

Novel Crosslinked Starch Microspheres as Adsorbents of Cu²⁺

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ABSTRACT: A novel adsorbent, a crosslinked starch microsphere (CSM), was prepared from soluble starch and *N,N'*-methylenebisacrylamide. The microporous structure of the CSM was determined with scanning electron microscopy. The diameter distribution of the CSMs was quite uniform, and the average diameter of the microparticles was estimated to be 50 μm . Cu²⁺ was introduced into the CSM. The successful adsorption of Cu²⁺ in the CSM was con-

firmed with Fourier transform infrared spectroscopy. The crystal structure of the CSM was destroyed after the incorporation of Cu²⁺. This was proven with X-ray diffraction. The thermal stability of the CSM was weakened with the introduction of Cu²⁺ during simultaneous thermal analysis. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 487–490, 2010

Key words: adsorption; thermal properties

INTRODUCTION

The starch microsphere, known for its biocompatibility, biodegradability, and stability, has been studied in a wide range of application areas, such as biology, medicine, and drug delivery.^{1,2} Recently, the starch microsphere has attracted great interests as a novel adsorption material because of its microporous structure,³ high surface area,^{4,5} and easy accessibility with the presence of active groups, such as hydroxyl and amino groups.^{6,7} To date, however, there have been few publications reporting the starch microsphere as a metal-ion adsorbent.

In our study, a novel crosslinked starch microsphere (CSM) was synthesized from soluble starch and *N,N'*-methylenebisacrylamide. The CSM exhibited a microporous structure, good mechanical properties, and chemical activity. The CSM was used as an adsorbent of copper ion. The results show that Cu²⁺ was successfully adsorbed in the CSM. Interaction between Cu²⁺ and the active groups of the CSM was observed. The crystal structure and thermal stability of the CSM decreased after the incorporation of Cu²⁺. Our preliminary study demonstrated the

mechanism and possibility of CSMs as adsorbents of metal ions such as Cu²⁺, which suggests potential applications of CSMs in areas such as wastewater treatment, supported meal catalysts, biomimetics, and ion-exchange resins.

EXPERIMENTAL

Reagents and materials

Soluble starch was purchased from Junle Chemical Works (Peng-Zhou, Si-Chuan Province, China). Cyclohexane, chloroform, sodium hydroxide, Span60, Tween60, K₂S₂O₈, Na₂SO₃, *N,N'*-methylenebisacrylamide, ethyl acetate, acetone, anhydrous ethanol, and CuSO₄ were all obtained from Xian-Yang Guo-Zhong Synthesis and Laundry, Ltd. (Xian-Yang, Shaan-Xi Province, China). All of the chemicals were analytical reagents and were used as received.

Characterization

The morphology of the CSM was determined with a JSM-6460 scanning electron microscope (Electronics Enterprise, Tokyo, Japan). A D/max-2200pc X-ray diffractometer (Rigaku, Tokyo, Japan) was used to measure the crystal structure of the CSM. The presence of Cu²⁺ in the CSM was confirmed with a Vector 22 Fourier transform infrared (FTIR) spectroscopy (Bruker, Karlsruhe, Germany). The thermal analysis of the CSM was conducted with a SDTQ600 simultaneous thermal analyzer (TA, New Castle, DE). The

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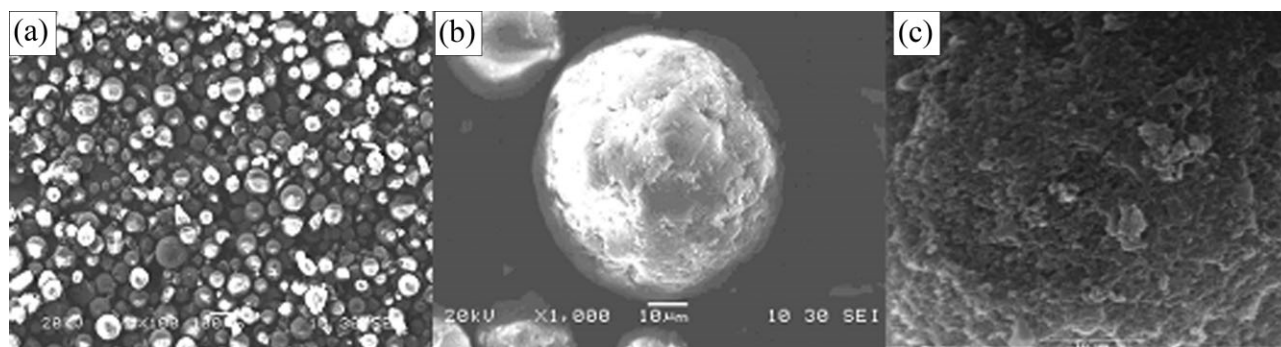


