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EVALUATION OF INSOLUBLE XANTHATE AND CROSSLINKED STARCH-GRAFT-POLYACRYLAMIDE-CO-SODIUM XANTHATE FOR THE ADSORPTION OF Cu(II) IN AQUEOUS SOLUTIONS

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SCIENTIFIC PAPER

UDC 547.815:678.745.8:544.723:66

DOI 10.2298/CICEQ141102002T

Article Highlights

- The adsorption capacity of CSAX for Cu(II) was higher than that of ISX
- The removal efficiency of ISX for Cu(II) was better than that of CSAX
- For CSAX, more N or S do not mean higher removal efficiency or higher adsorption capacity
- The adsorption mechanism of CSAX for Cu(II) is the physical adsorption and ion exchange
- CSAX was an alternative to ISX when treating heavy metal wastewater with turbidity

Abstract

The effectiveness of insoluble xanthate (ISX) and crosslinked starch-graft-polyacrylamide-co-sodium xanthate (CSAX) for Cu(II) removal from wastewater was evaluated. The two types of xanthates were characterized by SEM, XRD, FTIR and elemental analysis. Also, the factors influencing adsorption behaviors of copper ions from aqueous solutions were investigated. The results indicated CSAX had higher absorption capacity for Cu(II) than ISX because it contained more N and S. While as far as the removal efficiency was concerned, ISX was better than CSAX for its strong ligand-CSS groups. The removal efficiency of Cu(II) onto CSAX and ISX increased with the increase in pH. The mechanism for Cu(II) adsorption was ionic exchange for ISX whereas both ion exchange and physical adsorption contributed to adsorption by CSAX. The adsorption kinetics of ISX and CSAX for Cu(II) were favorably described by the pseudo-second-order kinetic model, and the adsorption isotherms were described well with the Freundlich isotherm model. The study with synthetic wastewater showed CSAX was a worthwhile alternative to the traditional ISX only when the wastewater contained both Cu(II) and turbidity.

Keywords: insoluble starch xanthate, crosslinked starch-graft-polyacrylamide-co-sodium xanthate, Cu(II) removal, adsorption kinetics, adsorption isotherm.

Water pollution caused by heavy metals has been a worldwide concern due to their hazardous and toxic effects on the environment, human beings, and animals. In the past few years, the removal of heavy metal ions from sewage and industrial wastewater has been given lots of attention, particularly in China

where soil and water have been seriously polluted by heavy metals [1-3]. Conventional methods for the removal of heavy-metal ions from wastewater including reduction precipitation, ion exchange and adsorption, electrochemical reduction, evaporation, reverse osmosis, and direct precipitation [4,5]. Among these methods, adsorption is generally preferred because of its high efficiency, easy management, relatively low cost, and especially availability of different adsorbents [6]. Therefore, the search for new highly effective, environmental-friendly and economic-viable adsorbents has become the focus of many studies [7].

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Paper received: 2 November, 2014
Paper revised: 9 January, 2015
Paper accepted: 20 January, 2015

In this respect, many natural polysaccharides and their derivatives containing various functional groups (chitin and its derivatives, modified cellulose, and modified starch, etc.) have gained great interest [8–11]. Starch is the most abundant biopolymer after cellulose and chitosan. In contrast to cellulose, starch is water-soluble, making it easy to be modified to incorporate active functional groups to improve its applications [12–15]. In 1970s, Wing *et al.* reported that insoluble starch xanthate (ISX) prepared by xanthation of a highly crosslinked starch, was effective for removing various heavy metal ions in the aqueous medium [16–19]. The manufacture process of this derivative as xanthation is a relatively simple, and starch itself is a cheap biopolymer; thus it is manufactured and widely applied. Recently, Chang *et al.* have synthesized a novel crosslinked starch-graft-polyacrylamide-co-sodium xanthate (CSAX) by cross-linking, grafting copolymerization and xanthation reaction, and stated that the CSAX is more effective than ISX in removing heavy metal ions [20–22].

A comparative study of ISX vs CSAX for the removal of heavy metals would greatly facilitate the choice of the more efficient adsorbent (ISX or CSAX). Cu(II) is a common and highly toxic heavy metal pollutant because it is widely used in paints and pigments, paper and pulp, fertilizer manufacturing, wood preservatives, and metal cleaning. Excessive intake of Cu(II) can be accumulated in the livers of human and animals, which leads to damage of liver and kidney, anemia, immunotoxicity, etc. [23]. The U.S. Environmental Protection Agency (U.S. EPA) requires that copper in drinking water does not exceed 1.3 mg/L. Therefore, in the present work, efforts were made to study the adsorption characteristics of Cu(II) in aqueous solutions onto ISX and CSAX. The two adsorbents were characterized by SEM, XRD, FTIR and elemental analysis. The influence of the element content, adsorbent dosage, solution pH, and contact time on the absorption performance was investigated. In addition, their absorption mechanism, isotherm and kinetics were also studied, which have not been reported in the previous literature.

EXPERIMENTAL

Materials

The cornstarch used was food grade (Tianjin DingFeng Factory, China). Epichloro-hydrin (EPI), acrylamide (AM), and ceric ammonium nitrate (CAN) (AR, Shanghai Chemical Reagent Factory, China) were used as the cross-linking reagent, graft monomer and initiator, respectively. Analytical grade ace-

tone, potassium hydroxide, hydrochloric acid and ethanol were supplied by Hangzhou Chemical Reagent Factory, China. The stock solution of 300 mg/L Cu(II) was prepared using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (AR, Shanghai Chemical Reagent Factory, China) and then diluted to appropriate concentrations for each test. Distilled water was used in the polymerization and preparation of the buffer solutions.

Preparation of ISX and CSAX

The synthesis procedure and the chemicals used for the preparation of ISX are described in Wing's study [17].

