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Study on synthesis and adsorption characterization of hydroxypropyl chitosan metal complex

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ABSTRACT

The studies on the modification of chitosan and the properties of its derivatives using physical fields (ultrasonic field) for raising the reaction speed and reaction yield have been carried out. The basic investigative data were provided for the development on the highly efficient, new water treatment agent. O-(hydroxyl isopropy1) chitosan-Fe(II) was synthesized via 1,2-epoxy-propane derived reaction of Fe^{2+} with chitosan. The structure of the product was identified by its transform Fourier infrared spectrum, UV spectrum, and X-ray diffraction. The adsorptive properties of hydroxypropyl chitosan-Fe(II) complex (HPCTS-Fe^{2+}) for heavy metal ions were researched. The experiments showed that the removal efficiencies were 99.8% and 78.8%, respectively, using 1% (g/mL) of the HPCTS-Fe^{2+}, pH5, initial concentration 1 mg/L Cu^{2+}, 0.1 mg/L Pb^{2+}, respectively, equilibration for 30 min. It showed that HPCTS-Fe^{2+} might be used as a new highly efficient water treatment agent for adsorbing heavy metal ions.

Keywords: Chitosan modification; Adsorptive properties; Ultrasonic enhance; Cu(II); Pb(II)

1. Introduction

Chitosan is the N-deacetylated product of chitin, one of the most abundant biopolymers in nature. Its chemical name is (1-4)-2-acetamido-2-deoxy-β-D-glucose. In recent years, chitosan and its derivatives have received considerable attention due to their potential beneficial activities, such as biocompatibility, nontoxicity, biological activity, and physical and chemical characteristics. It has broad application prospects in water treatment, chemical, textile, food, and medicinal fields. However, the intramolecular and intermolecular hydrogen bonding gives it a move closely crystal structure [1–4], so it is insoluble in water and most organic solvents, limiting its activity and applications. Only when the deacetylation degree is about 50%, the secondary structure is largely destroyed and the crystal degree declined. Hence it can then become soluble in water [5–7] to modify chitosan is an effective way to improve its performance.

The modification of chitosan mainly includes acylation, carboxylation, alkylation, esterification, Schiff base formation, crosslinking, and grafting. Modification rarely adopts effective selective reaction, because both of the hydroxyl and amine groups in chitosan have reactivity. So it often gains a mixture of various derivatives reacting in different positions. It is hard to make in-depth analysis of the relationship between structure and properties and to further research the theoretical investigation and its application [8–10]. Therefore selective reaction of chitosan to gain a more definitive chitosan derivative is the key to solve the above problem, few reports pay attention in this regard.

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This study applied ultrasonic technology to speed up the chitosan modification and improve the reaction yield of chitosan and its derivatives. Through the positioning hydroxypropyl group, new hydroxypropyl chitosan chitosan-Fe (II) compounds have been shown to have excellent adsorption performance.

2. Experimental

2.1. Instrumentation

Automatic X-ray diffraction D/max-IIIA, Japan's Neo-Confucianism company; Atomic adsorption spectrophotometer Thermo M6, America's Fisher Technology Co., Ltd.; Ultraviolet spectrophotometer Uv2550, Island Tianjin Instruments (Suzhou) Co., Ltd.; Fourier infrared analyzer PK-6000 and Origin 6.0 data processing system, America Mattson Company.

2.2. Chemicals and reagents

Chitosan (molecular weight 5 million, the deacetylation degree of 93.6%); ammonium ferrous sulfate; propylene epoxide; and ethanol.

