

Preparation and Characterization of Magnetic Resin Made from Chitosan and Cerium

YU Lina^{1),2)}, WANG Dongfeng^{1),*}, LI Haiyan¹⁾, LIU Bingjie¹⁾, WANG Xingyu¹⁾, and XU Ying¹⁾

1) College of Food Science and Engineering, Ocean University of China, Qingdao 266003, P. R. China

2) Shandong Peanut Research Institute, Qingdao 266100, P. R. China

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Abstract In this study, the water-based ferromagnetic fluid and magnetic resin made from chitosan and cerium complex (MRCCC) were successfully prepared by using the chemical co-precipitation technique and by the reversed-phase suspension cross-linking polymerization. MRCCC presented uniform and narrow particle size distribution as determined by the Laser Particles Sizer. The Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC) and X-ray powder diffraction (XRD) study demonstrated that there were iron and cerium existing in MRCCC. The movement of MRCCC under magnetic field proved its magnetic property. The swelling kinetics in water or solutions with different pH indicated that MRCCC could be applied in solutions with pH greater than 1.0. The ferromagnetic fluid particles were stable in MRCCC soaked in solutions with pH >2.0. In view of these results, MRCCC can be used as material for separation, clarification, adsorption, sustained release and hydrolysis activity.

Key words magnetic resin; chitosan; cerium; preparation; characterization; properties

1 Introduction

In general, all the lanthanide ions (Lns) belong to the 'type a' metal cation, which refers to alkali metal, alkaline earth metal and high oxide number light transitional elements, according to the classification of Ahrlund, Chatt and Davies (Frederick, 1980). Therefore, some common electron donor atoms can combine with Lns into complex bond to form Lns coordination compounds. According to the research reports (Liu *et al.*, 2007; Lin *et al.*, 2006; Shanguan and Qu, 2006; Wang *et al.*, 2007), these Lns coordination compounds have hydrolysis phosphate ester bond and peptide bond activity, and especially the hydrolysis activity of the cerium coordination compound is greater than those of many other Lns coordination compounds (Wang *et al.*, 2005; Kitamura *et al.*, 2003; Franklin, 2001; Sumaoka *et al.*, 1997).

Chitosan is composed mainly of β -(1-4)-2-amino-2-deoxy-D-glucopyranose and β -(1-4)-2-acetamido-2-deoxy-D-glucopyranose repeating units, the content of the former being more than 60%. Chitosan can absorb transition metal ions and Lns, because the C-2 amino group nitrogen atom or C-6 hydroxyl group oxygen atom can provide isolated pairs of electrons to metal ions so that the coordination effect occurs between chitosan and metal

ions. In recent years, some complexes made from chitosan cerium (Ce^{4+}) have been produced and proven to have hydrolysis phosphate ester bond and peptide bond activity. For example, a kind of film preservative of chitosan Ce^{4+} complexes suitable for use in fruits and vegetables was prepared by Wu *et al.* (2006). At room temperature, cucumbers coated with this film preservative can be stored for more than 12 d. The result showed that the degradation effect of parathion in cucumbers coated with the film preservative was more remarkable than that in natural degradation. In addition, a resin type of chitosan Ce^{4+} complex microspheres (RCCM) has also been successfully prepared and applied to the clarification of beer fermentation liquid and concentrated apple juice, in order to hydrolyze sensitive protein and to degrade methamidophos and parathionmethyl, respectively (Yu *et al.*, 2006; Wang *et al.*, 2006).

In recent years, magnetic chitosan microspheres have attracted increasing attention owing to their unique magnetic features, good biocompatibility and low toxicity; they can be utilized almost exclusively in some medical techniques, drug delivery, separation and adsorption (Denkbaş *et al.*, 2002; Park *et al.*, 2005; Donia *et al.*, 2008). It would be advantageous to prepare magnetic resin microspheres made from chitosan and cerium complex (MRCCC) for the clarification of fruit and vegetable juice based on the good hydrolysis phosphate ester bond and peptide bond activity of RCCM. On the other hand, separation of MRCCC from the reaction medium can be

* Corresponding author: Tel: 0086-532-82031575

E-mail: wangdf@ouc.edu.cn

easily conducted within a magnetic field.

Studies have shown that the reduction of sensitive protein in beer and some fruit or vegetable juice can prevent the turbidity phenomenon during their storage. In addition, pollutions arising from organophosphorous pesticides in fruit and vegetable juice may exist. Therefore, it is necessary to use a new kind of clarification material, which has hydrolysis for phosphate ester bond and peptide bond, in the production process of beer and fruit or vegetable juice, in order to reduce the content of sensitive protein and organophosphorous pesticides. MRCCC may become the material suitable for this purpose, because it has not only hydrolysis phosphate ester bond and peptide bond activity but also the property of magnetism. In this study, the water-based ferromagnetic fluid and the MRCCC were prepared, using the chemical co-precipitation technique and the reversed-phase suspension cross-linking polymerization, respectively. The characterization of MRCCC involved physical and chemical techniques. Laser Particles Sizer was employed to determine the average particle diameter and the particle size distribution. The analysis on the structural interactions caused by the incorporation of the metal ions in the resins was studied by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and X-ray powder diffraction (XRD).

2 Materials and Methods

2.1 Chemicals

Chitosan with deacetylation degree of 95% (Manufacturer's data) was provided from Lizhong Chitosan Company Limited (China). Ferric sulfate, ferrous sulfate and ammonia were analytical reagents produced by Sino-pharm Chemical Reagent Co., Ltd. China. Cerium ammonium nitrate was analytical reagent supplied by Shanghai Shanpu Chemical Industrial Co., Ltd. All other reagents were of analytical grade.