Step 1: Preparation of crosslinked starch. 50 g of corn starch was added into 75 mL 1% NaCl solution in a beaker and heated to 30 °C in a water bath. 20 mL 15 mass% KOH solution was added to this slurry, then 3.5 mL epichlorohydrin was added in dropwise. The reaction was kept for 16 h to obtain the crosslinked starch. The product was washed with deionized water and ethanol, then filtered by vacuum and dried at 133 °C for 2 h.

Step 2: Xanthation of crosslinked starch. Prepared slurry with 5 g crosslinked starch and 20 mL distilled water, then heated at 30 °C in a water bath. A mixture of 4 mL H_2O containing 1 g NaOH and a certain amount of CS_2 were added in the above liquid and stirred for 2 h. The precipitate was washed with distilled water, ethanol, acetone, and dry in vacuum oven at 27 °C to a constant weight.

Three different ISXs were prepared and designated as ISX1, ISX2, and ISX3. The sulfur content in the three different ISXs was controlled by the addition of CS_2 at 0.3 g, 0.7 g, and 1.25 g with 5.0 g cross-linked starch in the xanthation step, respectively.

The synthesis of CSAX was conducted in accordance with the procedure described in Chang's study [20].

Step 1 was to prepare cross-linked starch, which was the same as step 1 of ISX.

Step 2 was the preparation of cross-linked starch-grafted polyacrylamide (CSA).

3.0 g of crosslinked starch was mixed with 50 mL of distilled water to prepare starch slurry at 80 °C in a water bath. Then, 6.0 g of AM monomer and 10 mL CAN (which was used as radicals initiator) solution (6 mmol L^{-1}) were added to the slurry. The experiments were conducted under a nitrogen atmosphere with constant stirring at 35 °C for 3 h (the grafting efficiency reached the maximum value of 72.7% and the molecular weight of graft PAM pendant chain reached 2.67×10^7). Then the graft copolymer was washed with acetone to remove the unreacted mono-

mer. Afterward, it was filtered and dried at 50 °C in a vacuum oven.

Step 3 was the preparation of CSAX.

CSA (1 g) was xanthated by dropwise addition of 3 mol/L NaOH and a certain amount of CS₂ into the sealed conical flask and stirring magnetically at 30 °C in a water bath for 3 h until it turned saffron yellow. The precipitate was washed with acetone (50%) three times, pure acetone one time, filtered and dried at 27 °C to a constant weigh.

As for CSAXs, three different amounts of CS₂ (0.8, 1.7 and 3.5 g) were added with 1.0 g crosslinked starch-graft-polyacrylamide in the process of xanthation to prepare CSAX1, CSAX2 and CSAX3.

Characterization methods

X-ray diffraction (XRD) patterns of ISX and CSAX were obtained using a DX-2600 X-ray diffractometer (Dandong Fangyuan Instrument Company, China) operating at 40 kV and 40 mA. The surface morphology of ISX and CSAX was examined using a S-4800 scanning electron microscope (Hitachi, Japan). The FT-IR spectra of ISX and CSAX were recorded on the NEXUS470 (Nicole Instrument Corporation, USA) using the KBr dispersion method. Elemental analysis of dry samples was performed on a Flash EA-1112 elemental analyzer (Thermo Fingnigan Corporation, Italy), and carbon, hydrogen, nitrogen and sulfur contents were determined.

Adsorption experiments

In general, batch adsorption experiments were conducted in 250 mL conical flasks containing 100 mL of Cu(II) solution with the initial concentration of 30 mg/L (unless otherwise stated) and a certain amount of adsorbent. The mixtures were shaken at 180 rpm in a thermostatic water-bath shaker with controlled adsorption time and temperature. After adsorption equilibrium was reached, the solution was filtered and residual Cu(II) and Na⁺ concentrations in the filtrate was analyzed by an AA800 atomic absorption spectrometer (PerkinElmer, USA).

The effect of solution pH on the Cu(II) adsorption was studied in the pH range from 2 to 7 at 298 K. The pH was adjusted using 0.1 M NaOH or 0.1 M HCl solutions. The adsorption isotherm was studied at different initial copper concentrations ranging 30-300 mg/L at 298 K at an initial pH value of 5.3. All our experimental data were the average of triplicate determinations. The relative standard errors of the data were less than 5%.

The amount of Cu(II) adsorbed on the adsorbent (Q in mg/g) was calculated using Eq. (1):

$$Q = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where C_0 and C_t (mg/L) are the initial and final concentrations of Cu(II) at time t , respectively; V is the total volume of the aqueous solution (L); W is the mass of adsorbent (g). The removal efficiency of Cu(II) was calculated using Eq. (2):

$$\text{Removal efficiency (\%)} = 100 \frac{C_0 - C_e}{C_0} \quad (2)$$

RESULTS AND DISCUSSION

Characterizations of the two adsorbents

Scanning electron microscopy (SEM) was used to study the granular morphology of starch, ISX and CSAX.

Figure 1 shows that native starch granules appeared dispersedly with a smooth, oval, regular surface, and had particle diameter with about 10 μm. While the granules of ISX possessed obvious deformations because the cross linking and xanthation reactions led to an altered uneven surface, creating pores and adhesion of small particles on the surface, but the particle diameter did not change obviously. CSAX showed a rougher surface, and the particles were conglomerated closely. In addition, the granules became significantly bigger than starch or ISX due to graft copolymerization, and particle diameter increased to over 100 μm.

