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Optimization and thermodynamic assessment of ferrite (Fe$_3$O$_4$) synthesis in simulated wastewater

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Abstract

The effect of temperature, pH, the rate and time of oxidation, the concentration of ferrous ion in the starting suspensions as well as the amount of oxidant acting on the process of Fe$_3$O$_4$ synthesis by Fe(OH)$_2$ suspensions are investigated. After 2 h reaction at 90 °C under the oxidation of 10 g/L NH$_4$NO$_3$, solution containing 0.25–0.35 mol/L iron(II) ion initially would yield the greatest amount of Fe$_3$O$_4$, up to 95% Fe$_3$O$_4$ could be formed. pH of the solution should be controlled between 9.0 and 11.0. X-ray diffraction (XRD) analysis shows that the product has spinel structure, which indicated that the product is Fe$_3$O$_4$. Transmission electron microscopy (TEM) images show that the crystal size of ferrite is around 0.2 μm. The equilibrium composition of the synthesis reaction of Fe$_3$O$_4$ is optimized by the minimization of the free energy of thermodynamics. It was found that the optimal condition for the synthesis of Fe$_3$O$_4$ obtained through experiment is correspondent with that obtained through computer calculation. In the Fe$_3$O$_4$ formation area given by Kiyama [M. Kiyama, Conditions for the formation of Fe$_3$O$_4$ by the air oxidation of Fe(OH)$_2$ suspensions, Bull. Chem. Soc. Jpn. 47 (7) (1974) 1646–1650], the content of the product formed is not the same everywhere. The main factor that influences the content of the product is the amount of oxidant.
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1. Introduction

Heavy metal pollution of water is becoming a global issue and is associated with a broad spectrum of human activities, ranging from the most basic agricultural practices to the most high-tech industrial processes. Industrial manufacturing operation and mining are typically responsible for heavy metal pollution. Excessive exposure to heavy metals would be toxic to human beings and other creatures. And the famous Minamata disease striking Japan in the middle years of 20th century was one of the most massive pollution problems and had aroused worldwide attention to heavy metal pollution.

In 1979, Tamaura et al. employed "wet method" of ferrite production to the treatment of wastewater containing heavy metals and gained Fe$_3$O$_4$ [1], which has been popularly used as magnetic material, recording material and pigment [2]. The studies of wet method in the treatment of heavy metal-polluted water

attract many researchers ever since. For example, Barrado et al. applied the Taguchi design to the removal of toxic metals from waste waters by precipitation as magnetic ferrites [3]; optimal conditions are investigated, among which temperature, concentration of iron(II) and pH are considered factors [4,5]. In fact, the investigation into the mechanism of ferrite-formation began much earlier.

Wet method was first studied in 1959 [6]. Strong alkali, oxalic acid or ammonium oxalate were added to the water solution containing ions of iron and other metals, and ferrite product can be gained after a process of aeration oxidation (or co-precipitation), washing and drying, molding and sintering. Feitknecht found that the transformation of Fe(OH)$_2$ into Fe$_3$O$_4$ is complicated and a series of iron oxide by-products can be formed if the synthesis condition is not well-controlled. Also in 1959, Bernal et al. found that Fe$_3$O$_4$ would not be well-formed in a strong alkali solution or under an over oxidation condition, and the final products are α-FeOOH and γ-Fe$_2$O$_3$; while in a weak alkali condition, the final product would become γ-FeOOH if iron(II) ions are excess in the solution [7]. In early 1970s, Takada and Kiyama proposed the wet method of ferrite production formally

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Nomenclature

a_{ij}	atom number of the number j element in compound i
B_j	total mole number of the number j element
G	Gibbs free energy
m_i	molality of compound i
n_i	mole number of compound i
z_i	valency of compound i

Greek letters

γ_i	activity coefficient of compound i
λ_j	Lagrange undetermined constant
μ_i	chemical potential of compound i
μ_i^0	standard chemical potential of compound i

and widely investigated the conditions of $Fe(OH)_2$ oxidized into Fe_3O_4 [8]. Temperature, pH and concentration were thought to be the main factors for ferrite-formation and there was a relationship between these factors (Fig. 1). Later, researchers found that $Fe(OH)_2$ can be transformed to a pure by-product, γ-Fe_2O_3, which could be directly transformed into Fe_3O_4 though iron(II) ion absorption [11,12]. Tamaura et al. put forward a three-stage theory of Fe_3O_4 formation during air oxidation in 1981 that the oxidation proceeds in the following stages: (1) formation of iron(III) oxides and slower formation of Fe_3O_4; (2) rapid formation of Fe_3O_4; (3) linear formation of Fe_3O_4 [13]. And two ferrite-formation pathway were discovered: (1) γ-FeOOH oxidized from is transformed into ferrites by adsorption of iron(II) and (2) green rust II formed from $Fe(OH)_2$ containing sulfate can be spontaneously transformed into ferrites without any oxidants [12–15]. The two above-mentioned reactions constitute the mechanism of ferrite-formation through oxidation method.