2.2 Preparation of Water-Based Ferromagnetic Fluid

Water-based ferromagnetic fluid was produced by chemical co-precipitation technique. Solutions of 0.1 molL^{-1} ferric ion and 0.08 molL^{-1} ferrous ion were added to distilled water (the brown solution). Strong ammonia (50 mL) kept in a basic buret was added immediately to the solution at a rate of 3 mL min^{-1} and stirred for 20 min when the dropping was finished. The vessel containing the reaction product was put on a permanent magnet (co-precipitation reaction) for 2 h, and then the resultant magnetic particles were concentrated on the magnet region of the solution under the influence of magnetic field. Then, 100 mL aqueous ammonia (5%) was added to the magnetic particle aggregation after the upper solution was removed, and the mixture was stirred at 600 r min^{-1} for 20 min. The vessel was put on the permanent magnet again after this for magnetic particles to aggregate. Afterward, 100 mL distilled water was added to the aggregation and the mixture was stirred for 20 min and precipitated once again. This

process was repeated for four times. Finally, 50 mL distilled water was added to the magnetic particle aggregation and the mixture was stirred for 20 min to become the water-based ferromagnetic fluid.

2.3 Preparation of MRCCC

MRCCC was prepared by reversed-phase suspension cross-linking polymerization. A solution containing 10% chitosan and 0.5% cerium ammonium nitrate was prepared using aqueous acetic acid (2%). The water-based ferromagnetic fluid was added to the solution at a proportion of 25%, stirred and mixed with a glass rod, and then ultrasonically blended for 10 min (the black solution). This solution was added to liquid paraffin in a ratio of 1:1 and stirred for 10 min. Emulsions would be formed when adding span-80 (1.5%) and acetic ester (10%) under stirring conditions (300 r min^{-1} for 20 min at room temperature). When the temperature was increased to 40°C , the beforehand cross-linking agent formaldehyde (8%) was added to the emulsion (300 r min^{-1} for 30 min). When the temperature was increased to 50°C , the cross-linking agent glutaraldehyde (4%) was added, the pH value was adjusted to 7.5 with 2 molL^{-1} sodium hydroxide, and then the emulsion was stirred at 175 r min^{-1} for 3 h. The resultant MRCCC was rinsed with petroleum ether, acetone, ethanol and distilled water successively. The particles were then dried by DZX-6 vacuum drying oven (50°C) for around 48 h and stored at room temperature.

2.4 Preparation of Magnetic Resin of Chitosan (MRC)

MRC was also prepared by reversed-phase suspension cross-linking polymerization. A solution of 10% chitosan was prepared using aqueous acetic acid (2%). The water-based ferromagnetic fluid was added to the chitosan solution according to a proportion of 25%, followed by the same procedures as with the MRCCC.

2.5 Measurement of Absolute Quantity and Magnetic Response of Water-Based Ferromagnetic Fluid

2.5.1 Measurement of absolute quantity

Five milliliter water-based ferromagnetic fluid was added to a pre-weighed bottle (G_1 , g). The total weight (G_2 , g) of the bottle (with the magnetic particles) was determined when water was removed from the samples at 75°C . The absolute quantity of water-based ferromagnetic fluid was expressed with the formula: $(G_2 - G_1)/0.005 \text{ (g L}^{-1}\text{)}$. The reported absolute quantity represented the Mean \pm SD of three independent measurements.

2.5.2 Measurement of magnetic response

A mixture solution containing 0.1 mL water-based ferromagnetic fluid and 20 mL solvent (50% ethanol solution) was obtained by supersonic vibration for 20 min. Changes in transparency over time with and without a magnetic field were measured at 360 nm using Unico 2102 UV-vis

spectrophotometer.

2.6 Characterization

The morphological characteristics of MRCCC were examined by VHX-600 super field depth three-dimensional microscopy. Average particle diameter and particle size distribution of MRCCC were studied by LS-CWM Laser Particles Sizer. The contents of rare earth elements and iron in chitosan, water-based ferromagnetic fluid powder, MRC and MRCCC were determined by ICP- AES. The FT-IR was carried out using NEXUE 470 FT- IR Nicolet (Wavenumber range 4000–400 cm^{-1}). The sample was prepared by the KBr pellet method. The DSC of the samples was carried out using Netzsch, Model 200PC DSC (Temperature range 25°C–400°C). The heating rate was 10°C min^{-1} and the cooling gas was nitrogen (20 mL min^{-1}). The XRD data was measured using Rigaku D/MAX 2500 XRD. The scanning speed was 2° min^{-1} with $\text{K}\alpha$ and 2θ from 10° to 70°.

2.7 Measurement of Swelling Kinetics of Resins

The swelling rate (SR) in a given period and the equilibrium swelling rate (ESR) in a given solution with a particular pH can represent the swelling kinetics of resins (Zhang *et al.*, 2007). A sample of 0.1 g (W_d) resins was swelled by distilled water or by solutions with different pH over a period of time at ambient temperatures. The weight of resins (W_w) was measured after the surface water or solution was removed by using filter paper. The swelling rate was $\text{SR} = (W_w + W_d) / W_d$, and the equilibrium swelling rate was $\text{ESR} = W_d / W_w$.

2.8 Measurement of Stability of Magnetic Particles in Resins

Resins (0.1 g) were soaked in solutions with different pH (100 mL, pH 1–8) for 96 h. The iron content in the supernatant was determined every 12 h by using o-phenanthroline spectrophotometry. Prior to each reading, the solution, containing 5.0 mL supernatant, 20.0 mL distilled water, 2.5 mL hydroxylamine reagent (1%) and 5.0 mL acetic acid-sodium acetate buffer (pH 4.5), was left for 5 min after pH was adjusted to 4.5 with ammonia. Then 5.0 mL o-phenanthroline solution (0.1%) was added to the solution and a total volume of 50.0 mL was obtained with distilled water. The absorbance was measured at 510 nm using Unico 2102 UV-vis spectrophotometer after standing for 15 min.