The XRD patterns of starch, ISX and CSAX are shown in Figure 2. The original starch shows scattering at 2θ 15.18, 17.15 and 23.19°, representing the diffraction peaks of the hydroxyl group, which are characteristic peaks of starch. However, the XRD curves of ISX express traditional "A" style, and only have a wide amorphous diffraction peak at 20.38°, which means that the crystallinity of ISX3 decreased remarkably than natural starch [24]. The diffraction spectrum of CSAX becomes much weaker than ISX, which indicates that its crystallinity was further reduced. It is attributed to the fact that the aggregation phase of original starch was changed from a semi-crystalline state to an amorphous aggregation state during the cross-linking and graft polymerization.

The chemical structures of starch, ISX and CSAX were identified with FTIR spectroscopy (Figure not shown). For CSAX, a broad absorption band at 3418 cm⁻¹ is due to the -NH stretching of the -NH₂ group (overlapped by -OH of starch). A smaller peak at 2931 cm⁻¹ is assigned to the -CH stretching vibrations. Absorption peaks at 1658 and 1563 cm⁻¹ are -C=O and -C=O (hydrogen bonded) stretching vib-

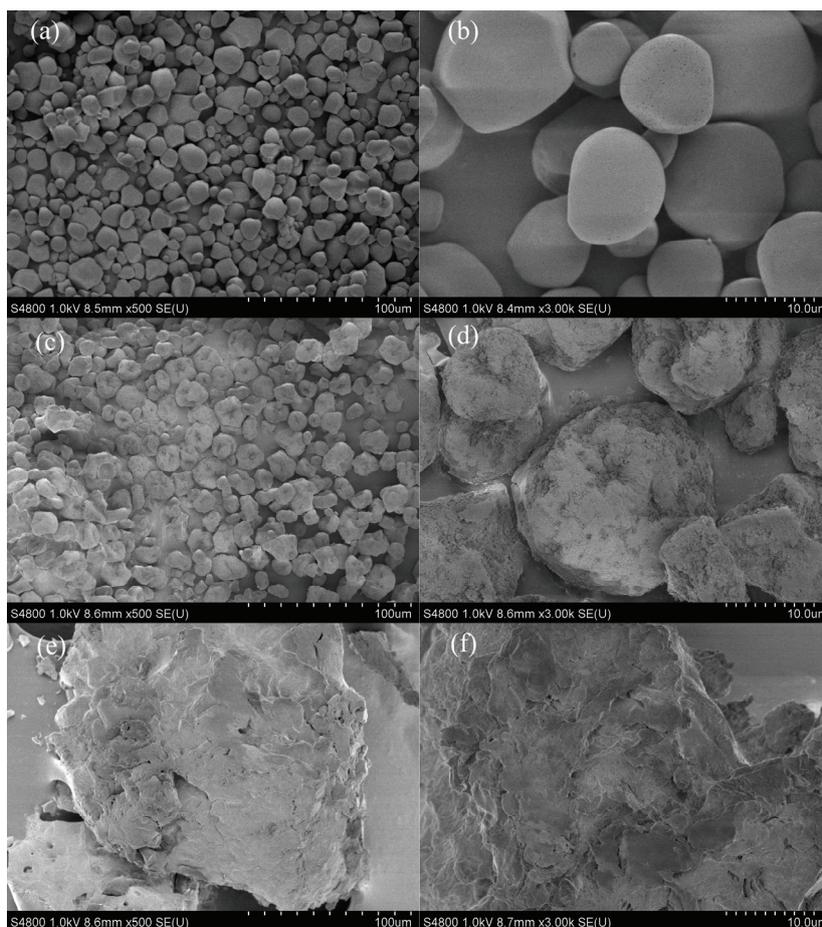


Figure 1. SEM images of starch (a,b), ISX (c,d) and CSAX (e,f).

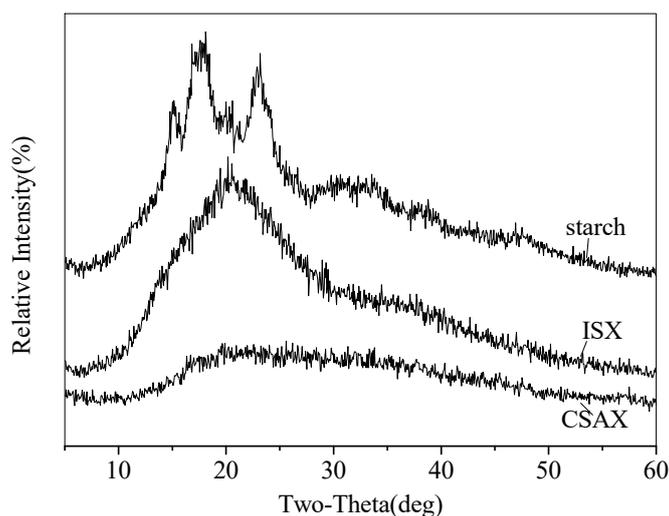


Figure 2. XRD patterns of starch, ISX, and CSAX.

ration of the $-\text{CONH}_2$ groups, and the peaks at 1750 cm^{-1} is for $-\text{COO}^-$ stretching. The absorption peak at 2450 cm^{-1} corresponds to the $-\text{SH}$ stretching vibration of the xanthate unit. The $-\text{CSSH}$ groups' spectra are displayed in the ranges of $1240\text{--}1200\text{ cm}^{-1}$, 1140--

1110 cm^{-1} , and $1070\text{--}1029\text{ cm}^{-1}$. The peak at 883 cm^{-1} may be attributed to the deformation of $-\text{CSS}^-$ [20]. Therefore, it is suggested that CSAX was synthesized successfully. For ISX, there were strong characteristic peaks at 1512 cm^{-1} for $-\text{C}=\text{S}$ and 853

cm^{-1} for the $-\text{CSS}^-$ deformation [17], indicating xanthate groups were induced on the starch molecular chain.

Elemental analysis of the dry samples shows the different element content of ISXs and CSAXs, and the results are shown in Table 1.