However, the formation condition of ferrite is still not clear enough, especially the detailed effects of certain conditions; reaction efficiency as well as the content and morphology of Fe_3O_4 in the final products are still under study. In this paper,
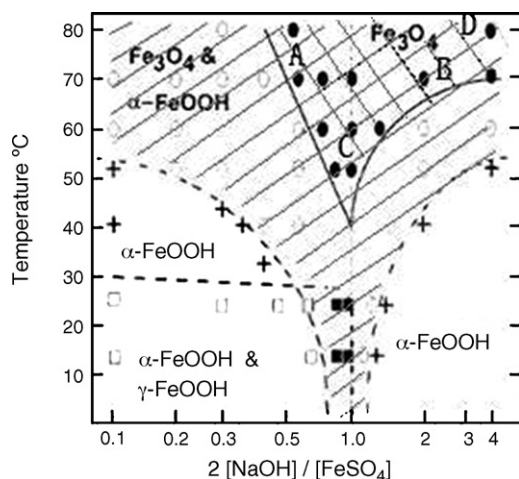
the transformation of iron(II) ion solution into ferrites by the oxidation of ammonium nitrate and air was investigated separately, trying to find out a cheaper and more effective oxidant for ferrite synthesis. Optimal synthesis condition of ferrite was studied by orthogonal tests, with the effects of different oxidants, air and NH_4NO_3 investigated as well, in order to make sure the influences of main factors on final products. The synthesis conditions of Fe_3O_4 with the oxidant of NH_4NO_3 were also assessed thermodynamically through the method of free energy minimization and self-compiling programs, intending to give a valuable reference to practical research.

2. Materials and methods

2.1. Chemicals and apparatus

$FeSO_4 \cdot 7H_2O$, NaOH, $SnCl_2 \cdot 2H_2O$, $K_2Cr_2O_7$, HCl, H_3PO_4 and H_2SO_4 are analytical grade. NH_4NO_3, $Na_2WO_4 \cdot 2H_2O$ and $TiCl_3 \cdot xH_2O$ are chemically pure. Commercial ferrite was purchased from Shanghai Iron Oxide Pigment Factory, PR China.

Schematic diagram of the reactor is shown in Fig. 2. The reactor was sealed with rubber septa. A glass electrode (Model 302-2, Shanghai Photoelectronic Devices Factory, PR China) and a calomel electrode (Model 232, Shanghai Photoelectronic Devices Factory, PR China) were connected to an ionic activity meter (Model Pxs-215, Shanghai Second Analytical Instrument Factory, PR China) to measure ionic activ-

Fig. 1. Phase diagram of relationship between oxidation condition and the formation of Fe_3O_4 [9,10]. [$FeSO_4$] is kept constant at 0.24 mol/L.
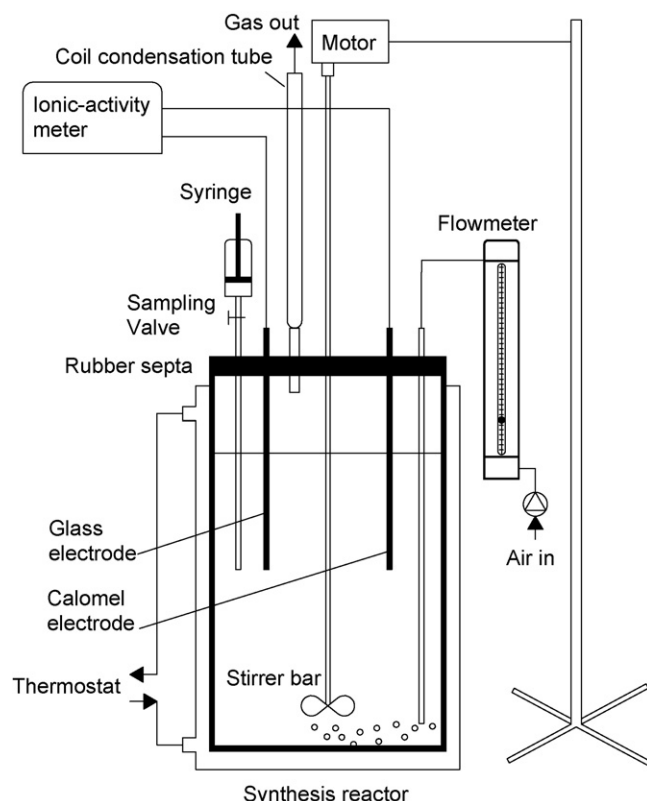

Fig. 2. Schematic diagram of synthesis reactor.

ity in the solution. The solution in the reactor was agitated with a mechanical agitator (Model GSP-80, Jiangsu Taixian Instrument Factory, PR China), and the stirrer was coated with Teflon. Air was pumped into the solution with an air pump (Model ACO-5503, Guangdong Haili Co., Ltd., PR China) and the flowrate rate was fixed with a gas flowmeter (Model LAB-4, Yuyao Zhenxing Flowmeter Instrument Factory, PR China). The temperature of the solution was kept constant with electric water bath (Model HWS12, Shanghai Yiheng Technology Co., Ltd., PR China). A coil condensation tube was used as a gas outlet as well as to cool down the gas.