2.9 Determination of Relative Magnetism

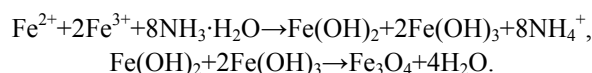
Magnetic materials (MRCCC, MRC and water-based ferromagnetic fluid particles) were placed on a clean glass panel. A magnet (8.2 cm long, 6.2 cm wide and 1.8 cm high, with a circular hole of 0.9 cm inner diameter) was horizontally moved from a certain distant to the magnetic materials. The distance between initial position of magnetic materials and stop position of magnet was determined when half of magnetic materials were absorbed

onto magnet.

3 Results and Discussion

3.1 The Absolute Quantity and Relative Magnetic Response of Water-Based Ferromagnetic Fluid

Water-based ferromagnetic fluid plays an important role in the preparation of MRCCC. The ferromagnetic fluid is a kind of colloid, in which magnetic particles are suspended in the carrier solution (Jakabský *et al.*, 2000). The equilibrium of attraction and expulsion among magnetic particles is a key aspect of ferromagnetic fluid. In this study, water-based ferromagnetic fluid was produced by chemical co-precipitation technique, with ammonia added drop by drop to the mixture solution of ferric saline and ferrous saline. Water-based ferromagnetic fluid was obtained through magnetic separation of reaction products. The theoretic reaction equations are as follows (Zhang *et al.*, 2006):



These equations show that the theoretic molar ratio is $\text{Fe}^{2+}:\text{Fe}^{3+}:\text{OH}^- = 1:2:8$. In reality, however, the ferrous ion content should be excessive due to the fact that the ferrous ion can be easily oxidized into the ferric ion. Therefore, the molar ratio of Fe^{2+} to Fe^{3+} used in the present study was 1.4:2. In general, as long as the molar ratio of Fe^{2+} to Fe^{3+} is not greater than 1:1, the Fe_3O_4 can be formed (He *et al.*, 2003). Additionally, the process $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$ is an endothermic process and heating can accelerate oxidization of Fe^{2+} into Fe^{3+} , because the standard molar enthalpies of formation of Fe^{2+} and Fe^{3+} are $-89.1 \text{ kJ mol}^{-1}$ and $-48.5 \text{ kJ mol}^{-1}$, respectively (Tremaine and Xiao, 1999). It was therefore necessary to keep relatively low temperature during the process of preparation of water-based ferromagnetic fluid. The absolute quantity of water-based ferromagnetic fluid was $(47.800 \pm 0.346) \text{ g L}^{-1}$ and that of iron was $(34.683 \pm 0.346) \text{ g L}^{-1}$. Fig.1 is the curve of magnetic response of water-based ferromagnetic fluid. The water-based ferromagnetic fluid was stable for its constant absorbance measured over a period of 20 minutes. Under magnetic field conditions, however, the fluid had responded, *e.g.*, the transparency increased from 4.88% at 30 s to 26.99% at 20 min.

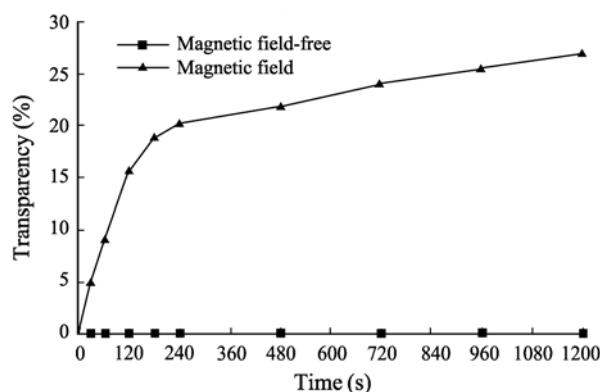


Fig.1 Curve of magnetic response of water-based ferromagnetic fluid.

3.2 Physical Properties of Magnetic Resins

If chitosan powder is mixed with water-based ferromagnetic fluid, it is hardly dissolved and the ferromagnetic fluid would be oxidized into deep red Fe_2O_3 . In addition, the prepared resins would not have magnetic property. Hence it is necessary to adequately dissolve chitosan using cerium ammonium nitrate before water-based ferromagnetic fluid is added to the solution. On the early stage of the reversed-phase suspension cross-linking polymerization, the operation should be carried out at room temperature, otherwise the coordination between the ferromagnetic fluid and chitosan will not happen and heating can accelerate the oxidation of Fe^{2+} into Fe^{3+} as stated previously. During the process of pre-cross-linking, small chitosan liquid gel can be formed and adsorption and coordination between iron and chitosan will occur upon stirring. In our experiment, glutaraldehyde was used as cross-linking agent to make chitosan liquid gel into solid gel particles.

MRCCC was a type of black and brown spherical resin with smooth surface. An analysis of the surface morphology with super field depth three-dimensional microscopy showed that there were salient and depression on the surface (Fig.2). As examined by LS-CWM Laser Particles Sizer, average particle diameter was about $181.567 \mu\text{m}$, with 100% particle diameter less than $363.078 \mu\text{m}$, and 90%, 50% and 10% particle diameter below $224.221 \mu\text{m}$, $175.123 \mu\text{m}$ and $121.223 \mu\text{m}$, respectively.