2.3. Procedures

2.3.1. Preparation of chitosan ferrous complexes

Accurately 0.1 g chitosan was weighed and dissolved in 20 mL 5% acetic acid water solution. The pH was adjusted to 2.5 with the addition of dilute aqueous ammonia, stirred, and ultrasonicated for 5 min at 200 Hz, until it turns homogeneous and colloid. Then, upon stirring certain concentrations of ammonium sulfate containing hydroxylamine hydrochloride were added at a constant speed until the final concentration of Fe^{2+} was 16 mg/mL. At that time, the volume of reaction system was 50 mL. The product was filtered after 0.5 h of continuous reaction and then precipitated with acetone–ethanol solution (1:1/V:V), wash the sediment with aqueous ethanol until no SO_4^{2-} was found in the washing liquid. Washing was repeated with anhydrous alcohol again, then dried in an oven to constant weight at 40°C. A yellow powder was obtained which is the chitosan ferrous complex.

2.3.2. Preparation of hydroxypropyl chitosan metal complex

About 2.0 g chitosan ferrous complex was completely dissolved in 33% NaOH and stirred well. After swelling remarkably at room temperature, it was refrigerated at least for 24 h; alkalizing chitosan was obtained. The chitosan was thawed, and superfluous lye was removed by squeezing. To that added 25 mL isopropanol and stirred for 30 min at room temperature. About 10% tetramethyl ammonium hydroxide 1.6 mL and 25 mL propylene oxide were added under stirring at room temperature. The solution wasstirred for 1 h at room temperature. Then the reaction containers were placed in an ultrasonic field to clean. The reaction was refluxed at 60–70°C for 6 h, filtered after cooling, then washed with isopropyl alcohol several times. Deionized water was added and dissolved at room temperature. After filtering, the filter liquor was neutralized by the addition of hydrochloric acid. The resultant precipitate was obtained by adding plenty of acetone, and washed with 95% ethanol twice. A colorless or pale yellow hydroxypropyl chitosan (HPCS) derivative was obtained when dried at 60°C.

3. Results and discussion

3.1. Effect of ultrasonic time on the chitosan modification reaction

The reactants were epoxypropane, catalyst, and chitosan and the ratio was 12 mL:1 mL:1 g. The reaction temperature was 60–70°C. Under 160 W ultrasonic conditions, chitosan reacted with the electrophilic epoxypropane. The relation between substitution degree and processing time can be seen in Fig. 1.

At the beginning of the first 1 h, the substitution degree had already reached 0.39 which showed the reaction had already begun. In 4 h, the substitution degree rapidly increased. Later, the etherification reaction reached an equilibrium state and the substitution degree hardly changed.

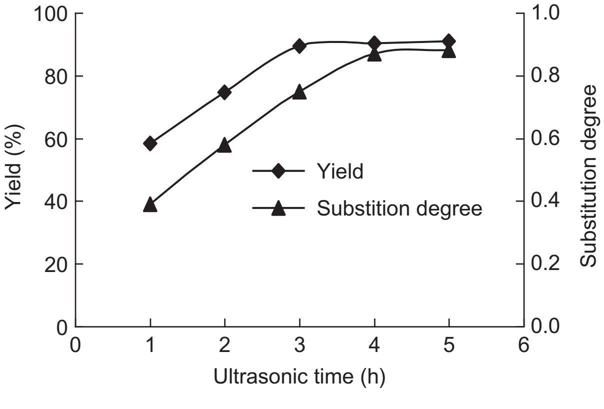


Fig. 1. Effect of ultrasonic irradiation time on the reaction.

3.2. Effect of ultrasonic power on the chitosan modification reaction

The reactants were epoxypropane, catalyst, and chitosan and the ratio was 12 mL:1 mL:1 g. The reaction temperature was 60–70℃ and ultrasonicated for 3h. Experiments were carried out under different ultrasonic powers and the results are shown in Fig. 2.

The result showed that the yield and the substitution degrees increased as the ultrasonic power increased. In less than 120 W, it grew very fast and increased to a great extent. When the power was greater than 120 W, it raised but with a slow speed and a small increase. Therefore, from the aspects of energy consumption, it was relatively economic to choose ultrasonic power of 120 W.

