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Influence of Ph Value and Temperature on the Formation of Iron Maltodextrin Complex

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This article deals with the influence of the pH value and temperature on the synthesis of iron maltodextrin complex from aqueous solutions of iron (III) chloride and maltodextrin. Products were characterized by X-ray diffractio, scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, and conductivity meter. The complex obtained at pH value from 3.0 to 11.0 contained iron in the form of akaganeite and had highest iron content and the yield at pH of 9.0. Temperature affected the formation of iron phase in the complex and the optimum value for the synthesis was 80°C. The complex obtained at optimum condition has iron content of 28.75 % and the yield of 78.96 %. Complex particles had a spherical shape with the diameter from 20 to 30 nm and consisted of akaganeite cores with a diameter of nearly 5 nm. The electric conductivity of the saturated complex solution was 30 μS/cm.

Key words: Iron; maltodextrin; complex; akaganeite; crystallinity; core

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Iron is one of the most trace essential elements in the human body [1]. It involves in many metabolism processes including oxygen transport (hemoglobin), oxygen storage (myoglobin), and DNA synthesis [1,2]. When iron absorption is low or distorted, the iron deficiency anemia (IDA) occurs [1,3,4].

IDA is a common problem occurring in ordinary people, especially in women [5,6]. The oral iron supplement is usually adequate for most patients but some people have an intolerance to oral iron, abnormal absorption due to surgery or gastrointestinal disease, significant bleeding, and non-compliance may make oral iron treatment in some patients inadequate [7,8]. These patients will benefit from parenteral iron.

Both oral iron (i.e. ferrous fumarate, and ferrous gluconate) and parenteral iron (i.e. iron dextran, iron sucrose, and iron sorbitol) have been used to treat iron deficiency for many years in both USA and Europe [7–10].

On account of its potential application against IDA, iron-polysaccharide complex has attracted the attention of scientists [11–15]. There are commercial products containing the complex. Many contributions involving the preparation of this complex from various sources of polysaccharide, such as starch, maltodextrin, and maltodextrin have been published [15–20] but the conditions of preparation of iron maltodextrin complex from ferric chloride and dextrin have not been investigated in detail yet.

This paper focuses on two important factors, pH value, and temperature, which influence the preparation of the complex.

MATERIAL AND METHODS

Reagents

The chemicals used in the experiments are $FeCl_3.6H_2O$, NaOH, maltodextrin (DE12), and ethanol. They are analytical grade and were used without any further purification.

Preparation of Iron Maltodextrin Complex

Iron maltodextrin complex was prepared by the

following processes: 3 g of maltodextrin was dissolved into 100 ml of distilled water and heated to 90°C. 1 M NaOH solution was added until pH 9.0 was reached, then it was continuously stirred and heated for 30 min. The obtained solution was poured slowly into 100 ml of 0.1 M $FeCl_3$ solution. The pH of the mixture was adjusted to definite value by slowly dropping 1 M NaOH solution, then continuously stirred and heated to a certain temperature for 4 h. The final solution was filtered and then mixed with an equal volume of ethanol. The resultant precipitate was separated by centrifuging and washed with a mixture of distilled water and ethanol, dried at 70°C for 48 h, and ground to fine powder.

Characterization

The phase compositions of the complex were analyzed using X-ray diffraction (XRD, Siemens D5000 diffractometer with Cu Kα radiation, λ = 1.54). The morphology of the complex was recorded by scanning electron microscopy (SEM, S 4800). Akaganeite particle size was estimated by transmission electron microscopy (TEM, JEM 1010). The iron content of the product was determined by atomic absorption spectroscopy (AAS, Thermo M-Series) according to the method by Galan [21]. The conductivity of complex aqueous solution was measured using Cobra unit with a conductivity probe K1-(PHYWE).

RESULT AND DISCUSSION

Influence of pH Value

To investigate the effect of pH value on the formation of the complex, the samples were prepared at different pH values, from 3.0 to 11.0. XRD patterns of all the samples (Figure 1) showed peaks at 2θ 11.9, 26.9, 35.1, 39.2, 46.4, 55.9 degrees, corresponding to the typical diffraction peaks of the akaganeite structure (β-FeOOH, JCPDS 34-1266) [22]. There were no typical diffraction peaks of other phases, indicating that in the complex, iron existed only in the form of akaganeite. The remarkable broadening of diffraction peaks shows that crystallite has small size small and the crystallinity of akaganeite in the complex is low [23]. To choose the optimum pH value, the samples were analyzed by AAS method to determine the iron content and the yield of the complexation process. Figure 2 shows iron content and the yield of the complex obtained at different pH values. Both iron content and the yield increased with an increase in pH from 3.0 to 9.0. Namely, iron content was 24.28% at pH of 3.0 and reached 27.38% at pH of 9.0. Similarly, the yield increased from 68.12% at pH of 3.0 to 78.95% at pH of 11.0. However, when pH attained 11.0 both iron content and the yield decreased to 28.15 and 78.22%, respectively.