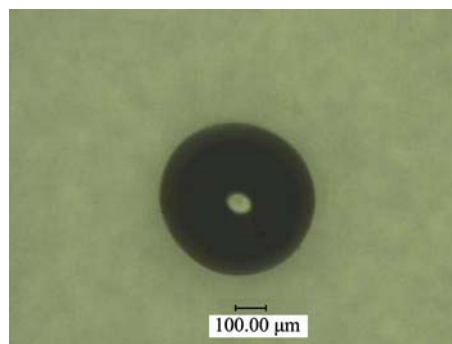


Fig.2 Microphotograph of MRCCC.

The contents of rare earth elements and iron in dried samples (1.0 g) of chitosan powder, water-based ferromagnetic fluid powder, MRC and MRCCC as determined by ICP-AES, are presented in Table 1. The cerium content of MRCCC was greatly higher than that of chitosan powder, water-based ferromagnetic fluid powder and MRC because cerium ammonium nitrate was added during the process of preparation of MRCCC. The quantity ratio of iron to chitosan was 0.173:1 in the preparation of MRC and MRCCC. The results (Table 1) showed that the contents of iron in MRC and MRCCC were similar and the average mass ratio of iron to magnetic resins was 0.019:1. Thus, 10.98% of the ferromagnetic fluid was encapsulated in the magnetic resins during the preparation and certain quantity of chitosan could only react with a fixed mass of ferromagnetic fluid.

Table 1 Contents of rare earth elements and iron in chitosan, water-based ferromagnetic fluid powder, MRC and MRCCC (Average of two experiments is presented. $P < 0.01$)

Metal	Chitosan (mg g^{-1})	Water-based ferromagnetic fluid powder (mg g^{-1})	MRC (mg g^{-1})	MRCCC (mg g^{-1})
Ce	0.0046	0.0574	0.0043	19.0120
Dy	0.0000	0.0080	0.0003	0.0121
Er	0.0060	0.0030	0.0025	0.0000
Eu	0.0000	0.0034	0.0003	0.0003
Gd	0.0014	0.0055	0.0011	0.0006
Ho	0.0000	0.0000	0.0000	0.0000
La	0.0006	0.0280	0.0011	0.0018
Lu	0.0000	0.0110	0.0012	0.0012
Nd	0.0004	0.0000	0.0000	0.0000
Pr	0.0000	0.0573	0.0047	0.0019
Sc	0.0005	0.0197	0.0016	0.0158
Sm	0.0013	0.0268	0.0238	0.0606
Tb	0.0000	0.0177	0.0024	0.0089
Tm	0.0000	0.0122	0.0044	0.0030
Y	0.0001	0.0022	0.0000	0.0001
Yb	0.0000	0.0072	0.0009	0.0012
Fe	0.0933	21.5745	19.3655	18.3215

3.3 FT-IR Spectroscopy

The FT-IR spectra of MRCCC, MRC and chitosan powder are shown in Fig.3 and the wave numbers of their main peaks are listed in Table 2. The peak consisting of ν (O-H) and ν (N-H) shifted to lower wave number from 3444 cm^{-1} in chitosan powder to near 3420 cm^{-1} in MRC and MRCCC, because the Schiff base II bond in MRC

and MRCCC induces weak association between hydroxylic hydrogen and II electron cloud. The characteristic adsorption peak of aldehyde group [ν (-CHO)] appearing at near 1716 cm^{-1} in MRC and MRCCC was the suspension aldehyde group, for one aldehyde group of glutaraldehyde can not react with amino group of chitosan. In MRC and MRCCC, it was found that the bending adsorption peak of $-\text{NH}_2$ (near 1597 cm^{-1}) and amide II (δ

(N-H) and ν (C-N)) disappeared but the characteristic adsorption peak of the Schiff base appeared at 1558 cm^{-1} . The result obtained above is consistent with the Schiff base mostly formed within range of $1540\text{--}1590\text{ cm}^{-1}$ (Santos *et al.*, 2005). The ν (C-O) intensity of C₆-OH decreased after the cross-linking reaction in chitosan. The possible reason might be that the chitosan long chain is turned into coiling and curling spatial structure and forms the hydrogen bond between primary alcoholic hydroxyl and nitrogen or hydrogen atom. In addition, the primary alcoholic hydroxyl has fairly high activity and can bond with aldehyde group of glutaraldehyde or metal ion. The ring-opening reaction of β -D-glucopyranose did not occur during the process of cross-linking reaction and the characteristic adsorption peak of β -D-glucopyranoside shifted from 897 cm^{-1} in chitosan to 916 cm^{-1} in MRCCC, possibly because the formation of hydrogen bond between amino group and hydroxyl group strengthens the force of glucose units in chitosan. The peaks located at 568 cm^{-1} and 564 cm^{-1} in MRC and MRCCC spectra, respectively, are the characteristic of stretching (ν (Fe-O)) and this indicates that Fe₃O₄ exist in MRC and MRCCC. The coordination bond between cerium and nitrogen atom from a-

amino group or acetyl amino group had been formed, as evidenced by the appearance of ν (Ce-N) at 543 cm^{-1} in MRCCC spectrum. Also in MRCCC spectrum, the stretching vibration adsorption peak of Ce-O appeared at 456 cm^{-1} and the secondary alcohol hydroxyl group had little change, indicating that the Ce-O bond was generated between cerium and primary alcohol hydroxyl group.

