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Synthesis of a novel flocculant on the basis of crosslinked Konjac glucomannan-graft-polyacrylamide-co-sodium xanthate and its application in removal of Cu^{2+} ion

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ABSTRACT

A novel functionalized polymeric flocculant on the basis of Konjac-graft-poly (acrylamide)-co-sodium xanthate was synthesized via copolymerization reaction of crosslinked Konjac glucomannan, acrylamide (AM), and sodium xanthate using epichlorohydrin (ECH) as cross-linker and ceric ammonium nitrate (CAN) as initiator in aqueous solution. The optimal synthesis conditions were as follows: KGM = 3 g, [ECH] = 4.9×10^{-3} mol/L at 35 °C for 2 h, then [CAN] = 4.0×10^{-3} mol/L, and the weight ratio of KGM and AM was 1:3 at 45 °C for 2.5 h, and then [NaOH] = 0.1 mol/L, $[CS_2] = 59 \times 10^{-3}$ mol/L at 30 °C for 2 h. The copolymer was characterized by FTIR, DSC and Elemental analysis. Flocculation test shows that in some extent, the cations, pH value, and turbidity are favorable for the removal of Cu^{2+} ions, but an excess dosage lead to an unobvious effect, and some anions express a negative effect on the Cu^{2+} removal. There exists the cooperation between Cu^{2+} ions and turbidity in the removal performance.

1. Introduction

Flocculant agents have been widely used for the treatment of life sewage, industrial effluents and mineral water in recent decades. Flocculants, on the basis of natural polysaccharides, are generally more effective than their inorganic counterparts due to the advantages of low dose, ease in handling, inertness to pH changes, formation of large cohesive flocculants and versatile tailor ability (Bratby, 1980). It is well-known that polyacrylamide is also a very efficient flocculent, exhibiting multifunctional properties of photo, biological and chemical degradation (Sorbie, 1991), however, as an organic flocculant, the major shortcoming of polyacrylamide is lack of self-degradable characteristic, resulting in "secondary pollution" of the environment. Moreover, it suffers poor shear stability. On the contrary, polysaccharides are shearing stable but poor flocculants. Therefore it is inevitable to make a match between the two. It was investigated that various natural products had been produced by grafting PAM to polysaccharides, such as guar gum (Nayak & Singh, 2001), sodium alginate (Tripathy & Singh, 1999), carboxymethyl cellulose (Biswal & Singh, 2004), amylase (Karmakar & Singh, 1998), dextran (Krishnamoorthi & Singh, 2007) and glycogen (Pal, Mal, & Singh, 2005), etc. Khalil and Abdel-Halim (2000) summarized that the modified starch was endowed with a dual function for chelating dissolved heavy metal ions and removing suspended particles in aqueous solution.

Konjac glucomannan (KGM) is a water-soluble non-ionic polysaccharide extracted from tubers of the Amorphophallus Konjac plant (Ratcliffe, Williams, Viebke, & Meadows, 2005). It consists of 1,4-lined-β-D-mannopyranose and β-D-glucopyranose units in a molar ratio of 1.6:1 with a low degree of acetyl groups (approximately 1 acetyl group per 17 residues) at the side chain C-6 position (FMC Corp., 1993; Kato & Matsuda, 1969; Katsuraya, Okuyama, Hatanaka, et al., 2003). Moreover, KGM is renewable and biodegradable natural polysaccharides, in which there are a large number of hydrophilic groups —OH. The hydrophilicity of these groups makes KGM the better raw material for super absorbency (Li, Liu, & Wang, 2005).

Modified KGM has been reported by many researchers (Li, Kennedy, Jiang, & Xie, 2006; Lu & Xiao, 2007; Tian, Hu, Zheng, et al., 2006; Yu, Huang, Ying, et al., 2007). The popularization of the copolymerization has largely retrenched the industry cost and improves the functional properties of natural polysaccharides (da Silva, de Paula, & Feitosa, 2007; Hebeish, AbdEl-Thalouth, El-Kashouti, & Abdel-Fattah, 2003). Attempts on removal of heavy metal ions, such as Cu^{2+}, Cr^{3+}, and Hg^{2+}, have been made to develop degradable flocculants on the basis of starch and other polysaccharides, but the synthesis based on KGM with dual function of trapping heavy metal ions and flocculating particle in aqueous solution, has not been reported yet.

In this research, a novel flocculant on the basis of crosslinked Konjac glucomannan-graft-acrylamide-co-sodium xanthate was synthesized by introducing PAM graft chains and xanthogenation with

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strong ligands. It was prepared by crosslinking KGM, using epichlorohydrin (ECH) as crosslinker, and then grafting polyacrylamide chains to crosslinked KGM by ceric ammonium nitrate (CAN) as an initiator. Then, a semi-manufactured goods, activated by NaOH, was xanthated by reacting with carbon disulfide. The final product obtained can not only remove dissociative heavy metal ions, but also reduce the component of turbidity-causing substances in water.