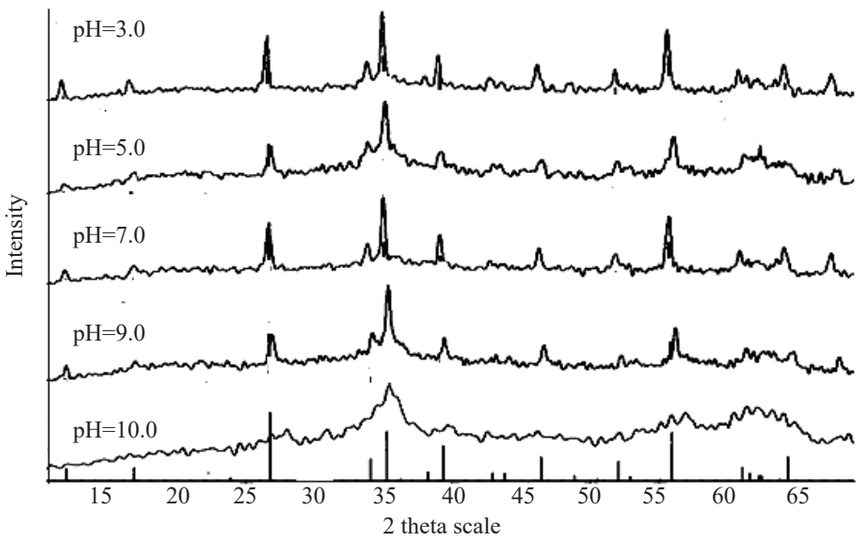

Figure 1. XRD patterns of the samples at different pH values.

The influence of pH value on iron content and the yield could be explained that at a pH value lower than 9, the akaganeite phase formed quickly and easily. In this condition, the polysaccharide molecules were not deprotonated, so they were difficult to stabilize the akaganeite particles in the solution. Therefore, the iron content and the yield was low. In contrast, at pH value higher than 9, although many polysaccharide molecules were deprotonated, the akaganeite phase was difficult to form, so the iron content and the yield was reduced.

In conclusion, the suitable value of pH was 9.0 and was chosen for the next experiments.

Influence of Temperature

The temperature of all the preparations were varied from 50°C to 90°C to find the suitable condition. The XRD data of the complex obtained at some temperatures were displayed in Figure 3. It was difficukt to observe any typical diffraction peaks on the XRD patterns of the samples obtained from 50°C to 70°C, indicating that powders obtained at these temperature values exist in the form of an amorphous phase [23]. XRD patterns of the samples obtained at 80°C and 90°C showed the typical diffraction lines of akaganeite structure, implying that the complex contained iron in the form of akaganiete. According to studies [13,16–18,24], iron polysaccharide complex is a combination of polysaccharide and akaganiete.

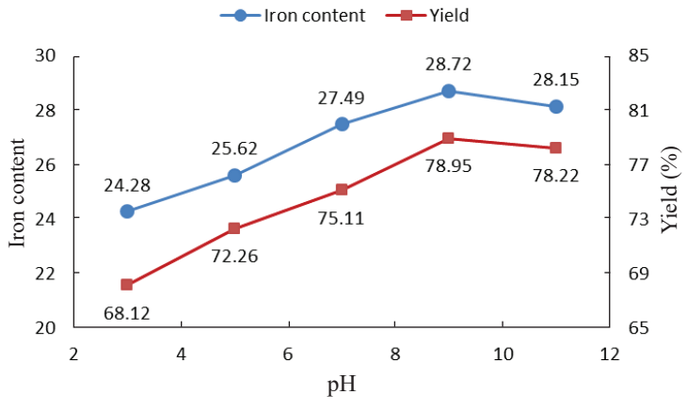

Figure 2. The iron content and the yield of the complex obtained at different pH values.