Table 1. Elemental analysis of CSAXs (mass%)

Sample	C	H	N	S
ISX1	25.70	4.72	0.00	0.71
ISX2	26.04	4.35	0.00	1.98
ISX3	26.87	4.11	0.00	2.46
CSAX1	29.81	5.07	3.09	8.32
CSAX2	30.29	5.26	3.65	5.03
CSAX3	32.62	5.58	4.17	3.95

Effect of adsorbent dosage and element contents on Cu(II) removal

The effects of the sulfur content and adsorbent dosage on the adsorption of Cu(II) on ISXs and CSAXs are shown in Figure 3. It shows that an increase in the adsorbent dosage resulted in an increase in removal efficiency of Cu(II), then the removal efficiency leveled off in all cases. This was due to the availability of more binding sites initially when the adsorbent dosage increased, and then the adsorption equilibrium was reached after a certain dosage.

In Figure 3a, Cu(II) removal efficiency was increased with the increase of sulfur contents in ISXs with the order of: ISX3 > ISX2 > ISX1. At 50 mg/L of adsorbent dosage removal of Cu(II) was found to be 92.29% for ISX3, 82.69% for ISX2 and 78.27% for

ISX1, respectively. With 200 mg/L dosage, the removal efficiency for Cu(II) was 99.91, 99.15 and 98.68% for the three ISXs, respectively. It is evident that the difference in Cu(II) removal efficiency of the three ISXs was more significant at low adsorbent dosage, and the removal efficiency was almost the same at high adsorbent dosage. For ISXs, the optimum removal efficiency of 99.89% was obtained at an dosage level of 150 mg/L. Therefore a dosage of ISX, ISX3 with 150 mg/L was used in the following adsorption experiments.

In Figure 3b, Cu(II) removal efficiency did not increase with the increase of the sulfur content in CSAX. However, it increased gradually with the increase of S content from 3.95 to 5.03% and N content from 4.17 to 3.65%, and it declined with the further increase of S content from 5.03 to 8.32% and increase of N content from 3.65 to 3.09%. The Cu(II) removal efficiency may relate to the ratio of N content to S content. When the N content was high (4.17%), it induced a high molecular weight of polymers and segmental overlapping of some grafted chains; when the S content was too low, there were not enough xanthate groups. It was not favorable for the adsorption in both cases. However, the Cu(II) removal was not optimal when the N content was low (3.09%) and S content was high (8.32%). It seems that a balance would exist between the two elemental contents [25], and only CSAX2 (N: 3.65% and S: 5.03%) exhibited the maximum Cu(II) removal efficiency of 94.17% at the dosage of 50 mg/L. For CSAX1 and CSAX3, their maximum removal efficiency of Cu(II) was 83.1 and 88.07%, which was always lower than CSAX2 even at

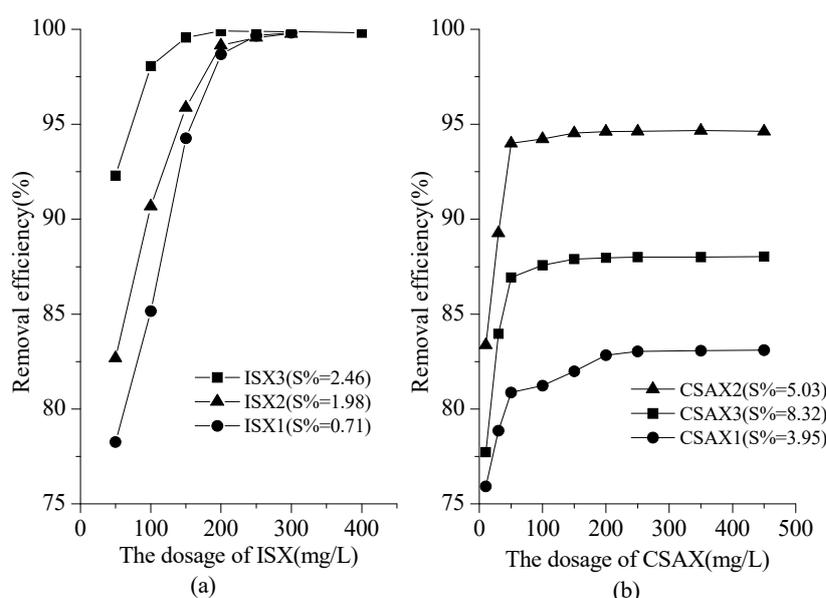


Figure 3. Effect of ISXs' (a) and CSAXs' (b) sulfur content and dosage on the removal of Cu(II).

high dosages. Hence, the following experiments on CSAX adsorption were carried out at the adsorbent dosage of 50 mg/L using CSAX2 as the adsorbent.

The removal efficiency and adsorption capacity are the two main characteristics for evaluating the adsorption ability of an adsorbent. The adsorption capacity is related to the quantity of effective functional groups, and the removal efficiency is depended on the binding affinity between effective functional groups and metal ions, so a high adsorption capacity does not mean high removal efficiency. For CSAX, there were many grafted pendant chain polyacrylamides [26], the amide groups can bind Cu(II), and the removal efficiency of crosslinked starch-grafted polyacrylamide(CSA) for Cu(II) was 76%. In CSAX, there were not only amide groups but also xanthate groups, and the append $-CSS^-$ groups increased the removal efficiency to be above 90%. The adsorption capacity was 567.42 mg/g for CSAX2, which was much higher than that of 199.78 mg/g for ISX3 at their optimal adsorbent dosages. This was attributed to more functional groups in CSAX2, which included amide groups on the pendant chain and xanthate groups on the starch main chain. However, CSAX2 showed a lower removal efficiency for copper ion than ISX3 although CSAX2 (S: 5.03%) had a much higher surfur content than that of ISX3 (S: 2.46%). The reasons may be: first, the binding affinity of amide group for Cu(II) was weaker than the strong ligand $-CSS^-$ groups, because the bond atom in $-CSS^-$ groups was S, the chelate complex formed between metal ions and S was very stable, and the solubility product (K_{sp}) values of metal sulfides are the lowest in all insoluble metal salts and metal hydroxides [27]; second, the steric hinderance effect of polyacrylamide pendant chains in CSAX inhibited the chelation of Cu(II) and $-CSS^-$ groups, and greatly reduced the utilization of $-CSS^-$ groups, which was much lower than that of ISX. That's also the reason that the removal efficiency for Cu(II) reached 99.91% at high dosages of ISX3 with only $-CSS^-$ groups.