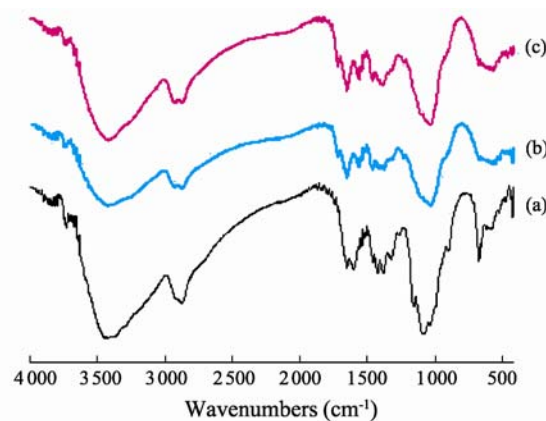


Fig.3 FT-IR spectrum (a) chitosan powder; (b) MRC; (c) MRCCC.

Table 2 Main wave numbers of chitosan powder, MRC and MRCCC

Peaks attribution	Chitosan powder (cm^{-1})	MRC (cm^{-1})	MRCCC (cm^{-1})
ν (O-H) and ν (N-H)	3444.86	3420.48	3419.62
ν (-CH ₃)	2917.82	2931.59	2926.33
ν (-CH ₂)	2875.65	2875.13	2869.90
ν (-CHO)	—	1715.89	1716.41
amide I (ν (C=O) and ν (C-N))	1649.84	1650.42	1650.61
δ (-NH ₂)	1597.87	—	—
ν (C=N)	—	1558.36	1558.93
amide II (δ (N-H) and ν (C-N))	1540.99	—	—
amide III (ν (C-N) and δ (N-H))	1259.77	1226.50	1231.07
ν (C-O-C)	1154.80	1098.33	1106.80
C ₆ -OH (ν (C-O))	1087.55	weaker	weaker
C ₃ -OH (ν (C-O))	1029.13	1025.81	1031.10
characteristic absorption peak of β -D-glucopyranoside	897.47	weaker	916.50
ν (Fe-O)	—	568.65	564.75
ν (Ce-N)	—	—	543.84
ν (Ce-O)	—	—	456.47

3.4 Differential Scanning Calorimetry (DSC)

The DSC curves for MRCCC, MRC, ferromagnetic fluid and chitosan powder are shown in Fig.4. In the first heating stage from $25\text{ to }200^\circ\text{C}$, the initial point was 47.99°C , the terminal point was 84.25°C , and the endothermic enthalpy was 46.26 J g^{-1} in the endothermic peak of MRCCC. The corresponding results for chitosan powder and MRC were 57.06°C , 82.88°C , 40.49 J g^{-1} and 52.24°C , 82.61°C , 47.32 J g^{-1} , respectively. The endothermic peak is mostly caused by the dehydration of chitosan macromolecule (Tang *et al.*, 2005). The maximum of endothermic peak in MRCCC was similar to those in MRC and chitosan powder. The endothermic enthalpy of MRCCC and MRC were greater than that of chitosan powder. Hydrogen bonds mostly existed between the amino group and water molecules in chitosan powder,

and therefore it needs lower energy to break those bonds. However, some amino groups of chitosan would react with glutaraldehyde to become the Schiff base after chitosan was prepared for spherical chitosan resins following the cross-linking polymerization. Thus new hydrogen bonds would be produced between the hydroxyl groups and water molecules, which combined with the amino groups initially. The breakup of those hydrogen bonds will require more energy, and therefore, the endothermic enthalpy of MRCCC and MRC are higher than that of chitosan powder.

In the second heating stage from $200\text{ to }400^\circ\text{C}$, the main exothermic peak in the DSC curve of MRCCC had an initial point of 222.05°C , a terminal point of 249.72°C and an exothermic enthalpy of 22.75 J g^{-1} . There are also two small exothermic peaks in the DSC curve of MRCCC. In the DSC curve of MRC, there were two exothermic

peaks, the higher one corresponding to an initial point of 207.83°C, a terminal point of 245.42°C and an exothermic enthalpy of 50.69 Jg⁻¹, and the lower one corresponding to 262.04°C, 273.38°C and 0.103 Jg⁻¹, respectively. However, there was only one exothermic peak in the DSC curve of chitosan powder, which had an initial point of 288.58°C, a terminal point of 326.09°C and an exothermic enthalpy of 124.20 Jg⁻¹. The exothermic peak may be related to the thermal and oxidative decomposition of chitosan, the thermolysis of the ferromagnetic fluid particles, and the volatilization and elimination of volatile products (Tang *et al.*, 2005). The thermal degradation temperature decreased in the order of chitosan powder, MRCCC and MRC. Chitosan has two kinds of hydrogen bonds; one is between the tertiary carbon hydroxyl group and the quintus carbon oxygen atom, and the other is between the sextuplicate carbon hydroxyl group and amino group (Rinaudo, 2006). Therefore, chitosan has both good crystallinity and good thermal stability. When the cross-linking spherical chitosan resins are prepared, the amino group will react with glutaraldehyde to form the Schiff base, destroying the hydrogen bond of chitosan. Consequently, the crystallinity and thermal stability of chitosan will decrease and MRC and MRCCC are less stable than chitosan powder under heating condition. As can be described by the glass transition temperature, for example, these values of chitosan powder, MRC and MRCCC were 290.05–300.60°C, 200.87–217.63°C and 198.21–214.96°C, respectively.

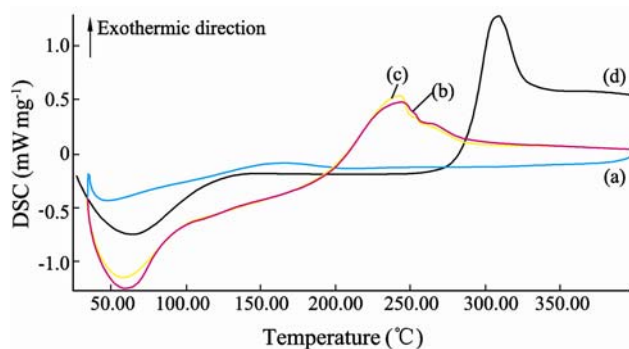


Fig.4 DSC of (a) ferromagnetic fluid powder; (b) MRC; (c) MRCCC and (d) chitosan powder.

