Synthesis and adsorption properties of cross-linked carboxymethyl starch (CMS)

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Abstract. Cross-linked carboxymethyl starch CMS was synthesized with cross-linked starch as raw material, sodium chloroacetate as etherification agent and sodium hydroxide as catalyst, and the structure of the product was characterized by FTIR, SEM and XRD. The optimum synthesis conditions of CMS were m (CSt): m (MCA) = 5:3, NaOH dosage 12 ml, reaction temperature 55 °C and reaction time 3 h. When the concentration of copper ion in the simulated water sample was 25 mg/L and the dosage of CMS was 2 g/L, the removal rate of copper ion was 96.0%, and the adsorption capacity of CMS was 15.4 mg/g.

1. Introduction

Nowadays, all kinds of industrial enterprises in the world still discharge a large number of heavy metal ions to the environment, such as cadmium, mercury, lead, arsenic, copper, zinc, nickel, etc. Because these heavy metals can’t be degraded by microorganisms, they become persistent pollutants, which greatly endanger the ecological environment and people's health [1-2]. In addition, heavy metals are valuable resources. It will cause great economic losses if the heavy metals can’t be recycled. Therefore, the treatment of heavy metal pollution is of great significance.

The common treatment methods for these dissolved heavy metals are chemical precipitation, electrolysis, reverse osmosis, ion exchange and adsorption. Among them, adsorption method is considered as one of the most effective wastewater treatment methods because of its high efficiency, simple operation and low cost [3]. Because of a large specific surface area, but few effective groups in the adsorbents, the absorption of common adsorbents, such as activated carbon [4-5] and zeolite, is mainly physical adsorption, which result in the non-selectivity for heavy metal ion adsorption. However, the synthetic adsorbents, such as polystyrene and phenolic resin, are difficult to be biodegraded because their matrix is synthetic polymer resin. If the waste resin is not treated properly, it will cause secondary pollution to the environment. Therefore, the development and research of the adsorption materials based natural synthetic organic polymers are focused on by researchers at home and abroad, mainly including starch, chitosan and cellulose.

Starch has many advantages, such as wide source, low price, and easy biodegradation and so on, which plays an important role in heavy metal adsorption materials [3,6]. As an anion group, carboxylic acid group can be combined with heavy metal ions in water by electrostatic force to realize the exchange and adsorption of heavy metal ions. Therefore, it is possible to obtain a heavy metal ion...
adsorbent by introducing carboxylic acid group into starch \cite{7-10}, which can replace the synthetic weak acid cation exchange resin.

In this paper, cross-linked carboxymethyl starch (CMS) was synthesized with cross-linked starch (CSt) and sodium chloroacetate (MCA) as raw materials and sodium hydroxide as catalyst. The structure of the product was characterized by IR, SEM and XRD, and the adsorption property of the product to copper ion was tested also.

2. Materials and methods

2.1. Reagents

Cross-linked starch (CSt) was self made. Sodium chloroacetate (MCA) was purchased from Shanghai Aladdin Chemical Co., Ltd., China. Sodium hydroxide was purchased from Tianjin Chemical Reagent No. 3 Factory, China. Hydrochloric acid was purchased from Beijing Chemical Works, China. Anhydrous ethanol was purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd., China. CuSO4·5H2O was purchased from Tianjin Yongda Chemical Reagent Co., Ltd., China. All the above ingredients except cross-linked starch were of analytical grade.

2.2. Synthesis of cross-linked carboxymethyl starch (CMS)

5 g of cross-linked starch and 20 ml of mixed solution of ethanol and deionized water (the volume ratio of the two was 1:1) were added into a three port flask. The system was placed in a water bath of 55 °C and stirred evenly under mechanical agitation, and then it was alkalized for 0.5 h by adding 12 ml of NaOH solution (15%). Then 3 g of sodium chloroacetate (dissolved in 10 ml deionized water) was added dropwise into the system and the reaction was carried out at constant temperature for 3 h. After the reaction, the pH value of the solution was adjusted to 7-8 with concentrated hydrochloric acid, and then the filter cake was obtained by filtration and washed with anhydrous ethanol for many times. The filter cake was vacuum dried at 50 °C, and the white powder obtained was CMS. The reaction processes occurred in the system are as follows. Formula 3 shows the side reaction process of hydrolysis of chloroacetic acid in alkaline solution.

