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Microwave assisted solid state reaction synthesis of methionine complexes of iron (II)

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Abstract

Methionine complexes of iron (II) were synthesized by employing a simple and novel microwave assisted solid state route in a domestic microwave (MW) oven (2.45 GHz frequency, 700 W power) and six crucial reaction parameters were investigated on the basis of their individual effects on the yield of the synthesized compounds. Results suggest that optimal synthesis conditions are microwave irradiation time, 260 s; the airflow temperature, 100 °C; and the amount of reactant, 1.5 g. The synthesized compounds were characterized by infrared spectrometry. From the results of chemical analysis and infrared spectrometric analyses, the minimum molecular formula of the synthesized compounds could be determined as $Fe(Met)_2 \cdot H_2O$, in which iron, nitrogen element and water account for 15.93%, 7.97% and 0.07%, respectively. The microwave method was found to be simple, fast and efficient, with high selectivity for the preparation of these compounds.

Keywords: Microwave irradiation; Solid state; Chemical reaction; Methionine complexes of iron (II)

1. Introduction

Iron, which is one of the most important microelements for human health and is known to interact with numerous other dietary components (Lynch, 1997), often exists in the state of complex in the body, which endows it a great deal of physiological function. Many materials, such as some closed ring tetrapyrroles: haem, chlorophyll, vitamin B12 and coenzyme F430, are capable of chelating a metal ion (Al-Karadaghi, Hansson, Nikonov, Jönsson, & Hederstedt, 1997). Iron in the form of complex may take part in the process of transportation and exchange of the oxygen in blood and also participates in other important metabolism as iron enzyme. However, because Fe^{2+} in the food has a low biological value it may exchange into the insoluble compounds, which are hard to be adsorbed for its characters of being prone to be oxidized and interrupted by oxalate, phosphate (Goldstein & Samuni, 2005). The deficiency of iron micronutrient is one of the most prevalent nutritional problems of humans in developing countries. It has been shown that growing children and women of reproductive age are most vulnerable to the deficiency (Bloem, 1995; Ribaya-Mercado, 1997). To overcome low efficiency of iron absorption has become a focus of recent investigations by nutritionists. Studies show that iron absorption in the body is influenced by several factors, including animal species, dietary factors, i.e. ascorbic acid (Monsen, 1988), pectin content, phytate (Morris & Ellis, 1982), protein sources and amino acids (Martinez-Torres, Romano, & Layrisse, 1981) and the other minerals. Amino acids, especially cysteine and reduced N-terminal cysteine peptides, are capable of enhancing iron uptake from both soluble and insoluble ferric iron (Glahn & Van Campen, 1997). The effects of these amino acids on iron absorption have also been studied in both human and rat models (Taylor, Martinez-Torres, Romano, & Layrisse,

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1986; Van Campen, 1973). Of the amino acid chelated products, Iron methionine also has more bioavailable iron than ferrous sulfate (Spears, Schoenherr, Kegley, Flowers, & Alhusen, 1992).

To the best of our knowledge, amino acid chelating metal ions are usually synthesized in solution (Saladini, Iacopino, & Menabue, 2000), which has involved lots of disadvantages, such as longer synthesis time, higher cost, environment pollution, wastes of large quantities of organic solvent and complicated synthesis technology (Halling, Ulijn, & Flitsch, 2005). These become a bottleneck to use the chelation reaction. Compared with traditional solution-state chemistry, solid-state synthesis via a route assisted by microwave irradiation has gained increasing attention due to simplification of reaction work-up and product isolation, rate-enhancements and higher product yields (Kirschning, Monenschein, & Wittenberg, 2001; Larhed & Hallberg, 2001). It has been recently found that apart from a wide variety of chemical reactions in the solution state to be accelerated by microwave irradiation of reactants (Landry, Lockwood, & Barron, 1995; Ramesh, Vaidhyanathan, Ganguli, & Rao, 1994; Vaidhyanathan, Ganguli, & Rao, 1994), relatively few reports have appeared on the microwave-assisted solid state synthesis, for example, of complex oxides like cuprates (Manoharan, Swati Prasanna, Rao, & Sahu, 2002), vanadates (Vaidhyanathan, Ganguli, & Rao, 1995), tungstates (Mingos & Baghurst, 1992), and ferrites (Krage, 1981). This indicates that application of microwave irradiation to organic synthesis possesses a promising future.