3.5 XRD Analysis

Fig.5 indicates five diffraction peaks, with 2θ being 30.65°, 35.88°, 43.74°, 57.68° and 63.07°, respectively, in the XRD curve of ferromagnetic fluid powder. The main composition of ferromagnetic fluid prepared by chemical co-precipitation technique in this study was Fe₃O₄, which is consistent with the diffraction peaks (30.12°, 35.48°, 43.12°, 57.02° and 63.62°) of standard Fe₃O₄ (Thünemann *et al.*, 2006). Moreover, the five diffraction peaks were also present in the MRCCC and MRC XRD curves, *i.e.* 30.40°, 35.92°, 43.14°, 57.81°, 63.21° and 30.50°, 35.75°, 42.39°, 57.53°, 62.99°, respectively. These results showed that the components of MRCCC and MRC had the ferromagnetic fluid and this is the main reason that MRCCC and MRC are magnetic.

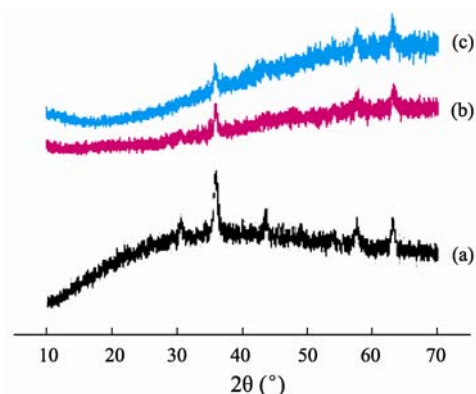


Fig.5 XRD spectra of (a) ferromagnetic fluid powder (b) MRCCC and (c) MRC.

3.6 Swelling Properties and Relative Magnetism

3.6.1 Swelling kinetics of the resins in water

The swelling kinetics of MRC and MRCCC in distilled water for 72 h are shown in Fig.6. Both MRC and MRCCC showed swelling properties in distilled water. Therefore, it can be deduced that the application of adsorption or recovery substances from aqueous solution through MRC and MRCCC is feasible. The swelling equilibrium of MRC and MRCCC were obtained within 48 h and 72 h, respectively. The cerium in MRCCC easily bonds with water molecule and the water content of MRCCC is more than that of MRC, so the equilibrium swelling ratio of MRCCC is greater than that of MRC.

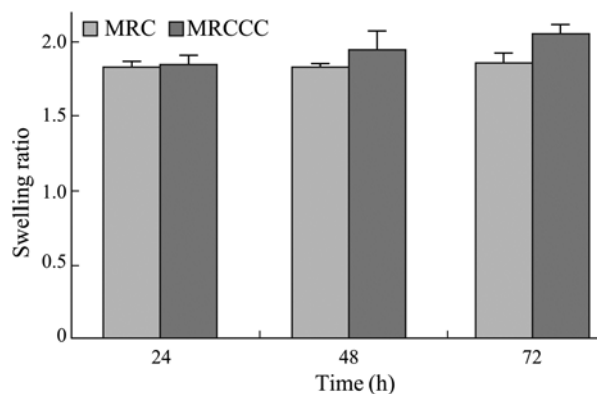


Fig.6 Columnar section of swelling rate of MRC and MRCCC. Average and standard deviations of three experiments are presented ($P < 0.01$).

3.6.2 Swelling kinetics of the resins in solutions with different pH

The measurement of equilibrium swelling ratio is shown in Fig.7, after MRC and MRCCC being soaked in solutions with different pH for 96 h. The MRC and MRCCC in solution with pH 1.0 lost the ferromagnetic fluid (see Section 3.6.3) and turned to yellow color at the end of the experiment. However, this did not occur in solutions with pH over 1.0. The minimum equilibrium swelling rate was obtained at 0.165 for MRC in solution with pH 9.0 and at 0.173 for MRCCC in solution with pH 11.0, while the maximum equilibrium swelling rates were 0.228 and 0.227, respectively. Therefore, MRC and MRCCC can

be applied in solutions with pH greater than 1.0.

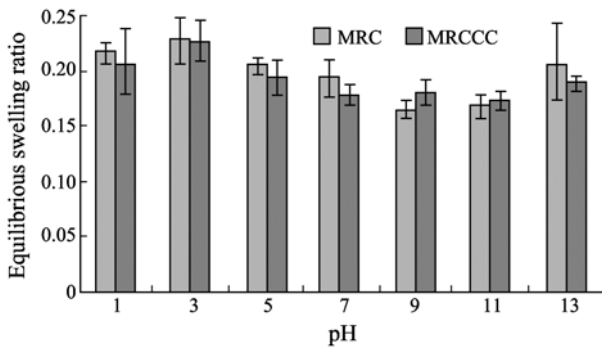


Fig.7 Columnar section of equilibrium swelling rate of MRC and MRCCC in buffer solutions with different pH. Average and standard deviations of three experiments are presented ($P < 0.01$).