2.2. Preparation of solutions

Deionized water was kept boiling for half an hour. It was then sparged with nitrogen for an hour to remove dissolved oxygen and carbon dioxide. Subsequently standard solutions with certain concentration were prepared by dissolving standard reagents into this water under the protection of nitrogen.

Glass electrode and calomel electrode were inserted into the reactor containing deoxygenated-deionized water under stirring at 25 °C. Certain amount of iron standard solution was added to the reactor after the water was sparged with nitrogen for 10 min. NaOH solution with a concentration of 2 mol/L was added to adjust the pH of the solution. The solution was then diluted to certain volume and it was called "reaction solution" in this experiment.

2.3. Reaction and sample handling

After the electrodes were removed from the reactor, the solution was heated to certain temperature. The reaction began after air or nitrate instead of nitrogen was sparged into the reactor and this moment was set as the "start time" of the reaction. After a period of time, sparging and stirring were stopped and an "end time" can be reached. Then the solution was kept still for 2 h under constant temperature. The deposition was washed with deionized water for five times and with acetone for three times. The sample acquired was dried under 60 °C and sealed in bottles for characterization.

2.4. Orthogonal test design—synthesis of Fe₃O₄ with air as oxidant

Table 1 shows the factors selected and their corresponding levels in orthogonal tests 1 and 2. In orthogonal test 1, temperature, pH value and solute concentration are considered as the main factors in Fe_3O_4 synthesis according to phase diagram given by Kiyama (Fig. 1). Effects of initial concentration of iron(II) ion (A), pH (B), synthesis temperature (C), reaction time (D), as well as the interaction between A and C, A and B, B and C were taken into account in a $L_8(2^7)$ orthogonal test.

Another modified $L_{16}(2^{15})$ orthogonal test (test 2) was taken subsequently based on the results of the first test, and E factor, ventilation rate, was added. The interaction between A and C, A and B, D and E were taken into account in test 2.

In the modified $L_{16}(2^{15})$ orthogonal test, the first column was not evaluated. Columns 2 and 3, 5 and 6, and 7 and 8 were combined into three columns respectively with the principles as follows: $(1, 1) \to 1$, $(1, 2) \to 2$, $(2, 1) \to 3$, $(2, 2) \to 2$, and factors A, B and D were evaluated to the three columns respectively. Columns 10 and 11 were evaluated with A and C as an interaction contribution, and so did columns 12 and 13 with B and C as well as columns 14 and 15 with D and E [16].

The methods for Fe_3O_4 yield comparison among factors estimated were as follows: (1) For a two level factor, average values of Fe_3O_4 yield of each level would be compared directly; (2) As for a three level factor, average values of Fe_3O_4 yield of each level were defined as $\bar{A}_1$, $\bar{A}_2$ and $\bar{A}_3$; they should be compared with their correction value $\bar{A}_1 + w$, $\bar{A}_2$, $\bar{A}_3 - w$, respectively ($w = (\bar{A}_{2b} - \bar{A}_{2a})/2$, where $\bar{A}_{2a}$ is the average value of level 2, the column of which was combined from $(2, 2)$, and $\bar{A}_{2b}$ is the average value of level 2, the column of which was combined from $(1, 2)$).

2.5. Sample analysis

Total iron content in the solution was determined by titanium(III) chloride reduction methods [17]. Acid-soluble iron(II) content was determined by potassium dichromate titration

Table 1
Orthogonal tests 1 and 2—factors selected and their levels

Factor	Symbol	Level 1		Level 2		Level 3	
		Test 1	Test 2	Test 1	Test 2	Test 1	Test 2
Initial Fe²⁺ concentration (mol/L)	A	0.25	0.15	0.35	0.25	–	0.35
pH value	B	9.0	9.0	10.0	10.0	–	11.0
Synthesis temperature (°C)	C	70	80	80	90	–	–
Reaction time (h)	D	2	2	3	3	–	4
Ventilation rate (L/min)	E	–	5	–	10	–	–
Interaction effect considered (test 1)	A × C, B × C, A × C						
Interaction effect considered (test 2)	A × C, B × C, D × E						