In recent years, although microwave irradiation has been applied to organic synthesis in solid state, including carbohydrates (Ge, Pang, & Luo, 2006; Li, Le, Cheng, Wang, & Shi, 2006; Li, Le, Shi, 2006; Liu, Li, Fang, & Chen, 2005) and amino acids (García-Tellado, Loupy, Petit, & Marrero-Terrero, 2003; Gelens et al., 2005; Lopez-Cobenas et al., 2006; Su, Wan, Zha, & Mu, 2001), to the best of our knowledge, there have been no reports of microwave assisted solid state synthesis of methionine complexes of iron (II) in the literature. The purpose of this paper is to determine optimal synthesis parameters of methionine complex of iron (II) in solid state reaction under microwave irradiation, in order to base for large-scale use. Therefore, effects of irradiation time, quantity of initiator, the particle size of reactants, quantity of adsorbent material, airflow temperature and the rate of airflow on the yield of the prepared complexes were investigated in the present study. The synthesized compounds were analysed by infrared spectroscopy.

2. Materials and methods

2.1. Chemicals

The methionine and the ferrous sulphate ($FeSO_4$) are supplied by China medicine ShangHai chemical reagent company (Shanghai, China); all other reagents, unless specified, were of analytical grade and were used without further purification.

2.2. Ligand synthesis

The chemical reaction (methionine complexes of iron (II)) was carried out in a closed glass container containing 20 g reactants (methionine and ferrous sulphate), various amounts of water as initiator and of silica dioxide as adsorbent material. The reaction mixture was then exposed to microwave irradiation in a modified domestic microwave oven (Haier company in China, operation frequency: 2450 MHz) for various time intervals with stirring. At the same time, airflow was introduced into a buffer bottle for timely removal of by-product sulfuric acid. After the reaction was completed, the reaction mixture was cooled, smashed up and dissolved into deionized water. The resulting solution was collected by filtration, extracted with methanol and finally dried in air to obtain the desired product.

2.3. Experimental design

On the basis of single-factor experiment for the production of complexes, proper ranges of microwave heat time, airflow temperature, rate of airflow, and the amount of reactant were preliminarily determined. When microwave heat time and airflow temperature were, respectively, 180 s and 85 °C, percent of the synthesized compounds rapidly increased. When microwave heat time and airflow temperature exceeded, respectively, 300 s and 95 °C, percent of the synthesized compounds reached peak value. This indicated that there existed a potential relation between percent of the synthesized compounds and reaction factors. Therefore, a three levels, three variables quadratic regression composite rotatable design was applied to determine the best combination of reaction variables for the production of methionine complexes of iron (II). Based on the investigations on single-factor experiment, the variables considered were microwave heat time, airflow temperature, and the amount of reactant in the experimental design (Table 1).

2.4. Analytical methods

2.4.1. Determination of nitrogen and ferrous ion content

Nitrogen content was determined according to the method of Kjeldahl described by Benton (1991).

Table 1
The levels of factors

Coded levels	Heat time (s)	Airflow temperature (°C)	Amount of reactant (g)
r	260	100	2.3
1	240	90	2.0
0	210	75	1.5
−1	180	60	1.0
−*r*	160	50	0.7

The synthesized compounds were analyzed for quantifying ferrous ion content. Ferrous ion was able to form a colored complex with 1,10-phenanthroline; therefore, its concentration was determined by using the spectrophotometer (SHIMADZU, UV-1201, Japan) with the light wavelength set at 510 nm according to the method described by Miglioranza et al. (2003).