3.3. Infrared spectrometry

The structures of chitosan, chitosan ferrous complex, and the hydroxypropyl chitosan metal complex were investigated by FTIR in the wave number region between 400 and 4000 cm^{-1}.

Fig. 3 shows the comparison of a and b; vibration adsorption peak of N–H and O–H at about 3429 cm^{-1} moved to the high frequency which showed that –NH_2 and –OH participated in the complexing reaction. The bending adsorption peak of N–H at 1514 cm^{-1} in the CTS was resolved into two adsorption peaks at 1496 cm^{-1} and 1581 cm^{-1} in the CTS-Fe^{2+}. The adsorption peak of ν_{C-N} at 1346 cm^{-1} moved to the higher frequency which further illustrated complexion of –NH_2 and Fe^{2+}. After the complexion of secondary hydroxyl group (–OH) and Fe^{2+}, the adsorption peak at 1,138 cm^{-1} moved to the high frequency about 10 cm^{-1}, and the adsorption strength lessened which indicated that complex reactions also took place between secondary hydroxyl group and Fe^{2+}.

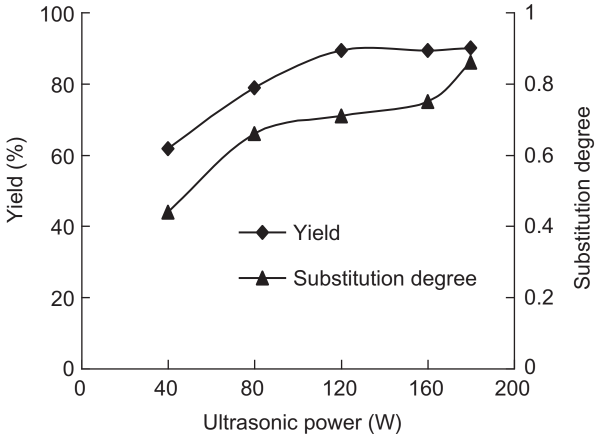
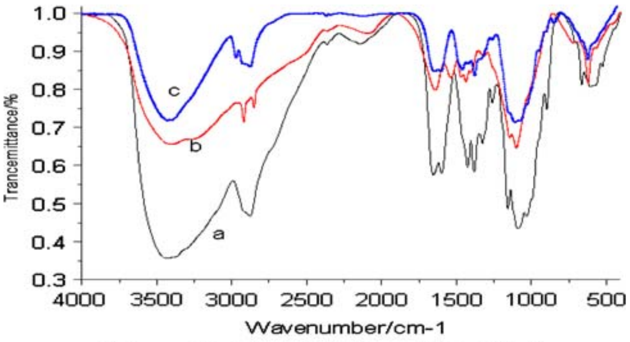


Fig. 2. Effect of power densities of ultrasonic field on the reaction.



Note : a=CTS, b=CTS-Fe^{2+}, c=HPCTS-Fe^{2+}

Fig. 3. IR spectra of CTS, CTS-Fe^{2+}, and HPCTS-Fe^{2+}.

Comparing b to c, after CTS-Fe^{2+} was hydroxypropylated, because of the formation of new bond of C–O and C–O–C, C–O absorption peak on the secondary –OH moved to the 1,200 cm^{-1} and transformed into one peak with increased intensity. The adsorption strength of C_6–OH at 1,030 cm^{-1} dropped obviously which meant the main reaction took place in C_6–OH.

3.4. Ultraviolet spectrometry

CTS and CTS-Fe^{2+} were dissolved into 0.1 mol/L hydrochloric acid solution, respectively, and scanned with ultraviolet spectroscopy between 190 and 400 cm^{-1}.

Fig. 4 shows pure CTS having only one strong but narrow at 202 nm. Compared with CTS, CTS-Fe^{2+} has a red shift about 20 nm. It has a wide and strong peak at 222 nm. Besides, it has another new peak at 336 nm which leads to the change of electronic spectrum. So it can be proved that Fe^{2+} binds to CTS and because of the combination of –NH_2 and Fe^{2+}, the strength of C–N decreases to a certain extent suggesting that the adsorption is mainly located in –NH_2.