\[
\text{St} \quad \text{O} \quad \text{H} \quad \text{OH}^+ \quad \text{St} \quad \text{O}^- + \text{H}_2\text{O} \quad (1)
\]

\[
\text{St} \quad \text{O}^- + \text{Cl}^- + \text{H}_2\text{COOH} \quad \text{St} \quad \text{O}^- + \text{H}_2\text{COO}^- + \text{Cl}^- \quad (2)
\]

\[
\text{OH}^- + \text{Cl}^- + \text{H}_2\text{COOH} \quad \text{H}_2\text{COOH} \quad \text{H}_2\text{COO}^- + \text{Cl}^- \quad (3)
\]

2.3. Characterization of cross-linked starch and CMS

Infrared spectra of cross-linked starch and CMS were measured via a SP100 Fourier-transform infrared (FTIR) spectrometer (PerkinElmer, USA.) using the potassium bromide pellet method. The wavenumber range was 4000-400 cm\(^{-1}\). XRD patterns of the samples were obtained using a Ultima IV X-ray diffractometer (Rigaku, Japan) equipped with a Cu-ka radiation source operated at 40 kV and 40 mA, with the diffraction angle scanned at a speed of 4°/min over a 2θ range of 10-60°. SEM images were observed on an Inspect S50 scanning microscope (FEI, USA). The acceleration voltage was 5 kV and the magnification was 2000 times.
2.4. Adsorption experiments
The reserve solution of copper ions (1 g/L) was prepared by dissolving 3.9063 g CuSO$_4$·5H$_2$O in 1000 mL deionized water. The water sample to be tested of copper ions (25mg/L) was prepared by removing 5 mL reserve solution into 200 mL deionized water. A certain amount of CMS was accurately weighed and put into the water sample. The water sample was stirred by magnetic agitation for 40 min at 500 r/min, and then precipitated for 5 h. The concentration of Cu$^{2+}$ in the supernatant was determined by sodium diethylaminodithiocarbonate spectrophotometry via a TU-1900 Dual-beam Ultraviolet-Visible Spectrophotometer (Beijing General Analytical Instrument Co., Ltd., China). According to the following formulas, the adsorption capacity of CMS ($Q$, mg/g) and the removal rate of Cu$^{2+}$ ($P$, %) are calculated.

$$Q = \frac{(C_0 - C_1)V}{m}$$  \tag{4}

$$P = \frac{C_0 - C_1}{C_0} \times 100\%$$  \tag{5}

In the formulas, $c_0$ and $c_1$ are the initial and final concentrations of Cu$^{2+}$ in supernatant, respectively, mg/L, $V$ is the volume of Cu$^{2+}$ solution.

3. Results and discussion

3.1. Synthesis conditions of CMS
Based on the removal rates of copper ion by CMS, the synthesis conditions were selected.

3.1.1. Effect of reaction temperature on adsorption performance. The effect of reaction temperature on the adsorption performance of CMS was studied. The dosage of CMS was 2 g/L, and the results are shown in Figure 1. The reaction temperature had a great influence on the adsorption performance of CMS. With the increase of reaction temperature, the removal rate of copper ion increased also, while when the temperature was higher than 55 °C, the removal rate decreased. This is mainly because when the temperature is too high, the hydrolysis reaction of chloroacetic acid is accelerated (formula 3). At the same time, gelatinization occurs on the surface of starch particles, which hinders the penetration of etherifying agent molecules into the inside of starch particles.