2.4.2. Infrared spectrum analysis

The powder sample and KBr were dried at constant temperature container until use and ground to reduce the particle size to less than 5 mm in diameter. A small amount of sample powder was sealed within a KBr pellet by a hydraulic press (200 kg/cm^2, 15 s) and then the spectrum of sample was recorded by using Nexus Fourier transform infrared spectroscopy (America Thermo Nicolet Co., scanning range: 7800–350 cm^{-1}, resolution: 0.5 cm^{-1}, with DTGS detector, signal-to-noise ratio: 0.09 cm^{-1}) in the region 500–4000 cm^{-1} in KBr pellet. The spectrum was collected with a resolution of 2 cm^{-1} by coadding the results of 16 scans.

3. Results and discussion

3.1. The mole ratio of methionine to ferrous ion

Different mole ratios of methionine to ferrous ion are important to the synthesis of methionine complexes of iron (II). Compared with the conventional solution method, microwave assisted solid state reaction synthesis of the complexes is advantageous for designing of the polymeric frameworks due to availability of selective donor sites which could facilitate coordination to metal ions with diverse electronic properties, coordination numbers and geometries (Bagnell, Kreher, & Strauss, 2001). If the mole ratio is too small, the complex formed is instable due to lack of stable ring structure. In contrast, it will be a waste of methionine, if the mole ratio is too large. Therefore, the coupling was performed at 80–100 °C with a 2:1 [n(Met)/n(Fe)] mole ratio in this study.

3.2. Effect of microwave irradiation time on the yield of the synthesized compounds

Microwave heating has been demonstrated to be a very promising non-conventional tool for the solid state laboratory synthesis of many compounds. In the microwave assisted solid-state reaction synthesis of methionine complexes of iron (II), microwave irradiation time is one of the crucial factors to raise the yield of the synthesized compounds. Here, microwave irradiation time was, respectively, set at 30, 60, 90, 120, 150, 180, 210, 240 and 270 s to examine the influence of irradiation time on the yield of the synthesized compounds when other reaction conditions were as follows: initiator (water) 12%, adsorbent material (silicon dioxide) 14%, reactants particle size 120 mesh, the airflow temperature 80–100 °C, and the airflow rate 11–13 g/s.

As shown in Fig. 1a, the yield of the synthesized compounds increased with the increase of irradiation time. The synthesized compounds achieved a maximum percentage of 80% when the irradiation time was 180 s. After this point, the yield of the synthesized compounds started to decrease with increasing the irradiation time. Excessive microwave irradiation drastically raises reaction temperature. Although the increased reaction temperature promotes the chemical reaction, at the same time it also hastens the decomposition of the synthesized compounds. When the speed of the latter exceeds that of the former, the yield of the synthesized compounds starts to decrease. Therefore, 180 s irradiation time was adopted in the work.

3.3. Effect of addition of initiator on the yield of the synthesized compounds

Addition of a small amount of water to the reaction mixture (methionine and ferrous sulphate) in the solid state