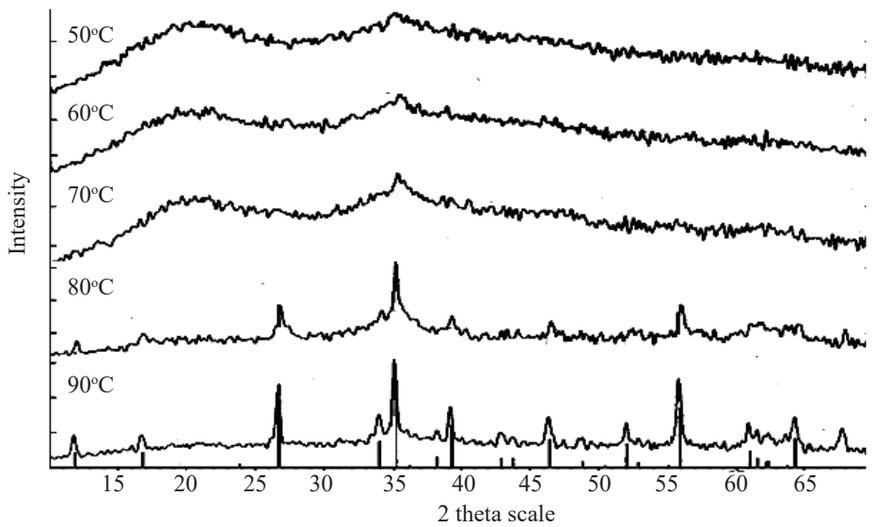

Figure 3. XRD patterns of samples formed at different temperatures.

Two samples formed at 80°C and 90°C were analyzed for iron content and the yield estimated was the average size of akaganeite crystallite using Scherrer equation [23]. The results are given in Table 1. The iron content and the yield of the two samples were nearly the same, suggesting that the temperature had no effect on these values of the complex. However, the average size of the akaganite crystallite in the sample synthesized at 80°C was 7 nm while that of the sample obtained at 90°C was 13 nm. The influence of the temperature on the average particle size might be explained that at high temperature the rate of the hydrolysis reaction was fast, for many small grains to combine to form bigger ones. From these results, the temperature of 80°C was chosen for preparation of the iron and maltodextrin complex.

Characterization of the Complex

FT-IR analysis. FT-IR spectra of maltodextrin and the complex are given in Figure 4. Both maltodextrin and the complex have bands between 3100 cm^{-1} and 3600 cm^{-1} assigned to the stretching vibration of O-H in maltodextrin, akaganeite and water [13]. The bands at 2926 cm^{-1} and 2924 cm^{-1} corresponded to C-H stretching which belongs to the structure of maltodextrin [13,17,25]. The FT-IR spectra also had bands at 698, and 700 cm^{-1} which contributed to O-H bending. In addition, the band at 465 cm^{-1} (Figure 4b) corresponds to the stretching of Fe-O in akaganeite [11,13,16,17]. According to this result, it could be concluded that the complex was the combination of maltodextrin and akaganeite.

SEM and TEM analysis. SEM image of the complex is given in Figure 5a. It contained spherical particles. Their shape and size was quite uniform. The particle borders were clear, and the diameter of particles ranged from 20 nm to 30 nm.

There was no appearance of the rod-like crystal of akaganeite. Therefore, it could be assumed that akaganeite particles were capsulated by maltodextrin molecules to form a core-shell structure. To determine the size and the shape of akaganeite cores, the complex

Table 1. Iron content, yield, and particle size of the complex obtained at 80°C and 90°C.

Temperature	Iron content	Yield	Average size of crystallite
80°C	28.75%	78.96%	7 nm
90°C	28.77%	78.94%	13 nm

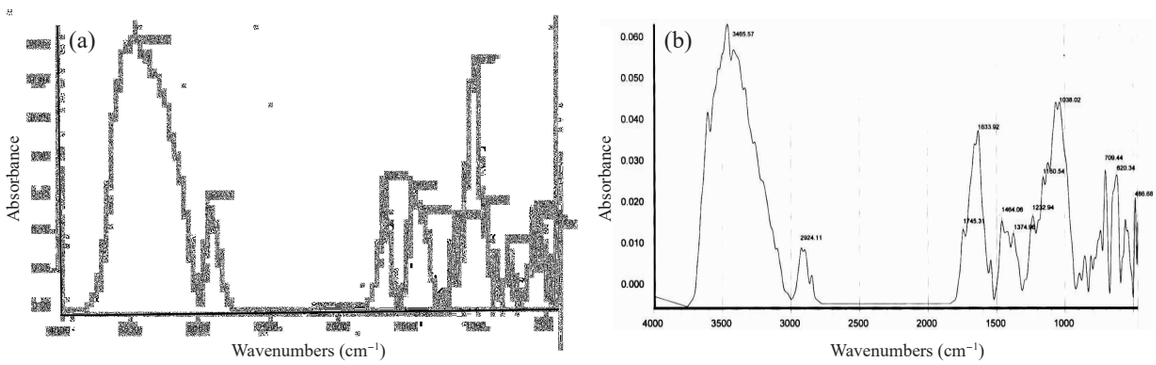

Figure 4. FT-IR spectra of maltodextrin (a) and the complex (b).