Effects of pH on Cu(II) removal

The influence of the initial pH on the adsorption of Cu(II) onto ISX and CSAX was examined in the pH range of 2.0-7.0 (Figure 4). Copper is present in aqueous solution in the forms of Cu^{2+} , $Cu(OH)^+$ or $Cu(OH)_2$. At $pH \leq 5$, Cu(II) ions are the main species in the solution[28]. In Figure 4, it can be seen that the removal efficiency of Cu(II) of ISX or CSAX attained 45-55% even at pH 2; this was because the pK_a value for the xanthate-xanthic acid dissociation was reported to be 1.70 [29]. The xanthate groups existed in

the form of CSS^- at pH 2, which could bind Cu(II) through electrostatic attraction. When pH increased, more xanthogenic acid groups of adsorbents could ionize to negative xanthogenic acid radical groups, so that the chelation between xanthogenic acid radicals and Cu^{2+} increased, leading to high removal efficiency of Cu(II). When pH exceeded 4.0, the capacity of CSAX increased still while that of ISX kept constant.

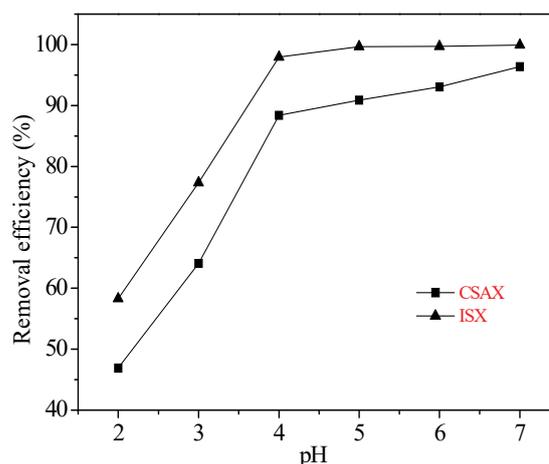


Figure 4. Effect of pH on the removal of Cu(II) by CSAX and ISX.

The effect of pH can be explained by pH_{pzc} values. The pH_{pzc} of ISX and CSAX are 7.16 and 7.93, respectively. When pHs of solutions were lower than pH_{pzc} of ISX or CSAX, the surface of the adsorbents was positively charged and unfavorable for binding Cu^{2+} . Generally, the net positive charge decreased with increasing pH value and led to decrease in the repulsion between the sorbent surface and metal ions, thus the adsorption capacity was enhanced. The removal efficiency of Cu(II) of ISX or CSAX attained 45-55% even at pH 2, indicating that initial pH has much smaller influence on ISX or CSAX because of the presence of strong acid xanthate groups that are difficult to be protonated. These negative groups have high affinity for the binding of positive charged metal ions, even at a relatively low pH, probably by means of the ion exchange [30].

In order to study the probable mechanisms for Cu(II) interaction with ISX and CSAX, concentrations of Cu(II) and sodium were detected before and after the absorption. When copper concentration was removed from 30 to 1.64 ppm (decreased by 0.443 mmol) with 50 mg/L CSAX at pH 5, the simultaneous release of sodium into the filtrate was increased from 0 to 5.89 ppm (increased by 0.256 mmol). The mole ratio (Cu:Na) corresponding to the changes was 1:0.58, and ionic exchanges between Cu and Na did not

occur in the theoretical ratio of 1:2. This can be explained as follows: the amide groups on the PAM pendant chains of CSAX can bind Cu(II) as mentioned before, so chemical absorption also contributed to the reaction between Cu ions and CSAX. Moreover, some of the free metal ions possibly remained inside the granule due to the porous and layered structure of CSAX, interacting electrostatically with the starch chains. Therefore chemical interactions and the physical entrapments of Cu(II) could be two additional mechanisms for Cu(II) removal by CSAX. For ISX, Cu(II) concentration was decreased from 30 to 0.58 ppm and meanwhile sodium concentration was increased from 0 to 9.89 ppm in the filtrate with 150 mg/L ISX at pH 5; the mole ratio between Cu adsorbed and Na desorbed was 1:1.9, nearly to the theoretical ratio of 1:2, so the adsorption mechanism for Cu(II) xanthate was mainly ionic exchange.

Adsorption kinetics

The removal efficiency of Cu(II) adsorbed on ISX and CSAX at different time are presented in Figure 5.

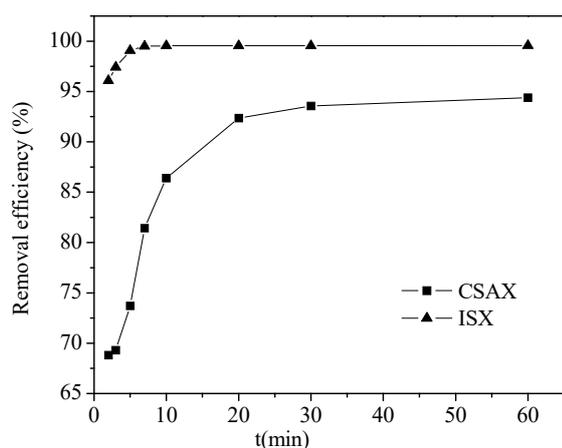


Figure 5. Effect of contract time of Cu(II) ions adsorption onto ISX and CSAX.