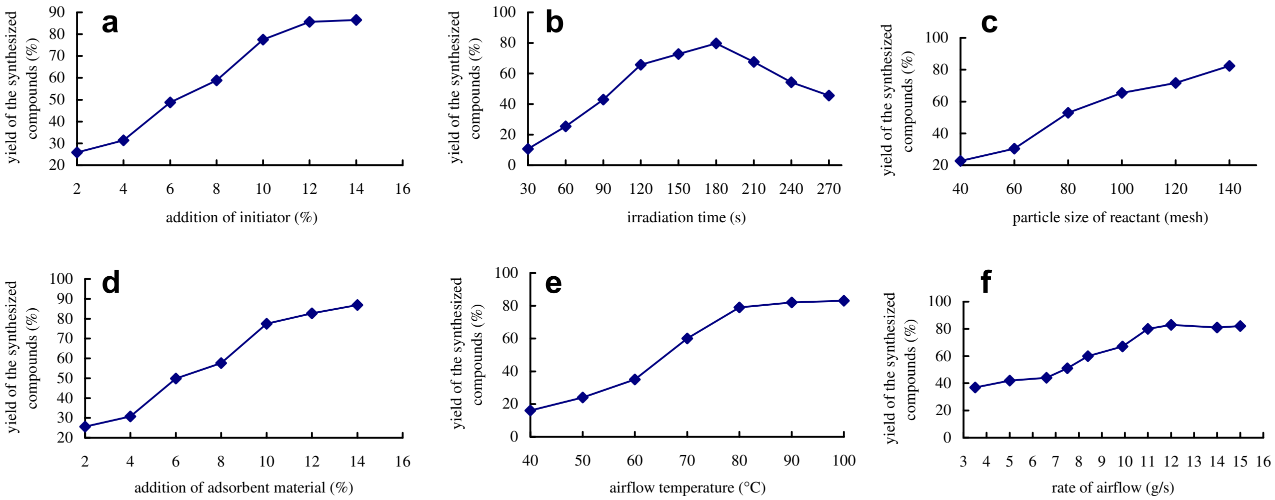

Fig. 1. Variation of the yield of the synthesized compounds with microwave irradiation time (a), addition of initiators (b), particle size of reactants (c), addition of adsorbent material (d), the airflow temperature (e) and the rate of airflow (f) during the reaction process.

under microwave irradiation enhanced the activity of the adsorbent material and absorption of microwave energy, and for that reason, the experiments were performed in the presence of an initiator (water). Some solvents, like water, ethanol, acetic acid and methanol, which are used as initiators, can effectively absorb microwave energy to accelerate the reaction. Once the reaction is initiated, the acid consumed can be quickly supplied from product of the reaction. As a result, this can absorb microwave energy again to accelerate the reaction. Although the addition of an initiator to the reaction mixture cannot have a significant effect on the degree of reaction of the materials, it may in theory accelerate the reaction speed at the start of the reaction. Moreover, the synthesized compounds may avoid to burn out and decompose due to the addition of the initiator. This provides an advantage for the reaction (Sakai, 1987).

In this research, quantity of water as an initiator was set at 2%, 4%, 6%, 8%, 10%, 12% and 14% of the total reaction mixture to investigate the influence of the initiator on the yield of the synthesized compounds when other reaction conditions were similar to those described in Section 3.2. It could be demonstrated that the yield of the synthesized compounds increased with an increasing quantity of initiator (Fig. 1b). Therefore, it may be concluded that the yield of the synthesized compounds is proportional to the quantity of initiator under the experimental conditions employed in this work. The yield of the synthesized compounds was close to the peak value when the quantity of initiator was set at 12%. The percentage value started to slowly increase with the continuously increasing quantity of initiator. When the quantity of initiator increased, the concentration of reaction mixture decreased. Decreased concentration of reactants was a disadvantage to the chemical reaction. In order to improve reaction yields and reduce reaction times, 12% of the initiator, using statistical model, was found to be acceptable.

3.4. Effect of particle size of reactants on the yield of the synthesized compounds

The degree of accessibility between the reactant particles, the speed of crystallization and self-renewal of grain on the surface of product are the three crucial factors that determine the speed of the chemical reaction in the solid state under microwave irradiation (Glas & Thiel, 1998). In this research, particle size of reactants was in turn set at 40, 60, 80, 100, 120 and 140 mesh. Other reaction conditions were similar to those described in Section 3.2. Fig. 1c shows the effect of particle size of reactants on the yield of the synthesized compounds. The results indicated that particle size of reactants was inversely proportional to the yield of the synthesized compounds. In other words, the smaller the particle size of reactants was, the higher the yield of the synthesized compounds. The yield of the synthesized compounds was close to the peak value (82.41%) when particle size of reactants was 140 mesh. Examination of the data in Fig. 1c reveals that reducing the particle size of reactants may enhance the yield of the synthesized compounds by facilitating the intimate contact between the reactant particles. However, this will also increase the processing cost of raw materials used in the study. Therefore, 120 mesh particle size was adopted to economically perform the synthesis in this work.