3.5. XRD analysis

Fig. 5 shows that chitosan has strong diffraction peak about 10° and 20° indicating crystallinity. That is because there are a lot of –OH and –NH_2 in chitosan molecules. They form the hydrogen bonds which give chitosan its molecular structure. The diffraction peak of modification product of HPCS around 10° weakened obviously and even disappeared. The diffraction peak around 20° broadened and its intensity decreased. This shows diffuse scattering that peak is weak and sample crystallinity has decreased

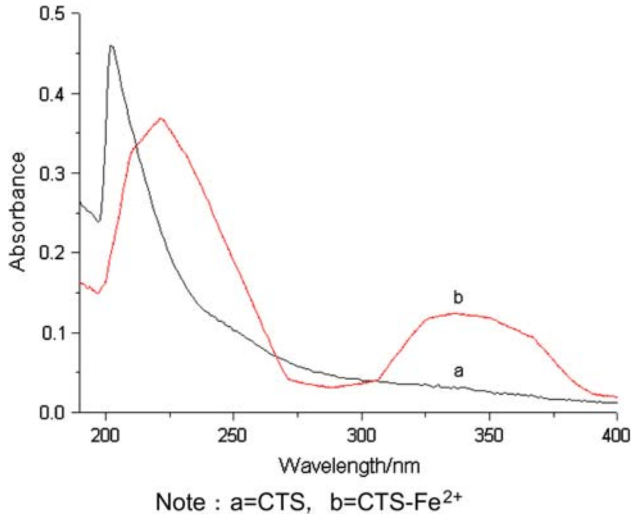


Fig. 4. UV spectra of CTS and CTS-Fe^{2+}.

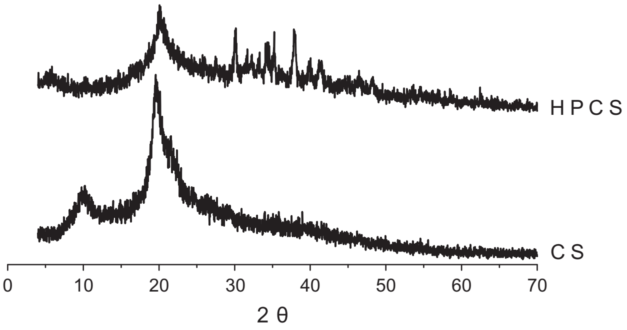


Fig. 5. X-ray diffraction of chitosan and O-(hydroxyl isopropy1) chitosan.

significantly. After the modification of hydroxypropyl, chitosan's crystallinity has changed to a certain degree. Hence there is a greater amorphous area in the structure which leads to modified, improved water solubility. From the perspective of crystal structure, the raw material chitosan has mainly α-chitosan structure. After the modification reaction, the diffraction peak at around 10˚ weakened obviously and even disappeared which shows the product has turned into β-chitosan.

3.6. Adsorption Cu^{2+}

About 0.02 g, 0.1 g, 0.05 g, 0.2 g, and 0.15 g HPCTS-Fe^{2+} were weighed in five 50 mL conical flasks, respectively, then added 20 mL 1 ppm Cu^{2+} standard solution, kept under stirring for 0.5 h and filtered. The residual Cu^{2+} concentration in the filtrate was detected by flame atomic absorption spectrophotometry. In Fig. 6 the standard curves shows linearity.

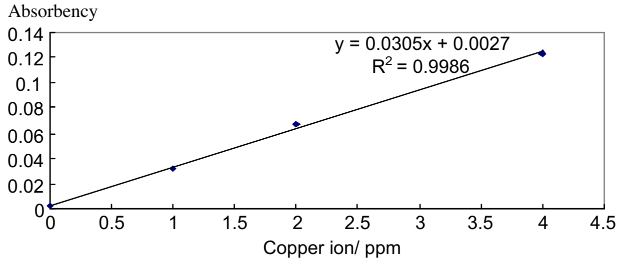


Fig. 6. Adsorption standard curve of copper ion.