The removal efficiency of Cu(II) on ISX and CSAX increased rapidly in the initial stage, and ISX reached equilibrium rapidly at 10 min while it was 60 min for CSAX. This indicates that Cu(II) can rapidly chelate with the xanthate groups of ISX, and the adsorption time of CSAX was relatively long because of the steric effect of graft macromolecules. Pseudo-first-order (Eq.(3)) and pseudo-second-order (Eq.(4)) kinetic models were applied to determine kinetic parameters and explain the mechanism of Cu(II) on ISX and CSAX [31,32]:

$$Q_t = Q_e[1 - \exp(-k_1 t)] \quad (3)$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (4)$$

where Q_e and Q_t (all in mg/g) are the adsorption amounts of Cu(II) on the adsorbent at equilibrium and at any time t , respectively; k_1 is the rate constant of the pseudo-first-order adsorption; and k_2 is the rate constant of the pseudo-second-order kinetics. The experimental data before adsorption equilibrium was used to assess the adsorption kinetics, and the calculated kinetic parameters are tabulated in Table 2.

It is clear that the correlation coefficient (R^2) of the pseudo-second-order kinetic model (0.9999 and 0.9997 for ISX and CSAX) is much higher than that of the pseudo-first-order kinetic model (0.9768 and 0.9038 for ISX and CSAX). Besides, the adsorption capacities calculated (Q_e (cal.)) with the pseudo-second-order model (200.249 and 556.237 mg/g for ISX and CSAX) are close to the experimental results (Q_e (exp.)) (199.124 and 558.010 mg/g for ISX and CSAX). Therefore, the adsorption process of Cu(II) onto ISX and CSAX followed the pseudo-second-order kinetic model for the whole adsorption process. The similar observations were reported on the adsorption of Cu(II) from aqueous solution using adsorbents with active groups, such as phosphate group [24], amino group [33], and hydroxyl group [34].

Table 2. Kinetic parameters for Cu(II) adsorption onto ISX and CSAX

Model	Parameter	ISX	CSAX
Pseudo-first-order	k_1 / min^{-1}	1.67134	0.65511
	$Q_e / \text{mg g}^{-1}$	198.51239	527.29175
	R^2	0.72932	0.78051
Pseudo-second-order	$k_2 / \text{g mg}^{-1} \text{min}^{-1}$	0.0599	0.002337
	$Q_e / \text{mg g}^{-1}$	200.24925	556.23766
	R^2	0.99721	0.9869
Intraparticle	$k_i / \text{mg g}^{-1} \text{min}^{-1/2}$	0.95922	20.42736
	C	194.00207	423.7052
	R^2	0.5263	0.68039

The adsorption capacity of CSAX was higher than ISX, mainly due to its higher molecular mass and more active groups on its surface as discussed above. However, the values of k_2 for ISX were much higher than those of CSAX, indicating that the adsorption rate of ISX was faster than that of CSAX. A reasonable explanation of that is an easier access of the functional groups bound to Cu(II) for ISX than CSAX.

In general, the adsorption process may be described in three steps: mass transfer from fluid phase to the particle surface across the boundary layer, diffusion within the porous particle, and adsorption itself onto the surface. Considering the pseudo second-order model cannot identify the diffusion mechanism, the intraparticle diffusion model was then tested as [35]:

$$Q_t = k_i t^{1/2} + C \quad (5)$$

where k_i is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$) and C is the intercept. The intraparticle diffusion model was utilized to determine the rate-limiting step of the sorption process. If the regression of q_t versus $t^{1/2}$ is linear and passes through the origin ($C = 0$), then intraparticle diffusion is the sole rate-limiting step. In the present study, neither of plots passed through the origin and present multilinearity, indicating that three steps take place (figure of Q_t versus $t^{1/2}$ not shown), the first, sharper portion may be considered as an external surface adsorption or faster adsorption stage. The second portion describes the gradual adsorption stage, where intraparticle diffusion is rate-controlled. The third portion is attributed to the final equilibrium stage, where intra-particle diffusion starts to slow down due to the extremely low adsorbate concentrations in the solution [30]. The values of R^2 , obtained from the plots of intra-particle diffusion kinetics are lower than that of the pseudo-second-order model (Table 2) but this model indicates that the adsorption of Cu(II) onto ISX and CSAX may be followed by an intra-particle diffusion model up to 10 min. This indicates that although intraparticle diffusion was involved in the adsorption process, it was not the rate-controlling step.

Adsorption isotherm

In this study, Langmuir, Freundlich and D-R isotherm models were applied to analyze the experimental data.

The Langmuir isotherm model, which is valid for monolayer adsorption onto a surface with finite number of homogenous sites, is expressed as follows [36]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \quad (6)$$

The Freundlich isotherm model, which is valid for multilayer adsorption on a heterogeneous adsorbent surface with sites that have different energies of adsorption, is expressed as follows [37]:

$$\lg Q_e = \lg K_f + \frac{1}{n} \lg C_e \quad (7)$$

where Q_m is the maximum adsorption amounts of Cu(II) in aqueous solutions at equilibrium (mg/g), b is the Langmuir constant (L/mg), and K_f (mg/g) and n are the Freundlich constants.

The parameters of the isotherm models determined from experimental data are summarized in Table 3. The relatively high correlation coefficients (R^2 in range 0.995–0.999) indicate that the experimental data fitted with the Freundlich isotherm model better than the Langmuir isotherm under the studied concentration range. The value of $1/n$ was less than 1, indicating favorable adsorption of Cu(II) onto ISX and CSAX. The Freundlich constant K_f of CSAX was higher than that of ISX, indicating that the adsorption capacity of CSAX for Cu(II) ions was higher.