3.5. Effect of addition of adsorbent material on the yield of the synthesized compounds

In the synthesis of the complex in the absence of solvent, both chloride and sulphate are often utilized as donor of metal ions. Acids produced by the reaction need to be neutralized by the addition of alkali. Some weak acid salts, such as acetate, whose by-product produced by the reaction is volatile acid which cannot stop the chemical reaction, are usually used as donor of metal ions. However, when strong acid salts, such as sulphate, are used, timely removal or neutralization of by-products (strong acid with a high boiling point) produced by the reaction becomes necessary for the maintenance of the chemical reaction initiated. Otherwise, these strong acids can accelerate decomposition of the synthesized compounds with increasing the temperature. In addition, the coordination capacity of different acid radicals is often affected by the discrepancy in electric charge, electron cloud density and steric hindrance. Both large steric hindrance of acid radicals and slight water solubility of methionine are the important causes of retarding the chemical reaction in solid state under microwave irradiation. Although ferrous acetate as donor of metal ion possesses the advantage described above, but its high cost makes the synthesis unpractical. Therefore, ferrous sulfate, which is cheap, was used in this work. Moreover, sulfuric acid produced by the reaction can be eliminated by the addition of adsorbent material. Usually, to choose adsorbent materials is important, because some of them may oxidize Fe^{2+} in the reaction. In the present study, silicon dioxide was chosen as the adsorbent material. Silicon dioxide has stronger adsorption capacity to acid and will not react with methionine and ferrous sulphates, so it does not promote decomposition of Met–Fe(II) chelates. Moreover, because silicon dioxide is water insoluble, it does not easily cause hot-spot areas under microwave irradiation and influence the extraction of the product.

In this study, the quantity of silicon dioxide as adsorbent material was set at 2%, 4%, 6%, 8%, 10%, 12% and 14% of the total reaction mixture to investigate the effect of the addition of adsorbent material on the yield of the synthesized compounds when other reaction conditions are similar to those described in Section 3.2. When the reaction was carried out in the presence of an increasing quantity of adsorbent material, the reaction was remarkably enhanced. The percentage of the prepared complex reached a peak value when the quantity of silicon dioxide was set between 12% and 14% (Fig. 1d). From these results, we infer that quantity of silicon dioxide between 12% and 14% is ideal for achieving the desired yield of the synthesized compounds considering concrete reaction condition.

3.6. Effect of airflow temperature on the yield of the synthesized compounds

In recent years the use of inorganic and organic reagents under solvent-free conditions has rapidly increased, as these reactions often involve milder conditions, easier work-up, and higher selectivity than similar reactions in solution. The rule of the solvent-free reaction makes it clear that the dispersion of reagents and the nucleation of product phases determine the time before the reaction is initiated (Larhed & Hallberg, 2001). Temperature significantly affects the two processes. The higher the temperature is, the faster the dispersion of reagent and nucleation of product phases. This makes the reaction easier to take place and shortens the reaction time. Temperature may initiate heterogeneously the processes of product grain growth, and when observed to do so the tendency for growth to take place in randomly orientated clusters suggests that temperature influencing nucleation and growth. Therefore, temperature of the reaction system is a key factor that strongly affects the nucleation speed of the product phases. The low reaction temperature will slow down the chemical reaction in solid state. The high reaction temperature is advantageous to the dispersion of reagent and the nucleation of the product phases (Xing et al., 2005).

In this study, airflow temperature was in turn set at 40, 50, 60, 70, 80, 90 and 100 °C. Other reaction conditions are similar to those described in Section 3.2. The effect of airflow temperature on the yield of methionine complexes of iron (II) was investigated in the range of 40–100 °C (Fig. 1e). Experimental results indicated that the yield of the synthesized compounds gradually increased with increasing temperature and reached approximately 80% at 80 °C. One potential cause for this may be that low airflow temperature can competitively absorb microwave energy, and that high airflow temperature can easily remove acid (the by-product produced by the reaction), and give an impetus to the nucleation of product phase. However, if the airflow temperature is too high, the relaxation time for microwave irradiation will change with the expansion of distance between molecules. The absorption efficiency of microwave radiation will decline. This causes microwave magnetron no-load operation, as a result of which microwave transmission becomes unstable and the chemical reaction is out of control (Galperin & Chao, 2000). In order for the domestic oven to operate it was essential that it was fully loaded at all times as it contained a safety mechanism that switched the magnetrons off when there was no-load operation within the cavity. In this work, it can be seen that good result can be obtained when the airflow temperature was controlled between 80 and 100 °C. So, airflow temperature range of 80–100 °C was adopted.