Figure 1 Scanning electron micrographs of CSMs at magnifications of (a) 100, (b) 1000, and (c) 1500 \times .

concentration of Cu^{2+} was measured with an AA-6800 atomic absorption spectrophotometer (Shimadzu, Tokyo, Japan).

Synthesis of CSM

Soluble starch (2 g) was dissolved in 20 mL of distilled water with mechanical stirring (pH = 8). The solution was heated to 80°C and kept there for 30 min to completely dissolve the starch. The temperature was subsequently reduced to 50°C. The starch solution was added to a 100-mL dispersion (1 g of Span 60/Tween 60 dispersed in 80 mL of cyclohexane and 20 mL of chloroform). The obtained water-in-oil emulsion was mechanically stirred for 30 min.

N,N'-Methylenebisacrylamide (0.2 g) was dissolved in 30 mL of chloroform in a three-mouthed flask, which was deoxygenated with nitrogen before use. $\text{K}_2\text{S}_2\text{O}_8$ (0.04 g) and Na_2SO_3 (0.03 g) were then added to the *N,N'*-methylenebisacrylamide/chloroform solution. The resultant solution was mixed with the starch emulsion obtained previously at 50°C for 2 h. The CSM was obtained after centrifugal separation. The resulting CSM was washed with ethyl acetate, acetone, and anhydrous ethanol in turn.

Adsorption of Cu^{2+} in the CSM

The static adsorptive method was used to determine the adsorption capacity of the CSM. The CSM (0.5 g) was added to 50 mL of aqueous CuSO_4 in a conical flask and then kept at 25°C for 24 h. After 24 h of isothermal adsorption, the CSM was filtered out from the solution. The residual Cu^{2+} in solution was determined with atomic absorption spectrometry. The adsorption capacity [Q (mmol/g)] was calculated with the following formula:

$$Q = (C_0 - C_e)V/W \quad (1)$$

where C_0 and C_e represent the concentrations of Cu^{2+} before and after adsorption (mmol/L), respectively; V is the solution volume of Cu^{2+} (L); and W is the mass of the CSM (g).

RESULTS AND DISCUSSION

Figure 1 shows the scanning electron micrographs of the CSM. A high density of microspheres with a uniform diameter distribution was observed. The average diameter of the CSMs was estimated to be around 50 μm . The highly microporous structure provided a high surface area for the CSM. The forces among starch molecules were enhanced as a result of the crosslinkage, which gave rise to a closer linkage of starch molecules. A three-dimensional structure containing microspheres was consequently formed from the water phase. Meanwhile, internal water in the microsphere was extruded, which left a lot of micropores on the resulting structure. The presence of micropores provided an extra advantage for the adsorption of metal ions.

FTIR spectroscopy

The FTIR spectra of soluble starch, CSM, and CSM- Cu^{2+} are shown in Figure 2. The band at 3445 cm^{-1} , related to the stretch vibration absorption of N-H and O-H,⁸ was enhanced in the spectrum of CSM [Fig. 2(b)] compared to that of soluble starch [Fig. 2(a)]. As

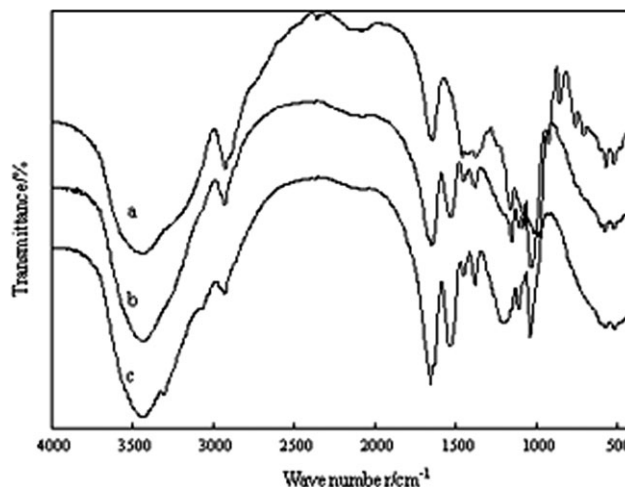


Figure 2 FTIR spectra of (a) soluble starch, (b) CSMs, and (c) CSM- Cu^{2+} .

