

Synthesis and Adsorption Properties of Insoluble Starch Xanthate (ISX)

Haihua Li^{1,2}, Lihui Zhang¹, Yuhua Gao² and Zhenfa Liu¹

¹ Institute of Energy Sources, Hebei Academy of Sciences, Shijiazhuang Hebei 050081, China;

² Hebei Engineering Research Center Water Saving in Industry, Shijiazhuang Hebei 050081, China

Email: 873756647@qq.com

Abstract. Starch xanthate was synthesized from corn starch and CS₂ under alkaline condition. The effects of catalyst dosage, CS₂ dosage and reaction temperature on sulfur content and copper ion removal rate were studied by single factor experiments, and the structure of the product was characterized by FTIR, SEM and XRD. The results showed that the optimum synthetic condition of ISX was NaOH dosage 16 mL, CS₂ dosage 2.5 mL, reaction temperature 35 °C and reaction time 2 h. The sulfur content of ISX synthesized under this condition was 7.54%, the removal rate of copper ion was 90.5%, and the adsorption capacity of ISX was 90.0 mg/g.

1. Introduction

Nowadays, all kinds of industrial enterprises in the world still emit a large number of heavy metal ions to the environment, such as cadmium, mercury, lead, arsenic, copper, zinc, nickel and so on. Because these heavy metals can not be degraded by microorganisms, they become persistent pollutants, which greatly endanger the ecological environment and people's health [1-3]. For the treatment of wastewater containing heavy metal ions, chemical precipitation, solvent extraction, membrane separation, electrolysis and ion exchange methods are commonly used [4]. However, these methods generally have the problems of high cost, complex operation and secondary pollution. Polymer heavy metal traps can combine heavy metal ions in a wide range of pH and ambient temperature to produce stable and insoluble metal chelates with high reaction efficiency and good selectivity, have obvious advantages in the treatment of heavy metal wastewater with low concentration (100 mg/L). They have become the key method for the prevention and control of heavy metals in water [5-7]. Synthetic organic macromolecule heavy metal collectors are mainly from petroleum products, and their prices are increasing year by year. Moreover, the toxicity of residual monomers limits their application in water treatment. Compared with the synthetic organic polymer, the modified natural macromolecule heavy metal collector has the advantages of high selectivity, non-toxicity and low price [8, 9].

Among many natural macromolecule heavy metal traps, the research and development of starch modification is particularly noticeable. Starch derivative flocculants have been used in wastewater treatment in the United States, Japan, Britain and other countries. Starch xanthate (ISX) is a starch derivative obtained by xanthation of starch with carbon disulfide after cross-linking under alkaline conditions [10]. Compared with other heavy metal traps, ISX is an economic and environmentally friendly adsorbent with simple synthetic process, good removal effect of heavy metal ions and low production cost.

In this paper, the synthesis conditions of ISX were systematically studied, and the structure of the



product was characterized. Copper sulfate solution was used to simulate heavy metal wastewater to study the adsorption performance of ISX for copper ions.

2. Materials and Methods

2.1. Reagents

Corn Starch, Reagent Grade, was purchased from Shanghai Aladdin Chemical Co., Ltd., China. CS₂, was purchased from Shanghai Aladdin Chemical Co., Ltd., China. NaOH, Acetone and CuSO₄·5H₂O were purchased from Tianjin Fuchen Chemical Reagent Factory, China. All the above ingredients except corn starch were of analytical grades.