![Figure 1. Effect of reaction temperature on removal rate of Cu$^{2+}$](image)

3.1.2. Effect of NaOH dosage on adsorption performance. The effect of the dosage of catalyst on the adsorption performance of CMS was studied. As shown in Figure 2, the removal rate of Cu$^{2+}$ increased first and then decreased with the increase of NaOH dosage. This is mainly because with the increase of NaOH content, the number of oxygen anion changed from hydroxyl in starch increases, which improves the rate of nucleophilic substitution reaction. On the other hand, a proper amount of alkali can promote the expansion of starch granules, which is conducive to the penetration of etherifying
agent into starch granules for reaction, and also improves the reaction rate. But when the alkalinity of the system is too strong, the side reaction of hydrolysis of chloroacetic acid is intensified, and then resulting in the decrease of the concentration of electrophilic reagent. In addition, excessive alkali can also cause the gelatinization of starch granules, which will increase the viscosity of the reaction system to hinder the movement of each reagent molecule, and reduce the number of effective collisions.

![Figure 2. Effect of catalyst dosage on removal rate of Cu\(^{2+}\)](image)

In conclusion, the best synthesis condition of CMS was \(m(\text{CSt}):m(\text{MCA}) = 5:3\), NaOH dosage 12 ml, reaction temperature 55 °C and reaction time 3 h.

3.2. Characterization of CMS

3.2.1. FTIR analysis. The CMS was characterized by IR. Compared with the infrared spectrum of cross-linked starch, a new absorption peak appeared at 1415 cm\(^{-1}\) in the infrared spectrum of CMS, which was the characteristic absorption peak of carboxylate. In addition, the absorption peak of C-O-C bond at 1021 cm\(^{-1}\) was significantly enhanced, which was due to the increase of the number of ether bonds in CMS macromolecules after cross-linking and etherification. The above analysis showed that after etherification, a large number of carboxymethyl anion groups were introduced into starch macromolecules.

![Figure 3. Infrared spectra of cross-linked starch and CMS](image)

3.2.2. SEM analysis. Figure 4 was the scanning electron micrographs of cross-linked starch (a) and CMS (b). The particles of cross-linked starch were spherical or polyhedral in shape, with smooth surface, large diameter, high arrangement regularity, and some particles had cavities. This is due to the interweaving of straight chain and branch chain inside the cross-linked starch molecule, which made the starch particles maintain certain integrity. After carboxymethylation, the particle size of CMS increased, and the surface regularity decreased, resulting in the appearance of distortion and a large number of dents.
3.2.3. XRD analysis. The X-ray diffraction spectra of cross-linked starch and CMS were shown in Figure 5. The peak shape of CMS changed greatly, not only the diffraction intensity was obviously weakened, but also the peak shape changed into dispersion peak. This showed that the crystalline area of cross-linked starch was destroyed after carboxymethylation. The reason for the above changes is that the carboxymethyl group is an anionic group and has a large steric hindrance. The hindrance effect weakens the intermolecular force of starch, especially the intermolecular hydrogen bond association, so that the integrity of starch crystal structure is destroyed and the crystalline zone is reduced. Compared with the cross-linked starch, CMS particles are more loosely so that molecules or ions can easily enter into its interior, which is conducive to the capture and adsorption of heavy metal ions by CMS. In addition, there were three peaks at 31°, 45° and 56° in the spectrum of CMS, which attributed to NaCl produced in the process of adjusting pH value.

![Figure 4. SEM images of cross-linked starch and CMS](image)

![Figure 5. XRD patterns of cross-linked starch and CMS](image)

3.3. Adsorption property of CMS

The concentration of Cu^{2+} of the simulated water samples used in the adsorption experiment was 25 mg/L and pH=7. The effect of CMS dosage on the removal rate of copper ion was tested at room temperature. The results were shown in figure 6. The removal rate of copper ion increased rapidly with the increase of dosage. When the dosage was 2 g/L, the removal rate of copper ion was 96.0%, and the adsorption capacity of CMS was 15.4 mg/g.
4. Conclusions
Cross-linked carboxymethyl starch CMS was synthesized with cross-linked starch as raw material, sodium chloroacetate as etherification agent and sodium hydroxide as catalyst. The optimum synthesis conditions of CMS were m (CSt): m (MCA) = 5:3, NaOH dosage 12 ml, reaction temperature 55 °C, reaction time 3 h.

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