Table 2
Analysis of $L_8(2^7)$ array—orthogonal test 1

Test	C	B	B × C	A	A × C	A × B	D	Content of Fe$_3$O$_4$ (%)
	1	2	3	4	5	6	7	
1	1	1	1	1	1	1	1	53.13
2	1	1	1	2	2	2	2	57.99
3	1	2	2	1	1	2	2	59.15
4	1	2	2	2	2	1	1	57.99
5	2	1	2	1	2	1	2	59.50
6	2	1	2	2	1	2	1	50.58
7	2	2	1	1	2	2	1	58.22
8	2	2	1	2	1	1	2	57.65
I	228.26	221.20	226.99	230.02	220.51	228.27	219.82	
II	225.95	233.01	228.22	224.21	233.70	225.94	234.29	
$\bar{\text{I}} = \text{I}/4$	57.065	55.30	56.75	57.51	55.13	57.07	54.96	
$\bar{\text{II}} = \text{II}/4$	56.49	58.25	56.81	56.05	58.43	56.49	58.57	
$\bar{\text{I}} - \bar{\text{II}}$	0.575	−2.95	−0.06	1.46	−3.30	0.58	−3.61	
Influence	6	3	7	4	2	5	1	

method [18]. The content of Fe$_3$O$_4$ was calculated as three times that of acid-soluble iron(II) in the samples.

Transmission electron microscope (Model JEM-100CX, JEOL, Japan), Electrooptics analytical balance (Model TG328A, Shanghai Balance Instrument Factory, PR China), X-ray diffractometer (Model XD-3A, Shimadzu Co., Japan) were employed to analyze the products.

2.6. Thermodynamic assessment of synthesis of Fe$_3$O$_4$

The following assumptions are incorporated into the model: (1) the initial compounds in the reaction system are: FeSO$_4$·7H$_2$O, NaOH, NH$_4$NO$_3$, and H$_2$O; (2) compounds that appear in the system after chemical equilibrium are: NaSO$_4$, (NH$_4$)$_2$SO$_4$, NaNO$_3$, HNO$_3$, H$_2$O, NH$_4$OH, Fe(OH)$_2$, Fe(OH)$_3$, α-FeOOH, γ-FeOOH, Fe$_3$O$_4$, Fe$_2$O$_3$ and HNO$_2$; (3) the solution is fully mixed up; (4) the temperature and pressure in the reactor is constant.

2.6.1. Solution principles for Gibbs free energy minimization

Based on three equilibrium conditions which are:

$$G = \sum_i \mu_i n_i \quad (i = 1, 2, \ldots, N) \tag{1}$$

$$\sum_i a_{ij} n_i = B_j \quad (i = 1, 2, \ldots, N; \ j = 1, 2, \ldots, M) \tag{2}$$

$$\sum_i z_i n_i = 0 \quad (i = 1, 2, \ldots, N) \tag{3}$$

a new function could be constructed as follows:

$$L = \sum_{i=1}^{N} \mu_i n_i - \sum_{j=1}^{M} \left[\lambda_j \sum_{i=1}^{N} (a_{ij} n_i - B_j) \right] - \lambda_{M+1} \sum_{i=1}^{N} z_i n_i \tag{4}$$

Suppose the mole numbers of all the compounds in the system are affiliated to the equilibrium conditions (1)–(3), a boundary condition should be reached in order to minimize the Gibbs free energy of the system:

$$\frac{\partial L}{\partial n_i} = 0 \tag{5}$$

A system of simultaneous nonlinear equations could be drawn from Eqs. (4) and (5):

$$\mu_i - \sum_{j=1}^{M} \lambda_j a_{ij} - \lambda_{M+1} z_i = 0 \quad (i = 1, 2, \ldots, N) \tag{6}$$

For Eq. (6), there are N equations, $M + 1$ constraint conditions (Eqs. (2) and (3)) and $N + M + 1$ unknown numbers (n_i and λ_j).

2.6.2. Target function and its solving

According to the assumptions, there will be 13 compounds in the system after equilibrium and these compounds are composed of six elements in all (Fe, O, H, N, S, and Na). The a_{ij} matrix could be evaluated as follows:

$$a_{ij} = \begin{array}{c} \\ {}_1Fe \\ {}_2O \\ {}_3H \\ {}_4N \\ {}_5S \\ {}_6Na \end{array}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 3 & 2 & 0 \\ 4 & 4 & 3 & 3 & 1 & 1 & 2 & 3 & 2 & 2 & 4 & 3 & 2 \\ 0 & 8 & 0 & 1 & 2 & 5 & 2 & 3 & 1 & 1 & 0 & 0 & 1 \\ 0 & 2 & 1 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 2 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