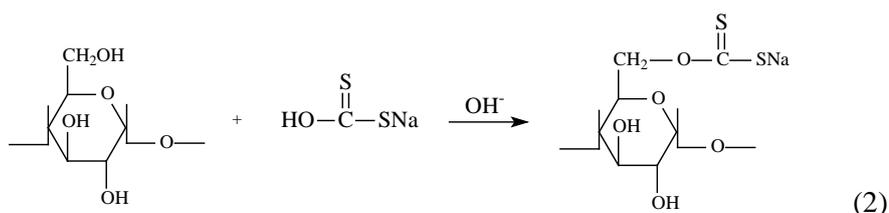
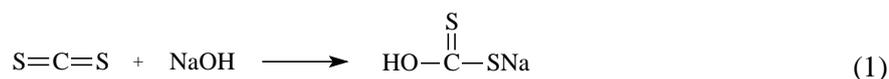
2.2. Synthesis of Cross-linked Starch [11, 12]

15 g corn starch was dispersed in 50 mL of the concentration of 1% NaCl solution and the resulting slurry was placed in a water bath preset at 30°C. Then, 15% NaOH solution 4mL and epoxy chloropropane (EPI) 1mL were added dropwise into the reaction system under continuous stirring, and reacted at constant temperature for 5 h.

The synthesized product was separated by filtration. The precipitate was dispersed in distilled water and adjusted pH by HCl to 7-8. Then, the product was washed by a lot of water and ethanol, finally, dried to constant weight in a vacuum oven at a 60 °C.

2.3. Synthesis of Insoluble Xanthate Starch (ISX)

5 g cross-linked starch was dispersed in a flask with three necks with 40mL deionized water placing in a 30°C water bath. The system was alkalinized for 0.5 h under stirring by adding 16mL of the concentration of 15% NaOH solution. After alkalinized, 2.5mL CS₂ was added in the flask under stirring and reacted for 2 h. Then, 25mL MgSO₄ solution (60 g/L) was added to the system and continued to react for 15 minutes. After the reaction, the cake obtained by filtering was washed with deionized water until its pH=7-8, and then washed with acetone three times to remove water from the product. The filter cake was vacuum dried for 2 h at 40°C, and the light yellow powder was ISX. The reaction processes were as follows:



2.4. Characterization of Corn and ISX

Infrared spectra of corn starch and ISX 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 a Inspect S50 scanning microscope (FEI, USA). The acceleration voltage was 5 kV and the magnification was 2000 times. The content of sulfur of ISX was determined by a vario mCRO cube element analyzer (Elementar, Germany).

2.5. Adsorption Experiments

The reserve solution of copper ions (1 g/L) was prepared by dissolving 1 g CuSO₄·5H₂O in 1000mL deionized water. The water sample to be tested of copper ions (25mg/L) was prepared by removing

5mL reserve solution into 200mL deionized water. A certain amount of ISX was accurately weighed and put into the sample. The sample was stirred by magnetic force for 40 min at 500r/min, and then precipitated for 4 h. The concentration of Cu^{2+} in water samples 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 formula, the removal rate of Cu^{2+} ($P\%$) was calculated.

$$P\% = \frac{c_0 - c_1}{c_0} \times 100\% \quad (3)$$

In the formula, c_0 and c_1 were the initial and final concentrations of Cu^{2+} in water sample, respectively, mg/L.

3. Results and Discussion

3.1. Synthetic Conditions of ISX

The sedimentation volume of the cross-linked starch was 19 mL. The synthetic conditions of ISX were screened based on the content of sulfur ($S\%$) and the removal rate of Cu^{2+} ($P\%$). The dosage of ISX was 250 mg/L.

3.1.1. Effect of NaOH Dosage. In xanthogen acidification of cross-linked starch, alkaline conditions are necessary, and the amount of alkali has a great influence on the degree of xanthogen acidification. The effect of NaOH dosage on the content of sulfur and the removal rate of Cu^{2+} were investigated under the conditions that CS_2 dosage was 2.5 mL, reaction temperature was 35 °C and reaction time was 2 h. As shown in figure 1, the sulfur content of ISX increased with the increase of NaOH dosage. When NaOH dosage was less than 16mL, the sulfur content of the product increased significantly. While continuing to increase the dosage of NaOH, the increase of $S\%$ slowed down. The tendency of the removal rate of Cu^{2+} by ISX was similar to that of $S\%$. This was mainly due to the sulfhydryl group as the functional group in ISX. With the increase of $S\%$, the content of sulfhydryl group in the product increased, and the removal rate of Cu^{2+} also increased. But the more alkali was used, the more deionized water was needed to wash and remove excess alkali, which results in waste of water. Therefore, the alkali dosage we choosing was 16mL.