3.6.3 Stability of magnetic particles in the resins

The stability of the ferromagnetic fluid in MRC or

MRCCC was determined with the iron concentration of supernatant after MRC or MRCCC was soaked in solutions with different pH for a certain period of time with the results shown in Table 3. The ferromagnetic fluid in MRC or MRCCC was not stable in solution with pH 1.0 and the iron was completely released out from resins. The MRC and MRCCC also turned into yellow color. The releasing rate of ferromagnetic fluid from MRC reached maximum at 36 h (9.414 mg L^{-1}), while that from MRCCC at 48 h (8.315 mg L^{-1}). The corresponding values were 8.904 mg L^{-1} and 8.325 mg L^{-1} at the end of the experiment. The results also indicated that MRC and MRCCC were less stable in solution with pH 2.0, for a small amount of ferromagnetic fluid was detected in the solution and MRC and MRCCC still retained black color. There was almost no ferromagnetic fluid released from MRC and MRCCC in solutions from pH 3.0 to pH 8.0. In other words, the application of MRC and MRCCC should be carried out in solutions over pH 2.0.

Table 3 Total iron concentration released from MRC and MRCCC in solutions with different pH

Time (h)		pH							
		1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0
12	MRC	6.327	0.083	0.000	0.000	0.000	0.000	0.000	0.000
	MRCCC	5.817	0.013	0.000	0.000	0.000	0.000	0.000	0.000
24	MRC	6.257	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	MRCCC	6.756	0.000	0.000	0.000	0.000	0.000	0.000	0.000
36	MRC	9.414	0.003	0.000	0.000	0.000	0.000	0.000	0.000
	MRCCC	7.615	0.000	0.000	0.000	0.000	0.000	0.000	0.000
48	MRC	6.726	0.043	0.003	0.003	0.000	0.013	0.000	0.000
	MRCCC	8.315	0.013	0.000	0.003	0.003	0.000	0.000	0.000
60	MRC	8.854	0.023	0.000	0.000	0.000	0.000	0.000	0.000
	MRCCC	7.835	0.023	0.003	0.000	0.000	0.000	0.000	0.000
72	MRC	8.564	0.023	0.000	0.000	0.000	0.000	0.003	0.013
	MRCCC	7.835	0.023	0.003	0.000	0.000	0.000	0.000	0.000
84	MRC	8.934	0.023	0.000	0.000	0.000	0.000	0.000	0.000
	MRCCC	6.317	0.023	0.000	0.000	0.000	0.000	0.000	0.000
96	MRC	8.904	0.023	0.000	0.000	0.000	0.000	0.000	0.000
	MRCCC	8.325	0.023	0.000	0.000	0.000	0.000	0.000	0.000

Notes: The unit of concentration is mg L^{-1} ; Average of two experiments is presented ($P < 0.01$).

3.6.4 Relative magnetic property

The determination of relative magnetic property of

ferromagnetic fluid powder, MRC and MRCCC was conducted according to the maximum distance they moved as shown in Fig.8. The relative magnetic property

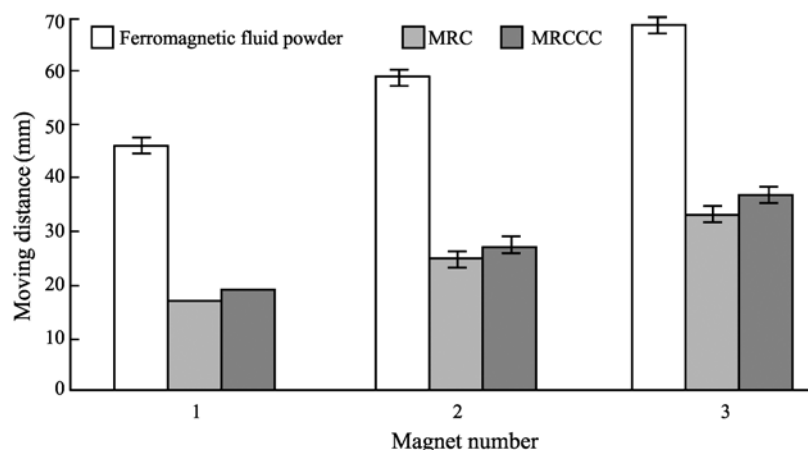


Fig.8 Relative magnetic property of ferromagnetic fluid powder, MRC and MRCCC. Average of two experiments is presented ($P < 0.01$).

of ferromagnetic fluid powder was most obvious among these three samples, because the average iron content in MRC or MRCCC was only 1.9%. In addition, the relative magnetic property of MRCCC was appreciably stronger than that of MRC owing to the magnetic material, cerium in MRCCC.

4 Conclusion

The water-based ferromagnetic fluid and MRCCC were successfully prepared by using the chemical co-precipitation technique or the reversed-phase suspension cross-linking polymerization, in this study. The absolute quantity of water-based ferromagnetic fluid was $(47.800 \pm 0.346) \text{ g L}^{-1}$ and the water-based ferromagnetic fluid was stable at non-magnetic field. MRCCC was a type of black and brown spherical resin with smooth surface. The ICP-AES, FT-IR spectrum and XRD studies demonstrated that there were iron and cerium existing in MRCCC. The application of MRCCC should be considered in solutions over pH 2.0 because the ferromagnetic fluid is stable in those solutions.