B_j could be expressed by the mole numbers of the initial compounds according to conservation of mass:

$$B_1 = n_{\text{FeSO}_4 \cdot 7\text{H}_2\text{O}},$$

$$B_2 = 11 \times n_{\text{FeSO}_4 \cdot 7\text{H}_2\text{O}} + n_{\text{NaOH}} + n_{\text{H}_2\text{O}} + 3 \times n_{\text{NH}_4\text{NO}_3},$$

$$B_3 = 14 \times n_{\text{FeSO}_4 \cdot 7\text{H}_2\text{O}} + n_{\text{NaOH}} + 2 \times n_{\text{H}_2\text{O}} + 4 \times n_{\text{NH}_4\text{NO}_3},$$

$$B_4 = 2 \times n_{\text{NH}_4\text{NO}_3}, \qquad B_5 = n_{\text{FeSO}_4 \cdot 7\text{H}_2\text{O}}, \qquad B_6 = n_{\text{NaOH}}$$

Table 3
Analysis of modified $L_{16}(2^{15})$ array—orthogonal test 2

	Vacant	A			B			D			C	E	A × C		B × C		D × E		Content of Fe_3O_4 (%)
	1	2		3	4		5	6		7	8	9	10	11	12	13	14	15	
1	1	1	(1)	1	1	(1)	1	1	(1)	1	1	1	1	1	1	1	1	1	53.13
2	1	1	(1)	1	1	(1)	1	1	(1)	1	1	2	2	2	2	2	2	2	51.51
3	1	1	(1)	1	2	(2)	2	2	(2)	2	1	1	1	1	2	2	2	2	53.83
4	1	1	(1)	1	2	(2)	2	2	(2)	2	2	2	2	2	1	1	1	1	51.86
5	1	2	(2)	2	1	(1)	1	2	(2)	2	1	1	2	2	1	1	2	2	64.48
6	1	2	(2)	2	1	(1)	1	2	(2)	2	2	2	1	1	2	2	1	1	71.54
7	1	2	(2)	2	2	(2)	2	1	(1)	1	1	1	2	2	2	2	1	1	70.73
8	1	2	(2)	2	2	(2)	2	1	(1)	1	2	2	1	1	1	1	2	2	66.44
9	2	1	(2)	2	1	(2)	2	1	(2)	2	1	2	1	2	1	2	1	2	65.05
10	2	1	(2)	2	1	(2)	2	1	(2)	2	2	1	2	1	2	1	2	1	85.08
11	2	1	(2)	2	2	(3)	1	2	(3)	1	1	2	1	2	2	1	2	1	61.81
12	2	1	(2)	2	2	(3)	1	2	(3)	1	2	1	2	1	1	2	1	2	70.38
13	2	2	(3)	1	1	(2)	2	2	(3)	1	1	2	2	1	1	2	2	1	56.49
14	2	2	(3)	1	1	(2)	2	2	(3)	1	2	1	1	2	2	1	1	2	67.14
15	2	2	(3)	1	2	(3)	1	1	(2)	2	1	2	2	1	2	1	1	2	65.05
16	2	2	(3)	1	2	(3)	1	1	(2)	2	2	1	1	2	1	2	2	1	89.02
I_j	483.52	492.65		488.03	514.42		526.92	546.01		497.63	490.57	553.79	527.96	521.94	516.85	514.99	514.88	539.66	$\sum_{i=1}^{16} y_i = 1043.54$
II_j	560.02	550.89		555.51	529.12		516.62	497.53		545.91	552.97	489.75	515.58	521.60	526.69	528.55	528.66	503.88	
$I_j - II_j$	−76.50	−58.24		−67.48	−14.70		10.30	48.48		−48.28	−62.40	64.04	12.38	0.34	−9.84	−13.56	−13.78	35.78	$S_{total} = \sum_{i=1}^{16} y_i - \left(\sum_{i=1}^{16} y_i\right)^2 /16 = 1793.76$
$(I_j - II_j)^2$	5852.25	3391.90		4553.55	216.09		106.09	2350.31		2330.96	3893.76	4101.12	153.26	0.1156	92.83	183.87	189.89	1280.2	
$S_j = (I_j - II_j)^2/16$	365.79	211.99		284.60	13.51		6.63	146.89		145.68	243.36	256.32	9.58	0.071	6.05	11.49	11.87	80.01	

Table 4
Analysis of variance in orthogonal test 2

Source	d.f. (degree of freedom)	SS (sum of squares)	MS (mean sum of squares)	F
A	2	496.59	248.295	51.46
B	2	20.14	10.07	2.087
C	1	243.36	243.36	50.44
D	2	292.57	146.285	30.32
E	1	256.32	256.32	53.12
$A \times C$	2	9.65	4.825	
$B \times C$	2	17.54	8.77	1.82
$D \times E$	2	91.88	45.94	9.52

Target function of the simulated reaction system evaluated according to Eq. (4) is:

$$L = \sum_{i=1}^{13} \mu_i n_i - \sum_{j=1}^{6} \left[\lambda_j \sum_{i=1}^{13} (a_{ij} n_i - B_j) \right] \qquad (7)$$