far as CSM-Cu²⁺ was concerned [Fig. 2(c)], a low shift of the band was observed. A small band found at 3350 cm⁻¹ in the spectrum of CSM-Cu²⁺ [Fig. 2(c)] indicated that the hydrogen-bonded association between -NH- or -OH decreased with the presence of Cu²⁺, whereas no such band was observed in the spectrum of either starch or CSM. A band observed at 2926 cm⁻¹ in the spectrum of starch [Fig. 2(a)] was attributed to the stretch vibration absorption of the anhydroglucose unit.⁹ The band upshifted to 3350 cm⁻¹ in the spectra of both the CSM [Fig. 2(b)] and CSM-Cu²⁺ [Fig. 2(c)], which suggested good interaction between starch and *N,N'*-methylenebisacrylamide. The two bands at 1647 and 1536 cm⁻¹ in the spectrum of the CSM [Fig. 2(b)] originated from C=O and N-H vibration absorption, respectively;¹⁰ this confirmed the presence of hydroxyl and amide groups in the CSM. These peaks were not observed in the spectrum of starch [Fig. 2(a)]. The C-O vibration absorption band upshifted to 1668 cm⁻¹ after the incorporation of Cu²⁺ into the CSM; this indicated interaction between Cu²⁺ and the oxygen atoms of the primary hydroxyl and second hydroxyl in the anhydroglucose unit of the CSM. The N-H vibration absorption band upshifted to 1543 cm⁻¹ after the absorption of Cu²⁺ in the CSM, which suggested good interaction between Cu²⁺ and the nitrogen atom. The FTIR results suggest that Cu²⁺ was adsorbed into the CSM not only through the physical way but also via interaction between the copper ion and active groups of the CSM.

X-ray diffraction (XRD)

Figure 3(a-c) shows the XRD spectrograms of soluble starch, CSM, and CSM-Cu²⁺, respectively. Three typical peaks at 15, 17, and 21° were found in the

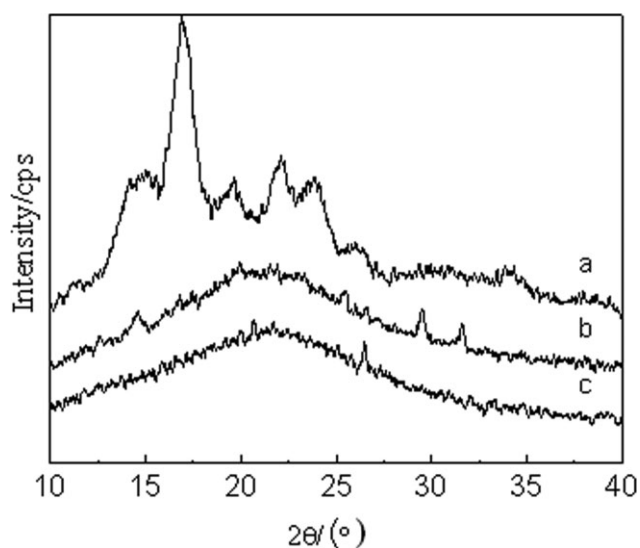


Figure 3 XRD spectra of (a) soluble starch, (b) CSMs, and (c) CSM-Cu²⁺.

