

The synthesising temperature is one of the critical parameters to achieve a desired size and morphology. It is found that the size of our particles shows that the largest particle are produced at 50°C. The particle size increases up to this temperature value and then starts to decrease. Decrease of the particle size after 50°C can be explained by the pH values which affect the number of OH^- ions on the surface. Increasing the number of the OH^- ions decreases the size of the particles as the electrostatic repulsions forces increase [15]. The largest particle size was obtained while the pH value is 11 in our experiments. According to results it is clear that the particle sizes change depends on whether the temperature is dominant factor or the pH value is dominant factor. Normal probability plot of particle size shown in Fig. 1b verify that an assumption of normality is approximately reasonable.

The magnetic properties and the particle size of MNP were compared by depending on different pH and temperature values via MSS program. The results show that the magnetic properties of particles depend on the initial parameters different than particle size. As shown in Fig. 2a, increase of the pH value has partially positive impact on saturation magnetisation of the MNPs at high temperatures [20]. However, the effect is opposite at low temperatures. It is clear that both pH and the reaction temperature determine the conformation of the crystal structure as well as the magnetic properties [21]. As shown in Figs. 1 and 2, if the desired properties of

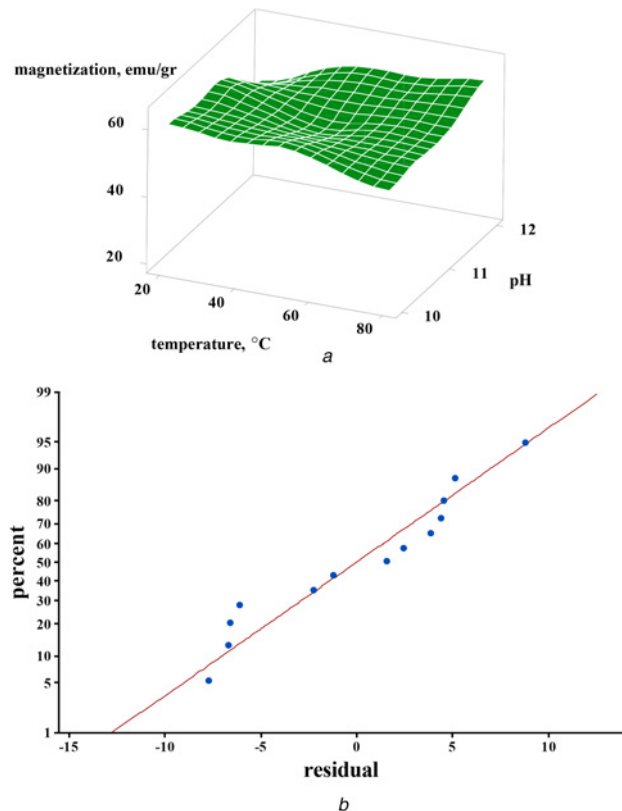


Fig. 2 Effect of initial conditions on
a Saturation magnetisation
b Normal probability graph of saturation magnetisation of MNPs

particles are small size and high saturation magnetisation, the pH value of 10–11 and temperature value of 20°C should be chosen as synthesis parameters.

The residual and percent of the normal probability graphs roughly follow a straight line in Figs. 1b and 2b. According to these results, the normal probability graphs of particle size and magnetic properties are suitable for modelling with the normal distribution. This shows that the points specified by the program are determined correctly and sufficient to produce the characteristic of the MNPs [22].

4. Conclusion: The main purpose of this Letter is to show that it is possible to eliminate the unnecessary experiments to understand main parameters in synthesis of MNP by using randomly generated tests of the MSS program. The program gives statistical results of the magnetic properties and particle sizes of the MNPs with respect to pH and synthesis temperature parameters. In this way, it is shown that the effect of these parameters can be predicted and MNPs with desired magnetic properties and dimensions can be produced. The results of our experiments are similar to the previous studies [8]. To obtain the particles which have small size and high saturation temperature one of the choices is the selection of pH around 10–11 and temperature lower than 50°C.

5. References

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