3.7. Effect of the rate of airflow on the yield of the synthesized compounds

The absorption of microwave energy is determined by the dielectric properties, the dielectric loss factor and the dielectric constant (Vaidhyanathan, Raizada, & RAO, 1997). The larger the dielectric loss factor and the dielectric constant are, the higher the absorption efficiency of microwave energy will be. Explanation for this may be that larger distance between molecules can promote gas molecules to effectively absorb microwave energy (Vallin, 2000).

In another set of experiments, the rate of airflow was in turn set at 3.5–15 × 100 g/s. Other reaction conditions are similar to those described in Section 3.2. As is shown in Fig. 1f, when airflow temperature was set at 80 °C, there would be a suitable distance between molecules, which results in the airflow coupling with the microwave irradiation and speeding up the reaction. A higher airflow rate may ensure quick removal of sulphuric acid, so it can increase the yield of the synthesized compounds. However, if the rate of airflow is excessively high, it can competitively absorb microwave energy and shift the position of thermodynamic equilibrium by removal of the water produced by the reaction. This was adverseous to affect the yield of the synthesized compounds, and we found that the yield of the synthesized compounds declined when the rate of airflow was too high. When the rate of airflow was set at 12 g/s, the yield of the synthesized compounds reached approximately 83 % in the reaction process. Therefore, we adopted an airflow rate of 11–13 g/s.

3.8. Optimization of the production of methionine complexes of iron (II)

Table 2 shows the experimental conditions and the results of the production of methionine complexes of iron (II) according to the factorial design. In this experiment, percent of the synthesized compounds in Nos. 3, 4, 7 and 8 groups was 20% higher than the corresponding value in Nos. 1, 2, 5 and 6 groups (Table 2). Percent of the synthesized compounds in No. 12 group was 34.59% higher than the corresponding value in No. 11 group and reached 83.51% (Table 2). Maximum yield of the complexes (83.51%) was recorded under the experimental conditions of microwave heating time, 210 s; airflow temperature, 100 °C; and amount of reactant, 1.5 g. The lowest yield of the complexes (48.92%) was observed in the test set No. 11 group (compared to all others). Statistical analysis revealed that the most relevant variable ($p < 0.001$) for the complexes production was airflow temperature and amount of reactant. The effect of microwave heat time on percent of the complexes is not significant. (Table 3). Airflow temperature, which determined initial condition of the reaction, was closely associated with the reaction speed. When airflow temperature is lower, only prolonging heat time (>160 s) cannot obviously raise percent of the synthesized compounds. Amount of reactant is a key factor to

Table 2
The data and results of experiments

Group	X_1	X_2	X_3	Heat time (s)	Airflow temperature (°C)	Amount of reactant (g)	Percent of the complexes (%)
1	−1	−1	−1	180	60	1.0	56.06
2	−1	−1	1	180	60	2.0	54.95
3	−1	1	−1	180	90	1.0	73.70
4	−1	1	1	180	90	2.0	71.37
5	1	−1	−1	240	60	1.0	59.67
6	1	−1	1	240	60	2.0	56.36
7	1	1	−1	240	90	1.0	79.20
8	1	1	1	240	90	2.0	75.80
9	−1.682	0	0	160	75	1.5	68.70
10	1.682	0	0	260	75	1.5	78.62
11	0	−1.682	0	210	50	1.5	48.92
12	0	1.682	0	210	100	1.5	83.51
13	0	0	−1.682	210	75	0.7	67.32
14	0	0	1.682	210	75	2.3	55.46
15	0	0	0	210	75	1.5	74.13
16	0	0	0	210	75	1.5	73.98
17	0	0	0	210	75	1.5	74.65
18	0	0	0	210	75	1.5	74.86
19	0	0	0	210	75	1.5	74.19
20	0	0	0	210	75	1.5	74.82

forming shape of filter mass. When the amount of reactant is 1.5 g, the effect is better.