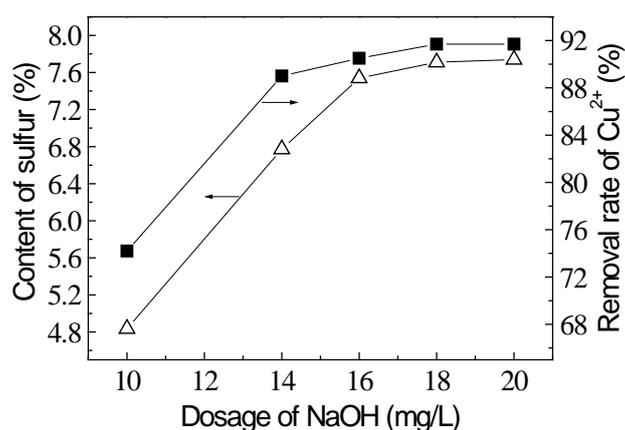


Figure 1. Effect of NaOH Dosage on Sulfur Content and Cu^{2+} Removal Rate

3.1.2. Effect of CS_2 dosage. As shown in figure 2, the $S\%$ increased with the increase of CS_2 dosage. When the dosage of CS_2 exceeded 2.5 mL, the sulfur content of the product decreased. This was mainly due to the fact that excessive CS_2 inhibited the opening of starch ring and reduced the reaction rate.

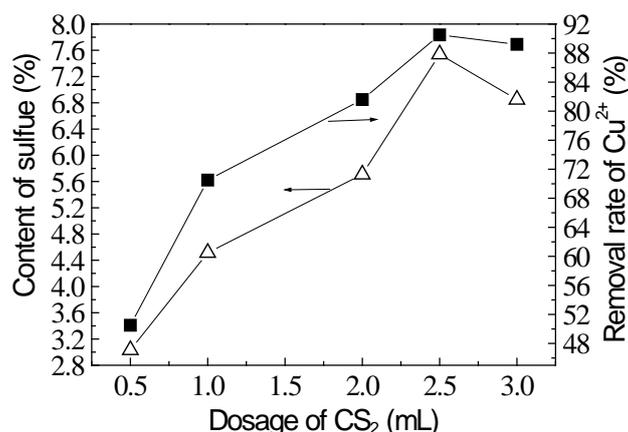


Figure 2. Effect of CS₂ Dosage on Sulfur Content and Cu²⁺ Ion Removal Rate

3.1.3. Effect of Temperature. It was reported that the temperature of xanthate acidification is generally 20-40°C, which mainly because the boiling point of CS₂ is very low (46-47 °C), and the water solubility of CS₂ is not good, and the reaction rate of xanthate with alkali is slow. Xanthan acidification was carried out at different temperatures to investigate the effect of temperature on the product. As shown in figure 3, when temperature was below to 35°C, S% gradually increased with the temperature increasing. While when the temperature was above 35°C, S% decreased rapidly. This was mainly because the reaction system of CS₂ and NaOH was heterogeneous, including solid-phase cross-linked starch, liquid-phase CS₂ and water, and gas-phase CS₂ and steam. high reaction temperature would cause the volatilization of CS₂, resulting in inadequate xanthate acidification reaction and the adverse side reaction. And the reaction was exothermic, and low temperature was conducive to the positive direction of the reaction. But the lower the reaction temperature, the longer the reaction time, so the temperature we choosing was 35°C.