The chemical potential of compound i is:

$$\mu_i = \mu_i^0 + RT \ln(\gamma_i m_i) \qquad (8)$$

A system of nonlinear functions could be deduced from Eqs. (2), (5), (7) and (8):

$$\mu_i^0 + RT \ln(\gamma_i m_i) - \sum_{j=1}^{6} (\lambda_j a_{ij}) = 0 \quad (i = 1, 2, \ldots, 13),$$

$$\times \sum_{i=1}^{13} a_{ij} n_i - B_j = 0 \quad (j = 1, 2, \ldots, 6) \qquad (9)$$

Activity coefficients of the compounds were calculated with the Pitzer's method and long-range electrostatic interaction and hard-core repulsion were taken into account [19]. Density and dielectric constant of H_2O were assumed to be constant with temperature. Only long-range electrostatic contribution was considered in the calculation of activity coefficients of NH_4OH, HNO_2, $Fe(OH)_2$ and $Fe(OH)_3$. And activity coefficients of H_2O, α-FeOOH, γ-FeOOH, Fe_3O_4 and Fe_2O_3 were approximately equal to 1. Parameters were obtained to from literatures [20,21].

Eq. (9) was solved with Newton's iteration method [22]. The initial values for iterative calculation were selected as follows: (1) the elements of S, Na and N exist in less compounds (2, 2 and 4 compounds respectively), mole number of compounds containing these three elements should be balanced firstly; (2) mole number of compounds containing the element Fe were balanced; (3) the rest elements were O and H; if mole number of H was twice of O, they will be considered as H_2O; if H is

Table 5
Fe₃O₄ yield among different levels

Factor	Symbol	Level 1 (%)	Level 2 (%)	Level 3 (%)	Level selected
Concentration	A	53.72	69.44	68.285	$A_2(A_3)$
Temperature	C	61.32	69.12	–	C_2
Reaction time	D	68.69	68.24	56.145	$D_1(D_2)$
Ventilation	E	69.22	61.22	–	E_1

Table 6
Fe₃O₄ yield under $D \times E$ interaction effect

	E_1 (%)	E_2 (%)
D_1	75.38	60.65
D_2	73.10	63.375
D_3	54.81	57.475

excess, reduce the number of HNO_3 and increase the number of NH_4NO_3 with the same amount until mole number of H was twice of O, and calculate it oppositely if the element O is excess.

The calculations were achieved with self-compiling MAT-LAB programs.

3. Results and discussion

3.1. Synthesis of Fe₃O₄ with air as oxidant

Table 2 shows the results of orthogonal test 1. It was found that in orthogonal test 1, the importance order of the influence factors in Fe_3O_4 synthesis was: $D > A \times C > B > A$. And temperature had only little effect on Fe_3O_4 yield. Fe_3O_4 content was between 53.13% and 59.15% in the eight experiments.

Levels of the factors in orthogonal test 2 were selected based on the results of orthogonal test 1. Table 3 indicates the analysis results of orthogonal test 2. Variance analysis could be drawn from Table 3. And Table 4 shows the variance comparison results of synthesis results with different levels. It is obvious in Table 4 that the main factors influencing Fe_3O_4 synthesis were: A, C, D, E, and $D \times E$. The content of Fe_3O_4 obtained varies little in the selected pH value range.

Table 5 shows the comparison of Fe_3O_4 yield among factors A, C, D and E. According to the comparison results of Table 5, levels 2 and 3 of A factor, level 2 of C factor, levels 1 and 2 of D factor and level 1 of E factor are selected respectively.

The interaction contribution of D and E was shown in Table 6. It could be deduced from Tables 5 and 6 that $D_1 \times E_1$ interaction contributes most in Fe_3O_4 synthesis, and the best synthesis condition for Fe_3O_4 synthesis is $A_2B_1(B_2B_3)$ $C_2(C_3)$ D_1E_1, which means that, after 2 h reaction at 90 °C under the aeration rate of 5 L/min, solution containing 0.25–0.35 mol/L iron(II) ion initially would yield the greatest amount of Fe_3O_4. pH value varying between 9.0 and 11.0 causes little difference to the content of Fe_3O_4.

Three parallel experiments was carried on under the synthesis condition of $A_2B_3C_3D_1E_1$, and Fe_3O_4 contents in the product were 91.55%, 91.15%, and 91.90%, respectively.

Another two experiments were carried over on the base of the $A_2B_3C_3D_1E_1$ condition. One prolong the synthesis time to 2.5 h without changing the other conditions, and the other increase the concentration of initial iron(II) ion to 0.45 mol/L without changing the other conditions. The contents of Fe_3O_4 in the products were 87.05% and 83.27%, respectively.