The regression equation describing the effect of the process variables (X_1, X_2, X_3) on percent of the synthesized compounds (Y) is given as $Y = 3.87X_1 + 16.07X_2 - 3.55X_3 + 1.70X_1X_2 - 1.09X_1X_3 - 0.43X2_2X_3 - 0.90X_1^2 - 8.34X_2^2 - 13.18X_3^2$.

The statistical significance of the regression equation was checked by *F*-test, and the results are summarized in Tables 3 and 4. The model *F*-value analysis of the regression equation indicated that there was a strong and significant influence of regression linear coefficients (X_1 and X_2) on the response value (Y). All the mutual interactions among the tested variables are insignificant. Although the determinant coefficients (R^2) of the regression equation are equal to 0.9846, the value of lack-of-fit for regression equation is not significant, indicating that both response value (Y) and factors had no significant ($p > 0.05$) linear effect on the model (Table 4). In addition, It was observed from the statistical analysis that rate of airflow is closely associated with airflow temperature and microwave heat time. Statistical analysis conducted on the data showed that airflow temperature and amount of reactant had significant ($p < 0.05$) effects on the percent of the complexes during the synthesis operation. It was found that airflow temperature had a positive correlation with the percent of the complexes, and that higher airflow temperature led to relatively higher yield. It was also found that microwave heat time had a positive correlation with the percent of the complexes, but the relationship was not significant. Even though the trends were similar, higher airflow temperature led to relatively higher yield than microwave heat time. However, the amount of reactant showed a negative correlation with the percent of the complexes.

Table 3
The variance analysis of each item in regression equation

Coefficients	d.f.	Sum of squares	Mean square	*F*-value	Significance
X_1	3	1397.58	465.86	162.28	**
X_2	3	428.83	142.94	49.79	**
Interaction	3	4.5646	1.5215	0.53	
Lack-of-fit	5	27.9716	5.5943	38.05	
Pure error	5	0.7351	0.1470		

Table 4
Variance analysis of each factor

Factors	d.f.	Sum of squares	Mean square	*F*-value	Significance
X_1	4	78.9639	19.4097	6.88	*
X_2	4	1390.1560	347.5309	121.07	**
X_3	4	394.5395	98.6348	34.36	**

The optimal conditions were thus approached using the model as follows: airflow temperature, 100 °C; microwave heat time, 260 s; and amount of reactant, 1.5 g.

3.9. Analysis of the synthesized compounds

3.9.1. Infrared spectrum of the synthesized compounds

Fig. 3 shows that after coordination compound formation (Met and Fe(II)), the absorption band of $v(NH_3^+)$ shifted from 2960 to 3465 cm^{-1}. The absorption peak of $v_{as}(NH_2)$ and $v_s(NH_2)$, respectively, appeared in the 3395–3345 cm^{-1} and 2924–2960 cm^{-1} regions which indicated the coordination formation of α-NH_2 and Fe(II). Because of the contribution to the ferrous ion from the shared electron-pair of nitrogen, the dipole–dipole interaction of C–N was intensified which led to a strong absorption peak of C–N at 1117 cm^{-1} in the infrared spectrum of methionine iron (II) complex. Figs. 2 and 3 indicate that there was no free –COOH group in methionine and methionine iron (II) complex because there was no absorption peak in the 1700–1750 cm^{-1} region; the strong absorption peak of hydroxyl at 3465 cm^{-1} indicated the existence of water. The two peaks at 555.6 and 442.4 cm^{-1} could, respectively, be assigned as $r(H_2O)$ and $w(H_2O)$ vibrational modes of the coordinated water. Because of the effect of overlapping and counteracting between the sterical vibration of coordinated water to carbonyl group and Fe(II) chelating –CO_2^- group of methionine, the Δv between $v_{as}(CO_2^-)$ and $v_a(CO_2^-)$ of complex was basically identical to the Δv of methionine; two new weak absorption peaks at 618.0 and 400.0 cm^{-1} in the infrared spectrum of methionine iron (II) complex could, respectively, be assigned as the absorption peaks of v(Fe–N) and v(Fe–O).