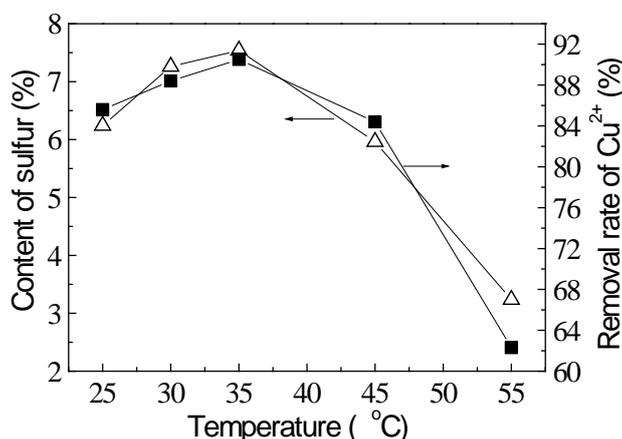


Figure 3. Effect of Temperature on Sulfur Content and Cu²⁺ Removal Rate

In summary, the optimum synthetic conditions of ISX were NaOH dosage 16mL, CS₂ dosage 2.5 mL, reaction temperature 35 °C, magnesium sulfate dosage 25 mL and reaction time 2 h. Under these conditions, S% of the product was 7.54% and the removal rate of Cu²⁺ was 90.5%.

3.2. Characterization of ISX

3.2.1. FTIR analysis. The FTIR spectra of corn starch and ISX were shown in figure 4. Compared with the FTIR spectrum of corn starch, the peak of ISX at 3700 cm⁻¹ was the absorption peak of Mg(OH)₂,

the absorption peak at 1702 cm^{-1} was the stretching vibration absorption peak of C=S, the characteristic absorption peak at 1517 cm^{-1} was the thiol group, and the deformation vibration peak at 853 cm^{-1} was the deformation vibration peak of -CSS- functional group. The emergence of a series of new peaks illustrated that xanthate group was introduced into starch molecular chain.

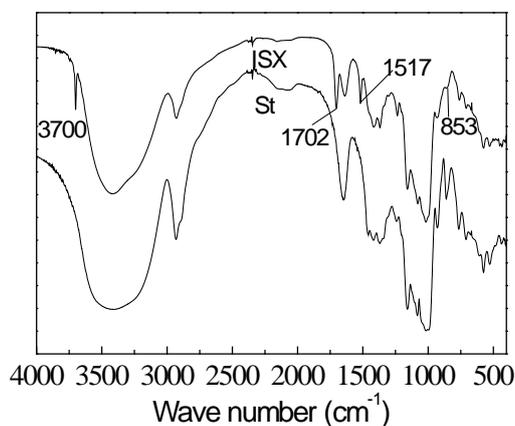


Figure 4. Infrared Spectra of Corn Starch and ISX

3.2.2. SEM Analysis. The surface morphology of corn starch and ISX particles was observed by SEM. As shown in figure 5, the granule surface of corn starch was smooth and oval. This was due to the interweaving of amylose and branched chains in starch molecules, which keeps starch granules intact (a). After xanthate acidification, the granule of ISX exhibited a rough surface with pits or holes (b), which was conducive to the adsorption of heavy metal ions.