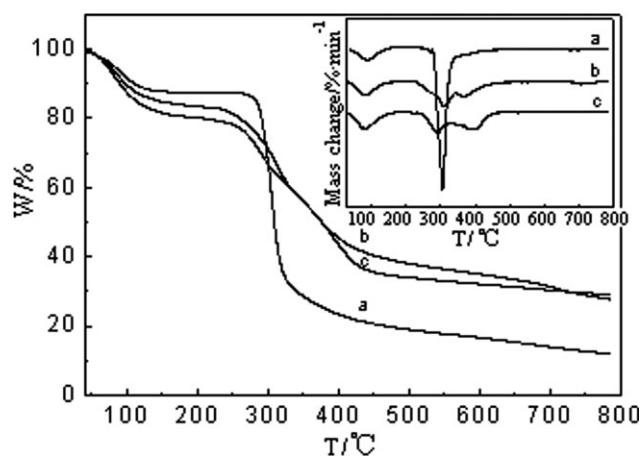


Figure 4 TG curves of (a) soluble starch, (b) CSMs, and (c) CSM-Cu²⁺ (T = temperature; W = weight fraction of the three samples). The inset shows DTG curves of (a) soluble starch, (b) CSMs, and (c) CSM-Cu²⁺.

spectrum of soluble starch [Fig. 3(a)]. The intensity of the peaks at 15 and 21° decreased significantly in the spectrum of the CSM, and no peak was observed at 17° [Fig. 3(b)]. This may have been due to the fact that the crystal structure of starch was destroyed after the crosslinkage of *N,N'*-methylenebisacrylamide. The crystallinity degree of CSM was determined to be 6.41%. In the spectrum of CSM-Cu²⁺, only one small peak was found at 21° with a smaller intensity than that in the spectrum of CSM; this suggested a further decreased crystallization capacity. The crystallinity degree of CSM-Cu²⁺ decreased to 0.48%, basically located in the disordered noncrystalline state. The absorbed Cu²⁺ incorporated with N or O, prevented interaction from intermolecular hydrogen bonds and led to worse crystallization of CSM.

Simultaneous thermal analysis

The thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of soluble starch, CSM, and CSM-Cu²⁺ are shown in Figure 4(a-c, including the inset). In the range 30–150°C, the first dehydration temperatures of CSM [Fig. 4(b)] and CSM-Cu²⁺ [Fig. 4(c)] were lower than that of soluble starch [Fig. 4(a)]. The largest weight loss was obtained in CSM-Cu²⁺; this indicated that the amount of free moisture in CSM-Cu²⁺ was greater than that in the CSM or soluble starch, whereas soluble starch contained the highest amounts of bound water. In the range 150–350°C, the rate of mass change of soluble starch was the highest, for the crosslinking action of *N,N'*-methylenebisacrylamide increased the thermal stability of the CSM and CSM-Cu²⁺. Also, the decomposition temperature of CSM-Cu²⁺ was lower than that of the CSM and soluble starch. The weight

loss of CSM-Cu²⁺ was greater than that of CSM because of the presence of Cu²⁺, which facilitated the strand break of CSM. As shown in the inset in Figure 4, one peak was observed at 365°C in the spectrum of the CSM, and one was found at 394°C in CSM-Cu²⁺, whereas no peak was present in the DTG curve of soluble starch. This peak probably arose from the thermal decomposition of the cross-linkage between *N,N'*-methylenebisacrylamide and α -D-glycosyl isothiocyanate. The glycosidic bond between the CSM and α -D-glycosyl isothiocyanate was weakened because of the incorporation of Cu²⁺. The breaking of the crosslinked bond, however, was buffered. The intramolecular and intermolecular hydrogen bonds of CSM were destroyed by Cu²⁺, which gave rise to the decreased crystallinity degree and worse thermal stability of CSM-Cu²⁺.

CONCLUSIONS

In this article, we presented the preparation of a novel metal-ion absorbent CSM from soluble starch and *N,N'*-methylenebisacrylamide. The CSM exhibited good mechanical properties, a microporous structure, and a high surface area. Cu²⁺ was adsorbed into the CSM with isothermal adsorption. Good performance of the CSM as an absorbent of Cu²⁺ was demonstrated. The presence of Cu²⁺ in the resulting CSM was confirmed with FTIR. The FTIR results also indicate that Cu²⁺ was adsorbed

into the CSM not only through the physical way but also via interaction between the copper ion and active groups of the CSM. The XRD results confirm that the crystal structure of the CSM was destroyed after the incorporation of Cu²⁺. The presence of Cu²⁺ also influenced the thermal stability of the CSM during simultaneous thermal analysis. Cu²⁺ facilitated the breaking of the glycosidic bond in the CSM molecule but buffered the break of the cross-linked bond.

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