Table 1
Adsorption effect on the Cu^{2+} with HPCTS-Fe^{2+} accession

HPCTS-Fe^{2+}/g	The remaining Cu^{2+} concentration/ppm
0.02	0.790
0.05	0.263
0.10	0.132
0.15	0.035
0.20	0.002

Table 1 shows different HPCTS-Fe^{2+} additives and residual Cu^{2+} concentration. As HPCTS-Fe^{2+} increases, the adsorption capabilities increase. When the amount of HPCTS-Fe^{2+} was up to 0.20 g, Cu^{2+} concentration decreased from 1 ppm to 0.002 ppm and the removal rate reached 99.8% (see Fig. 7).

3.7. Adsorption Pb^{2+}

About 0.02 g, 0.1 g, 0.05 g, 0.2 g, and 0.15 g HPCTS-Fe^{2+} were weighed in five 50 mL conical flasks, respectively, then added 20 mL 1 ppm Pb^{2+} standard solution, kept under stirring for 0.5 h, and filtered. About 1 mL filtrate was, diluted 10 times and the residual Pb^{2+} concentration was detected by flame atomic absorption spectrophotometry. Fig. 6 standard curve shows linearity. Table 2 shows different HPCTS-Fe^{2+} additives and residual Pb^{2+} concentration. As HPCTS-Fe^{2+} increases, the adsorption capabilities increase.

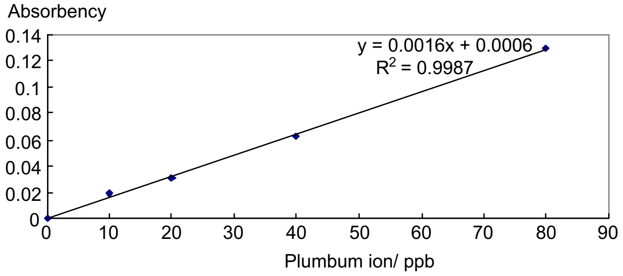


Fig. 7. Adsorption standard curve of plumbum ion.

Table 2
Adsorption effect on the Pb^{2+} with HPCTS-Fe^{2+} accession

HPCTS-Fe^{2+}/g	The remaining Pb^{2+} concentration/ppb
0.02	38.79
0.05	34.89
0.10	27.25
0.15	27.11
0.20	21.24

Note: Graphite furnace atomic absorption spectrophotometry precision is 10 times higher than the flame atomic absorption spectrophotometry, so chooses different units. 1 ppm = 1000 ppb.

When the amount of HPCTS-Fe^{2+} was up to 0.20 g, Pb^{2+} concentration decreased from 100 ppm to 21.24 ppm and the removal rate reached 78.76%.

4. Conclusions

Adopting ultrasonic technology and using epoxy propane as an etherifying agent, hydroxypropyl group was introduced into chitosan's C_6–OH making the new derivative move hydrophilicity than chitosan. Preparatory technological conditions were optimized. The condensation rate of products was 14–19% times greater than conventional methods, and saved consumption of raw materials. For chitosan derivatives, this research opens a new shortcut.

Through a coordination reaction and a grafting reaction, the synthesis of new chitosan derivatives was gained by controlling the reaction position. The structure of this new compound was characterized by ultraviolet spectrum, infrared spectrum analysis, and X-ray diffraction. The adsorption of Pb^{2+} and Cu^{2+} to the hydroxypropyl chitosan ferrous complexes showed good selectivity for Cu^{2+} with the removal rate of 99.8%. This provides the theoretical foundation for the development of new high adsorption materials in the water treatment with a broad application prospect.

Acknowledgments

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