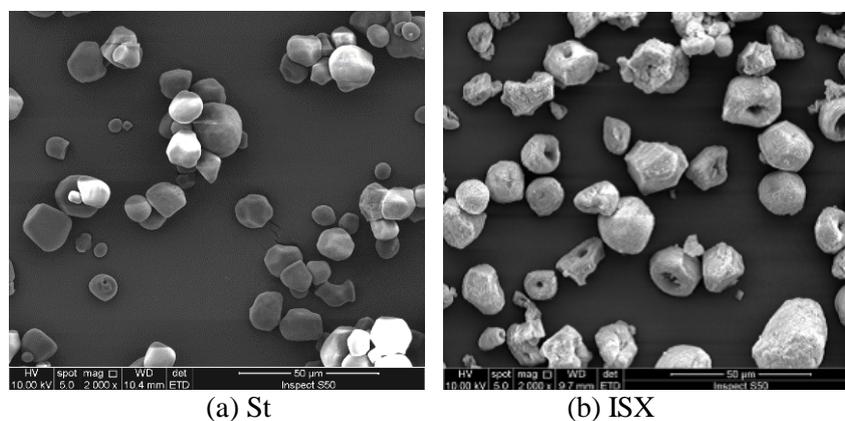


Figure 5. SEM Images of Corn Starch and ISX

3.2.3 XRD Analysis. The XRD patterns of corn starch and ISX were shown in figure 6. There were obvious diffraction peaks near 15° , 17° , 18° and 23° in the spectrogram of corn starch, which indicated that corn starch had complete microcrystalline region and belonged to typical A-type crystal. While the peaks disappeared completely at the same diffraction angle in the spectrogram of ISX, which might be due to the weakening of intermolecular forces of the starch molecular chains and the hydrogen bonds of hydroxyl groups. In the xanthate acidification, the crystal structure of starch was destroyed, while the activity and the porosity of starch increased which conducive to absorb heavy metal ions. In addition, the pattern of ISX showed two obvious diffraction peaks at 37.88° and 58.86° , the two peaks attributed to Mg(OH).

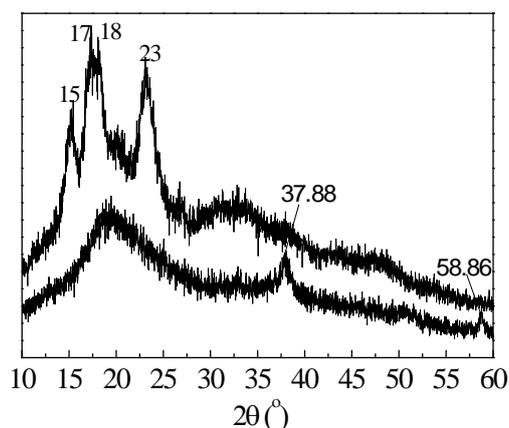


Figure 6. XRD Patterns of Corn Starch and ISX

3.3. ISX Adsorption of Copper Ions

The effect of dosage on the removal rate of Cu^{2+} was tested at room temperature using the simulated wastewater with Cu^{2+} concentration of 25 mg/L. As shown in figure 7, when the dosage of ISX was less than 250 mg/L, the removal rate of Cu^{2+} increased rapidly with the dosage increasing. While when the dosage was more than 250 mg/L, the increase of Cu^{2+} removal rate slowed down. When the dosage was 250 mg/L, the removal rate of Cu^{2+} was 90.5%, and the adsorption capacity of ISX was 90.0 mg/g.

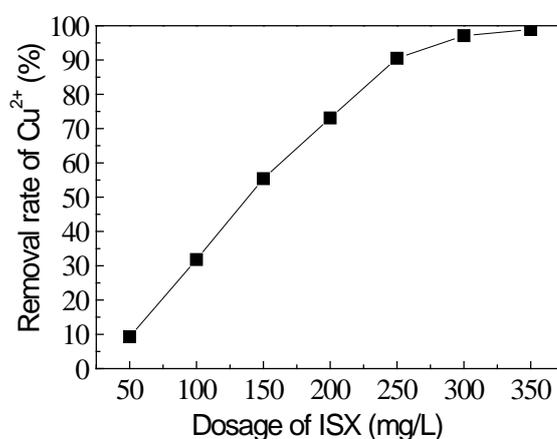


Figure 7. Effect of ISX Dosage on Removal Rate of Cu^{2+}

4. Conclusions

- 4.1. The synthetic conditions of ISX were screened by single factor experiments with the sulfur content of the product and the removal rate of copper ions as the evaluation criteria. The results showed that the optimum synthetic conditions were NaOH 16 mL, CS_2 2.5 mL, reaction temperature 35 °C and reaction time 2 h. Under these conditions, S% of the product was 7.54%, and the removal rate of copper ion was 90.5%.
- 4.2. The effect of ISX dosage on the removal rate of copper ion was investigated. The results showed that when the dosage of ISX was 250 mg/L, the removal rate of copper ion was 90.5%, and the adsorption capacity of ISX was 90.0 mg/g.

5. Acknowledgements

The research was sponsored by the National Natural Science Foundation of China (21376062), the Natural Science Foundation of Hebei Province (18964005D) and the Science and Technology Project

of Hebei Academy of Sciences (19701).

6. References

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