3.9.2. Elemental analysis and structure determinations of the synthesized compounds

The elemental analysis of the synthesized compounds showed N of 7.14% and Fe of 14.56%.

According to the infrared spectrum and chemical analysis, the sample molecular formula of $(Fe(Met)_2 \cdot H_2O)$ could represent the chemical structure of the synthesized compounds as is depicted in Fig. 4.

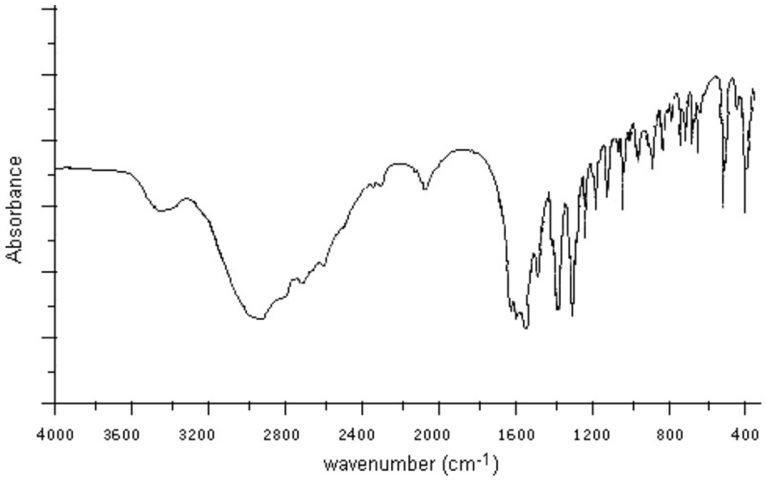

Fig. 2. Infrared spectrum of methionine.

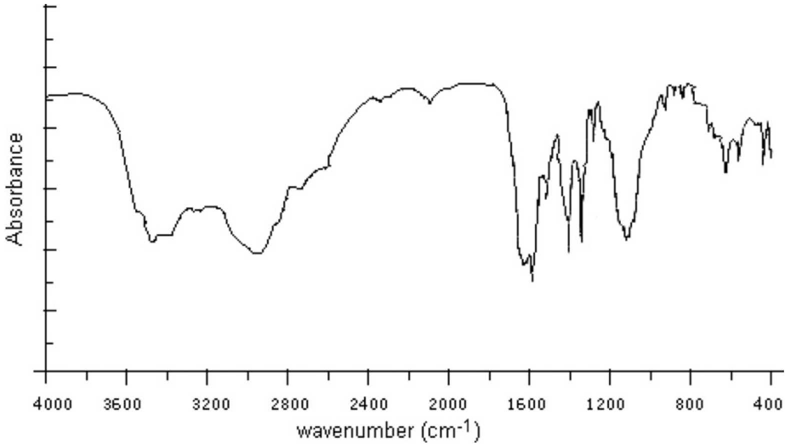

Fig. 3. Infrared spectrum of Met–Fe(II) complex.

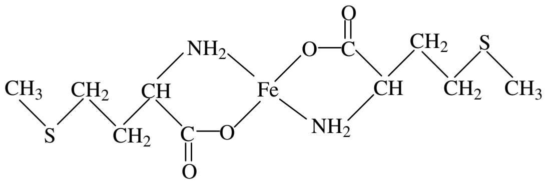

Fig. 4. The molecular structure of methionine complexes of iron (II).

4. Conclusions

A high yield of methionine complex of iron (II) was successfully achieved by employing a microwave assisted solid state route under the optimum reaction conditions, i.e., microwave heat time, 260 s; quantity of reactant, 1.5 g; and the airflow temperature, 100 °C. It was illustrated that combination of microwave irradiation and solid state chemistry in the synthesis of methionine complexes of iron (II) is very promising in the terms of mildness of reaction conditions, yields and time of reactions. It also has all the advantages devoted to solvent-free reactions, namely, environmentally friendly conditions, high chemoselectivity and absence of volatile and hazardous solvents.

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