It seems that Fe_3O_4 content in the product could not be enhanced to a percentage higher than 92% with air as the oxidant, neither through prolong reaction time nor through increase reactant concentration. The probable reason is that the oxidation
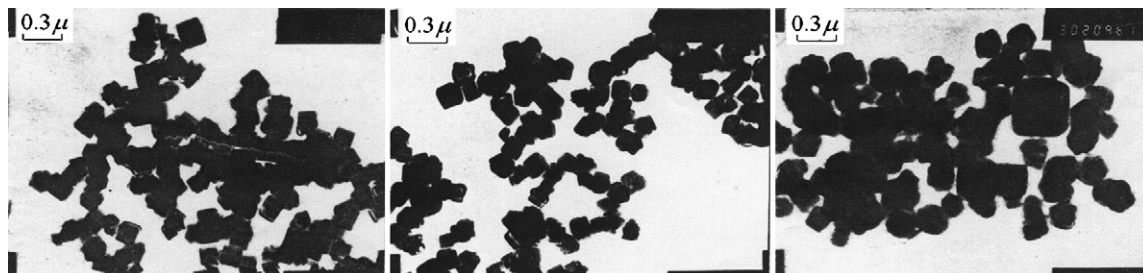
Fig. 3. TEM image of samples (left to right: sample 2; sample 3; sample 4).

ability of oxygen in the air is too strong that the surface of newly formed Fe_3O_4 particles will be oxidized.

3.2. Synthesis of Fe_3O_4 with NH_4NO_3 as oxidant

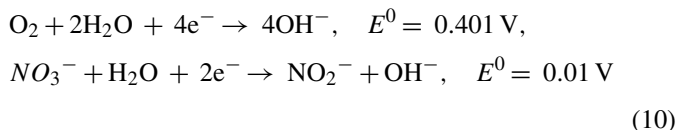Oxidation abilities of oxygen and NH_4NO_3 are compared in expression (10) as follows:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-, \quad E^0 = 0.401\,V,$$

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + OH^-, \quad E^0 = 0.01\,V$$

$$(10)$$

Table 7 shows Fe_3O_4 content in the products with the oxidant of NH_4NO_3. It could be seen in Table 7 that when the concentration of NH_4NO_3 was between 2.5 g/L and 10 g/L, Fe_3O_4 content in the products all exceed 95%. Fe_3O_4 yield reduced dramatically when concentration of NH_4NO_3 was below 2.5 g/L, which indicates that the amount of oxidant influences Fe_3O_4 synthesis most.

The TEM images of samples 2, 3 and 4 are illustrated in Fig. 3. Crystal size of samples 2, 3 and 4 are 0.18 μm, 0.16 μm and 0.20 μm, respectively.

The results also show that the best condition for Fe_3O_4 synthesis is—temperature: 90 °C, pH: 9–11, initial iron(II) ion concentration: 0.35 mol/L, NH_4NO_3 concentration: 10 g/L, and reaction time: 2 h. Under this condition, the product has the best morphology and undertone with a high Fe_3O_4 content (>95%). Table 8 shows that the lattice constant of sample 4 is

Table 7
Fe_3O_4 content in the products with the oxidant of NH_4NO_3

	Test label					
	1	2	3	4	5	6
NH_4NO_3 concentration (g/L)	1.25	2.5	6	10	15	25
Fe_3O_4 content (%)	63.78	96.28	96.09	95.67	91.02	88.36

Table 8
Comparison among samples

Sample	Sample description	
	Lattice constant (Å)	Fe_3O_4 content (%)
C.P. Fe_3O_4	8.404	98.00
Sample 4	8.411	95.67
Commercial ferrite	8.413	89.28

approximate to chemically pure Fe_3O_4 and commercial ferrite, while Fe_3O_4 content of sample 4 is higher than commercial ferrite. Spinel structure indicated in X-ray diffraction (XRD) image shows that the product is Fe_3O_4.

3.3. Thermodynamic assessment of Fe_3O_4 synthesis

Fig. 4a shows the effect of the amount of NH_4NO_3 on product yield. It could be deduced that in 400 mL solution containing 0.4 mol/L $FeSO_4 \cdot 7H_2O$ and 0.8 mol/L NaOH initially at 25 °C, the amount of NH_4NO_3 has great effect on synthesis product. The amount of NH_4NO_3 influences the distribution of iron in different species greatly. According to Fig. 4a, $Fe(OH)_2$ is the main product with a low oxidant concentration. As the oxidant amount increases, the amount of $Fe(OH)_2$ decreases sharply. Fe_3O_4 become the main product when the amount of NH_4NO_3 is about 1.25 g. As the amount of oxidant increases to about 1.6 g, almost all the $Fe(OH)_2$ are oxidized and trivalent species increase. As the amount of NH_4NO_3 exceeds 1.6 g, the amount of α-FeOOH increases greatly with a corresponding decrease in the amount of Fe_3O_4 and other by-products. From the aspect of thermodynamics, it seems that the amount of oxidant should be controlled below 4 g if a high content of Fe_3O_4 is to be obtained, otherwise α-FeOOH will become the main component of the product. The amount of NH_4NO_3 should also exceeds 1.25 g to avoid $Fe(OH)_2$ being the main product. And this result is generally consistent with the experimental results.