Table 3. Langmuir, Freundlich and D-R parameters for Cu(II) adsorption onto ISX and CSAX

Model	Parameter	ISX	CSAX
Langmuir	$Q_m / \text{mg g}^{-1}$	466.877	2229.856
	$b / \text{L mg}^{-1}$	1.8243	0.0615
	R^2	0.9765	0.9599
Freundlich	K_f	222.844	240.552
	$1/n$	0.2633	0.5183
	R^2	0.9995	0.9978
D-R	$Q_m / \text{mg g}^{-1}$	130.564	12268.832
	$K_D / \text{mol}^2 \text{Kj}^{-2}$	0.00204	0.00615
	$E / \text{kJ mol}^{-1}$	15.66	9.01
	R^2	0.9792	0.9802

The D-R isotherm model can be applied to distinguish between physical and chemical adsorption. The linearized D-R isotherm model can be written as [38]:

$$\ln Q_e = \ln Q_m - K_D \varepsilon^2 \quad (8)$$

where K_D is the constant related to adsorption energy (mol^2/kJ^2); ε is the Polanyi potential, which is equal to $R T \ln(1 + 1/C_e)$; R is the universal gas constant ($\text{kJ}/(\text{mol K})$); T is the temperature (K). The values of Q_m and K_D which were determined from the slope and intercept of the $\ln Q_e$ versus ε^2 plots (figure not shown) are

listed in Table 3. The relatively high correlation coefficients (R^2 in range 0.979–0.980) reflect that the experimental data agreed well with the D-R isotherm model. The mean free energy of adsorption (E_a in kJ/mol), defined as the free energy change when 1 mol of ion is transferred to the surface of the solid from infinity in solution, can be calculated as follows:

$$E_a = (2K_D)^{-1/2} \quad (9)$$

It is known that the magnitude of E_a is useful for estimating the type of adsorption. If this value is below 8 kJ/mol, the adsorption type can be explained by physical adsorption; if it is between 8 and 16 kJ/mol, the adsorption type can be explained by ionic exchange; if it is between 20 and 40 kJ/mol, it can be explained by chemical adsorption [29]. In this study, the value of E_a for ISX was found to be 15.66 kJ/mol, suggesting that the adsorption of Cu(II) onto ISX was typically an ionic exchange process; the values of E_a for CSAX was 9.01 kJ/mol, which is near to the limit value with 8 kJ/mol of ionic exchange and physical adsorption, implying that the adsorption of onto CSAX involved both ion exchange and physical adsorption. These conclusions was in agreement with the above analysis of the concentration changes of Cu and Na.

Through the above analysis, CSAX had the advantages of the low adsorbent dosage and high adsorption capacity while ISX had a higher removal efficiency and faster adsorption rate even though the optimum dosage of ISX was three times as much as that of CSAX. It should be noted that the production cost of CSAX was relatively high due to the grafting copolymerization and its post-processing treatment, so ISX seemsto be a much better adsorbent compared to CSAX as far as the removal of Cu(II) was concerned.

Treatment of water containing both turbidity and copper ions

The original concentration of Cu(II) in copper solution was 30 mg/L, and the adsorption experiment was carried out at room temperature and pH with 5.3. A certain dosage of kaolin suspension was added in the test solution with the turbidity of 100 NTU. Different dosages of ISX and CSAX were added in the testing solutions, respectively, and the results are shown in Figure 6. TR is defined as the turbidity removal when water sample contains only turbidity (100 NTU); CR_t is defined as the copper ions removal when water sample contains both turbidity (100 NTU) and copper ions (30 mg/L); CR is defined as the copper ions removal when water sample contains only copper ions (30 mg/L).

It was favorable for Cu(II) removal in the presence of kaolin suspension, and the effect was improved evidently with the increase of CSAX's dosage. The removal efficiency of Cu(II) was up to 96.98% and turbidity removal was 98.28% at the dosage of 50 mg/L. Copper removal efficiency was much higher than the efficiency of 94% for the sample which only contained copper ions.

The major mechanisms of flocculation by polymers are charge neutralization and bridging. For neutral or anionic flocculants, flocculation is caused mainly by polymer bridging [39–41]. The suspended particulates of kaolin in the testing solution were flocculated by PAM chains on the CSAX polymer due to a large amount of $-\text{CONH}_2$ groups in CSAX, and the floc had the "sweep" function for the insoluble colloidal chelate compounds of copper with CSAX and had the weak adsorption function for soluble copper ions. Moreover, some of its groups would be adsorbed at the particle surface when a CSAX polymer came into contact with a colloidal particle, and the remainder of

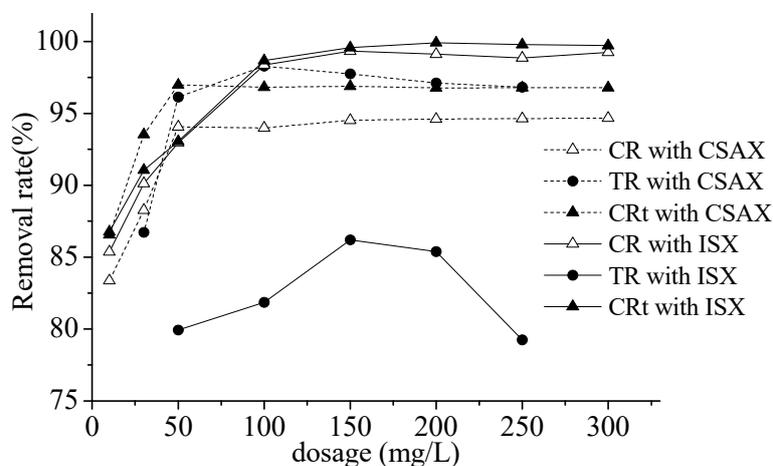


Figure 6. Treatment of water samples containing both turbidity and Cu(II) with ISX and CSAX.

the molecule (some xanthate groups) stretched into the solution. Adsorption can occur if residual Cu(II) in the solution contacted these extended segments by forming a particle-polymer-chelate compound complex [42]. Furthermore, kaolin itself can work as adsorbent and can remove partially the Cu^{2+} from water medium even without the addition of polymer [43]. Therefore, CSAX had good flocculation performance, and the flocculation greatly improved the removal performance of Cu(II).