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References

- Denkbaş, E. B., Kiliçay, E., Birlikseven, C., and Öztürk, E., 2002. Magnetic chitosan microspheres: preparation and characterization. *React. Funct. Polym.*, **50**: 225-232.
- Donia, A. M., Atia, A. A., and Elwakeel, K. Z., 2008. Selective separation of mercury (II) using magnetic chitosan resin modified with Schiff's base derived from thiourea and glutaraldehyde. *J. Hazard. Mater.*, **151**: 372-379.
- Franklin, S. J., 2001. Lanthanide-mediated DNA hydrolysis. *Curr. Opin. Chem. Biol.*, **5**: 201-208.
- Frederick, S. R., 1980. Terbium (III) and Europium (III) ions as luminescent probes and stains for biomolecular systems. *Chem. Rev.*, **5**: 541-552.
- He, Q. X., Yang, H., Chen, Q. Q., Liu, S. Q., and Huang, K. L., 2003. Study on preparative condition of magnetic Fe_3O_4 nanoparticle synthesized by method of microemulsification. *J. Magn. Mater. Devices.*, **34**: 9-11 (in Chinese with English abstract).
- Jakabský, Š., Lovás, M., Mockovčiaková, A., and Hredzák, S., 2000. Utilization of ferromagnetic fluids in mineral processing and water treatment. *J. Radioanal. Nucl. Chem.*, **246**: 543-547.
- Kitamura, Y., Sumaoka, J., and Komiyama, M., 2003. Hydrolysis of DNA by cerium (IV)/EDTA complex. *Tetrahedron*, **59**: 10403-10408.
- Lin, H. K., Liu, Q., and Lin, H., 2006. Study on kinetics and mechanism of mononuclear rare earth metal complexes in promoting the hydrolysis of p-nitrophenyl phosphate (NPP). *J. Mol. Catal. A: Chem.*, **259**: 11-16.
- Liu, Q., Chen, H. M., Lin, H., and Lin, H. K., 2007. Study on kinetics and mechanism of mononuclear rare earth metal complexes in promoting the hydrolysis of 2-hydroxy-propyl-p-nitrophenyl phosphate (HPNP). *J. Mol. Catal. A: Chem.*, **269**: 104-109.
- Park, J. H., Im, K. H., Lee, S. H., Kim, D. H., Lee, D. Y., Lee, Y. K., *et al.*, 2005. Preparation and characterization of magnetic chitosan particles for hyperthermia application. *J. Magn. Mater.*, **293**: 328-333.
- Rinaudo, M., 2006. Chitin and chitosan: Properties and applications. *Prog. Polym. Sci.*, **31**: 603-632.
- Santos, J. E. D., Dockal, E. R., and Cavaleiro, É. T. G., 2005. Synthesis and characterization of Schiff bases from chitosan and salicylaldehyde derivatives. *Carbohydr. Polym.*, **60**: 277-282.
- Shangguan, G. Q., and Qu, X. G., 2006. Study on the stability of polyazamacrocyclic-Eu (Tb) by potentiometry and catalytic hydrolysis on phosphate diester of BDBPH-Tb complexes. *Chin. J. Anal. Chem.*, **34**: 10-15.
- Sumaoka, J., Kajimura, A., Ohno, M., and Komiyama, M., 1997. Homogeneous metal complexes for DNA hydrolysis and their application to artificial restriction enzymes. *J. Inorg. Biochem.*, **67**: 361-361.
- Tang, W. J., Wang, C. X., and Chen, D. H., 2005. Kinetic studies on the pyrolysis of chitin and chitosan. *Polym. Degrad. Stab.*, **87**: 389-394.
- Thünemann, A. F., Schütt, D., Kaufner, L., Pison, U., and Mohwald, H., 2006. Maghemite nanoparticles protectively coated with poly (ethylene imine) and poly (ethylene oxide)-block-poly (glutamic acid). *Langmuir*, **22**: 2351-2357.
- Tremaine, P. R., and Xiao, C. B., 1999. Enthalpies of formation and heat capacity functions for maricite, $\text{NaFePO}_4(\text{cr})$, and sodium $\text{Na}_3\text{Fe}(\text{PO}_4)_2 \cdot (\text{Na}_4\text{H}_2\text{O})(\text{cr})$. *J. Chem. Thermodyn.*, **31**: 1307-1320.
- Wang, D. F., Luo, Y., Sun, J. P., Du, D. H., Wang, C. H., Zhou, X. L., *et al.*, 2005. The use of complexes of algae polysaccharides and Ce^{4+} to degrade compounds containing peptides or phosphate ester bonds. *Carbohydr. Polym.*, **62**: 1-5.
- Wang, D. F., Sun, J. P., Du, D. H., Sun, L. P., Chen, Z. D., and Xue, C. H., 2007. Degradation of extraction from seaweed and its complex with rare earths for organophosphorous pesticides. *J. Rare Earths*, **25**: 93-99 (in Chinese with English abstract).
- Wang, D. F., Yu, L. N., Su, L., Zhang, Y. W., and Wang, C. H., 2006. Resins of chitosan- Ce^{4+} complexes application in apple juice production. *Chin. Rare Earths*, **27**: 11-14 (in Chinese with English abstract).
- Wu, H., Wang, D. F., Yu, L. N., Li, H. Y., and Shi, Y. L., 2006. Preparation of chitosan-Ce (IV) complex and its effects on preserving cucumbers and degrading parathion. *J. Chin. Rare Earth Soc.*, **24** (suppl.): 176-181 (in Chinese with English abstract).
- Yu, L. N., Wang, D. F., Li, H. Y., Su, L., and Wang, J. L., 2006. Hydrolysis activities of resins of complexes made from polysaccharides and Ce^{4+} . *J. Rare Earths*, **24** (special): 125-129 (in Chinese with English abstract).
- Zhang, J., Zhang, S. T., Wang, Y. P., and Zeng, J. Y., 2007. Composite magnetic microspheres: Preparation and characterization. *J. Magn. Mater.*, **309**: 197-201.
- Zhang, W. J., Zhang H. F., and Li D. Z., 2006. Preparation of Fe_3O_4 magnetic fluid by one-step method with a microemulsion reactor. *Front. Chem. Chin.*, **3**: 272-276.

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