Differentiation appears between the results of thermodynamic assessment and experiment as the amount of oxidant exceeds 3.0 g. It may be due to the following reasons: (1) the assessment did not take dynamics into account, while the experiment is carried on in limited time span; (2) with the increase of amount of NH_4NO_3, ion strength in the solution changes greatly and it is not taken into account in the assessment.

Fig. 4b illustrates the effect of temperatures on synthesis product when the concentration of NH_4NO_3 was 2.5 g/L. With the temperature varying from 25 °C to 90 °C, the constitution of the product changes little. A high temperature is good for Fe_3O_4 synthesis.

R value is an index concerning the pH of the solution. In the range between 25 °C and 75 °C, the amount of Fe_3O_4 synthesized increases with the increasing of R value (Fig. 4c). As the temperature arises to 90 °C, it comes to the opposite. Fig. 4c indicates that there is some relationship between temperature and pH of the solution. And between 25 °C and 75 °C, the Fe_3O_4 yield
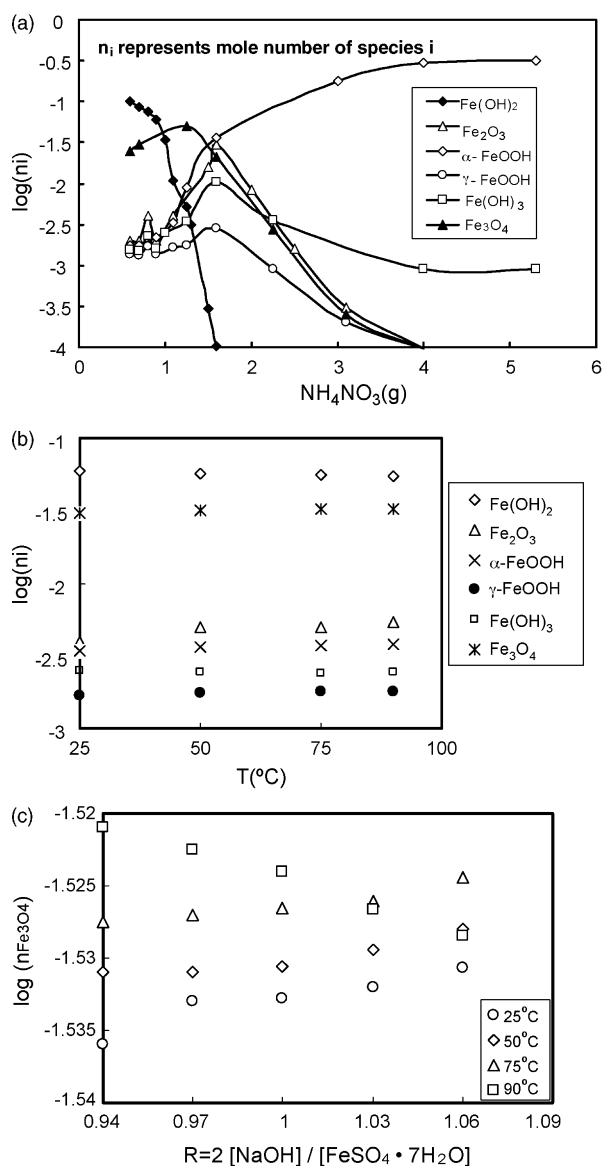
Fig. 4. Effect of NH_4NO_3 amount (a), temperature (b) and R value (pH) (c) on product yield.

stays constant despite the change of R value, which is consistent with the phase diagram shown in Fig. 1.

4. Conclusions

(1) Synthesis condition for Fe_3O_4 production was investigated with orthogonal tests under the oxidation of air. It seems that Fe_3O_4 content in the product could not be enhanced to a percentage higher than 92% with air as the oxidant, neither through prolong reaction time nor through increase reactant concentration.

(2) The results show that the best condition for Fe_3O_4 synthesis is—temperature: 90 °C, pH: 9–11, initial iron(II) ion concentration: 0.35 mol/L, NH_4NO_3 concentration: 10 g/L, and reaction time: 2 h. Under this condition, the product has the best morphology and undertone with a high Fe_3O_4 content (>95%).

(3) XRD characterization indicates that the product is pure magnetite with spinel structure.

(4) In the range between 25 °C and 75 °C, the amount of Fe_3O_4 synthesized increases with the increasing of R value. As the temperature arises to 90 °C, it comes to the opposite.

(5) Considering both the experimental results and assessment results, it is found that Fe_3O_4 yield differs in the Fe_3O_4 forming area given by Kiyama (Fig. 1). Fe_3O_4 yield in A and B area will be higher than that of C and D area.

Acknowledgements

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