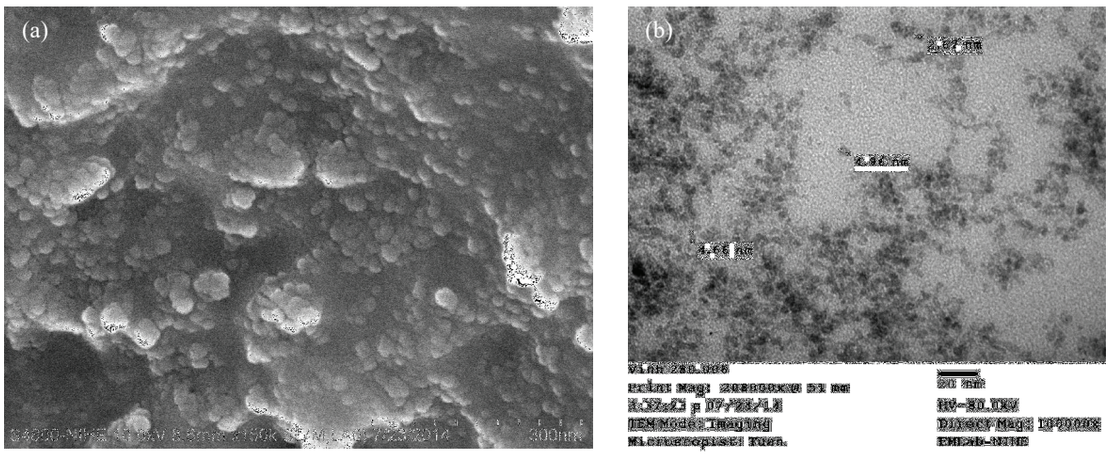

Figure 5. SEM (a) and TEM (b) images of the complex.

was dissolved in distilled water and then observed by transmission electron microscopy.

TEM image of the complex was given in Figure 5b. According to this result, akaganeite cores were quite small, nearly 5 nm. Their size and shape was quite similar.

Electric conductivity. The electrical conductivities of some solution were given in Table 2 and of the complex were showed on Figure 6.

From Table 2, the conductivity of the aqueous saturated solution of the complex was higher than that of distilled water but much smaller than the conductivity of the acetic acid solution (14 times); of potassium chloride solution (500 times); and of ferric chloride solution (nearly 800 times). Therefore, the complex could be said to be nonionic.

According to Figure 6, the conductivity of the complex was quite stable when time increased. It changed slightly about 0.02 µS/cm.

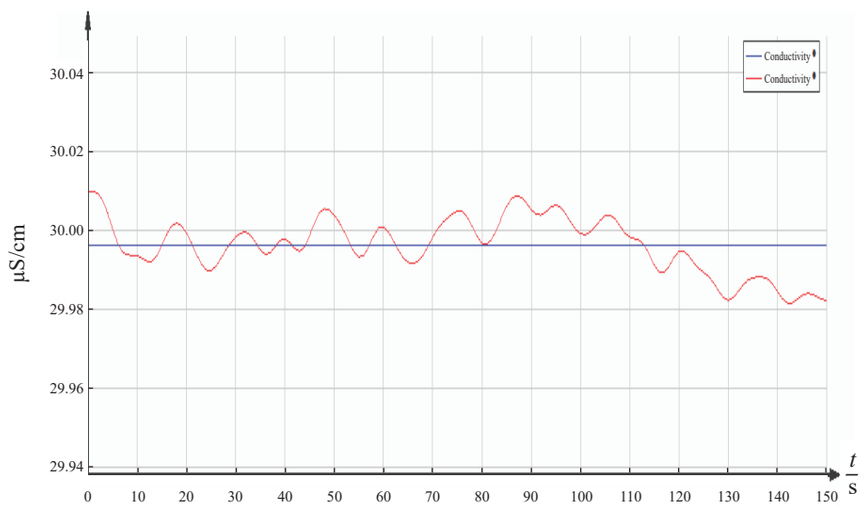

Figure 6. Electric conductivity of saturated solution of the complex.

Table 2. Conductivity of some solutions.

Solution	Conductivity (μS/cm)
Distilled water	7.0
CH_3COOH (0.1 M)	520
KCl (0.1 M)	15 000
$FeCl_3$(0.1 M)	23 760
Complex (saturated)	Approximately 30

CONCLUSION

The effects of pH value and temperature on the formation of iron maltodextrin complex was investigated. pH value did not affect the formation of akaganeite phase but influenced the iron content and the yield of the complex. The optimum pH for complex synthesis was 9.0. Temperature remarkably influenced the formation of akaganeite phase in the complex. The complex with iron in the form of akaganeite was only obtained at a temperature at or above 80°C. The comlex synthesized at 80°C and pH of 9.0 had iron content of 27.75% and the yield of 78.96%. The complex contained spherical particles with core-shell structure, in which the akaganeite core was capsulated by maltodextrin. The diameter of the complex particles ranged from 20 nm to 30 nm and of the akaganeite core was nearly 5 nm. The complex solution had a very low electric conductivity.

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