ISX's removal efficiency of Cu(II) did not change obviously when both turbidity and copper ions contained in water sample. The maximum removal efficiency was still 99.5% and the maximum removal turbidity efficiency was 86% when the dosage was 150 mg/L, as same as that of the water sample which contained only Cu(II). This was much lower than that of CSAX. Because ISX only had starch chain as the bridging unit, it was less effective than PAM chains for removing turbidity.

CSAX was much more effective than ISX for removing turbidity and little less effective than ISX for removing Cu(II) when water sample contains turbidity and Cu(II). Therefore, CSAX has some certain advantages in treating toxic metals effluent which contains both heavy metals and turbidity.

Table 4. Comparison of maximum sorption capacity of other xanthated sorbents

Adsorbent	$Q_{\text{max}} / \text{mg g}^{-1}$	Reference
Orange peel xanthate	77.60	[44]
Xanthated sugarcane bagasse	2.91	[45]
Xanthate-modified magnetic chitosan	34.5	[46]
Cross-linked xanthate chitosan	43.47	[47]
ISX	466.877	This study
CSAX	2229.856	This study

Table 4 lists a comparison of maximum adsorption capacity of Cu(II) with various xanthate adsorbents. It can be seen that ISX and CSAX have much higher adsorption capacity of 466.877 and 2229.856 mg/g for Cu(II), indicating that they have a significant potential for removal of Cu(II) from aqueous solutions.

CONCLUSIONS

In summary, based on the results of the present comparative investigation between ISX and CSAX, following conclusions were obtained.

1) Both ISX and CSAX can remove Cu(II) from aqueous solutions. The removal efficiency of Cu(II)

onto CSAX was determined by the contents of N and S while that of ISX was only related with the content of S. The absorption capacity of CSAX was much bigger than that of ISX while the removal efficiency of ISX was higher than CSAX.

2) The adsorption efficiency of Cu(II) onto CSAX and ISX increased with the increased dosage. Their adsorption kinetic process was well predicted by the pseudo-second-order model. Their equilibrium adsorption data fitted well with the Freundlich and D-R isotherm models, and the $1/n$ value for Freundlich isotherm showed that Cu(II) were favorably adsorbed by the CSAX or ISX.

3) The physical process and ions exchange process both contributed to the adsorption of Cu(II) onto CSAX, whereas the adsorption mechanism of Cu(II) for ISX was mainly the ion exchange.

4) Turbidity was favorable for the Cu(II) removal by CSAX. CSAX seems to be a worthwhile alternative to the traditional ISX in the process of treating wastewater containing both copper ions and turbidity.

Acknowledgements

This work was financially supported by the Science and Technology Plan Projects of Jiaying City, China (NO.2014AY21008), the Hi-Tech Research and Development Program of China (No. 2012AA06A304), the Platform Funds from Zhejiang Province (No. 2012F10028), the Research Project for Application of Public Technology of Zhejiang Province of China (No. 2012C31028), and the research funds from Nanhu College of Jiaying University (No. N41472001-3).

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NAUČNI RAD

EVALUACIJA NERASTVORNOG KSANTATA I UMREŽENOG SKROBA SA KALEMLJENIM KOPOLIMEROM POLIAKRILAMIDA I NATRIJUM-KSANTATA ZA ADSORPCIJU Cu(II) U VODENIM RASTVORIMA

U ovom radu je procenjena efikasnost nerastvornog ksantata (ISX) i umreženog skroba sa kalemljenim kopolimerom poliakrilamida i natrijum-ksantata (CSAX) za uklanjanje Cu(II) jona iz otpadnih voda. Dve vrste ksantata su okarakterisane elementarnom mikroanalizom, kao i SEM, XRD i FTIR metodama. Analizirani su i faktori koji utiču na adsorpcione karakteristike jona bakra iz vodenog rastvora. Rezultati su pokazali da CSAX poseduje bolji adsorpcioni kapacitet za Cu(II) od ISX, s obzirom na to da sadrži više azota i sumpora. S druge strane, što se tiče efikasnosti izdvajanja Cu(II) jona, ISX je bolji od CSAX zbog sadržaja jakih -CSS grupa. Uklanjanje jona bakra kod obe vrste ksantata se povećava sa povećanjem pH rastvora. Mehanizam Cu(II) adsorpcije na ISX je jonska izmena, dok su jonska izmena i fizička adsorpcija odgovorne za adsorpciju kod CSAX. Kinetika adsorpcije kod oba adsorbenta odgovara modelu pseudo-drugog reda, a adsorpcione izoterme odgovaraju Freundlich izotermama. Ispitivanje sa sintetičkim otpadnim vodama ukazuje na CSAX kao korisnu alternativu tradicionalnom ISX u slučaju kada otpadna voda sadrži i Cu(II) jone i zamućenje.

Ključne reči: nerastvorni skrobni ksantat, umreženog skroba sa kalemljenim kopolimerom poliakrilamida i natrijum-ksantata, uklanjanje Cu(II), kinetika adsorpcije, adsorpciona izoterma.