2. Experimental

2.1. Materials

Konjac power was provided by Enshi Konjac Factory, Hubei, and China. Acrylamide (AM, chemically pure) was supplied by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China, and the ceric ammonium nitrate by Tianjin Chemical Reagent Co., Ltd, Tianjin, China. Epichlorohydrin and Carbon disulfide was from Wuhan Organic Chemistry Reagent Factory, Wuhan, China. Kaolin (2%) and 1000 mg/L $CuCl_2$ solution were prepared as a stock solution. Other reagents were used as purchased. All the solutions in the experiment were prepared with distilled water.

2.2. Preparation of crosslinked KGM-graft-poly(acrylamide)-co-sodium xanthate (Delval, Janus, Vebrel, Morcellet, & Crini, 2001; Delval et al., 2003; Hocking, Klimchuk, & Lowen, 1999)

A series of reagents with different amounts of Konjac power, crosslinker, initiator, ceric ammonium and acrylamide was prepared by the following procedure: Certain amount of Konjac power and distilled water were put in a 500 mL three-necked flask equipped with a stirrer, a condenser, and a nitrogen line, then thoroughly mixed. The slurry was heated to 35 °C and the temperature was kept invariable in a water bath. Epichlorohydrin was added dropwise with slowly stirring. This crosslinking process was allowed to react at 35 °C for 2 h. Then the slurry was heated to 45 °C for 30 min under nitrogen atmosphere. Certain amount of CAN (dissolved by 1 mol/L nitric acid) was added to flask. The reaction was continued for 15 min, and then certain amount of AM solutions was added. The grafting polymerization process was kept at 45 °C for 2.5 h. Moreover, the slurry was cooled to 30 °C quickly and the nitrogen was stopped at the same time. Certain amount of NaOH solution and CS_2 were added into slurry slowly for xanthating. This xanthation reaction was not allowed to react at 30 °C for 2 h until its color turned to saffron yellow. Then the whole reaction was completed. Finally the product was cooled to room temperature, washed successively with anhydrous ethanol, and then dried in a vacuum oven at 60 °C to a constant weight. The dried product was milled, screened, and the samples used had a particle size in the range of 40–80 mesh.

2.3. Flocculation testing

In this test, 100 mL $CuCl_2$ solution was added to a 250 mL beaker. The pH, the concentration of cation and anion, sample dosage, and the turbidity of solution were adjusted to desired values. The mixture was agitated by stirring blades at a fast speed of 150 rpm for 2 min, then at a slow speed of 50 rpm for 10 min. Then the precipitates were allowed to settle for 15 min, the upper clear liquid was drawn. The heavy metal removal rate (Hr%) and turbidity removal rate (Tr%) was measured by atomic absorption spectrometer and the turbidity meter, respectively, and calculated as follows:

$$\text{Hr\%} = 100(C_0 - C_1)/C_0$$

where C_0 and C_1 are the metal ion concentrations of the initial suspension and supernatant, respectively.

$$\text{Tr\%} = 100(T_0 - T_1)/T_0$$

where T_0 and T_1 are the turbidities of the initial suspension and the supernatant, respectively.

2.4. Characterization

2.4.1. FTIR analysis

The FTIR spectrum of the sample was recorded in the range of 400–4000 cm^{-1} using KBr pellets with a Nicolet (USA) Nexus 470 FTIR spectrometer for investigation of intermolecular interaction. Spectra were signal with a resolution of 4 cm^{-1} at room temperature.

2.4.2. DSC analysis

DSC was performed using a DSC 204-F1 (NETZSCH, Germany) at a heating rate of 10 °C/min under nitrogen atmosphere. The temperature ranged from 30 to 400 °C.

2.4.3. Elemental analysis

Elemental analysis of dry samples was performed on a VarioMICRO Elementar analyzer (Germany). Carbon, hydrogen, nitrogen and sulfur were determined.

3. Results and discussion

3.1. FTIR spectra

Fig. 1 displayed the FTIR spectra of KGM and modified KGM. In Fig. 1a, 3419 cm^{-1} and 2923 cm^{-1} was due to the stretching vibration of OH and C—H in KGM. 711 cm^{-1} and 768 cm^{-1} were assigned to the pyranose ring vibrations, i.e., the characteristic absorption peaks of mannose in KGM. The weak absorption peak at 1720 cm^{-1} came from the small amount of acetyl group in KGM. In Fig. 1b, a broad absorption band at 3414 cm^{-1} is for the —NH stretching vibration of the —NH_2 group, the characteristic absorption at 1659 cm^{-1} and 1598 cm^{-1} corresponded to the C═O stretching vibration (—$CONH_2$). Two strong bands around 1030 and 1238 cm^{-1} resulted from —C—O—C— symmetrical and asymmetrical stretching vibration, respectively. The groups' spectra are displayed in the range of 1250–1200 cm^{-1}, 1140–

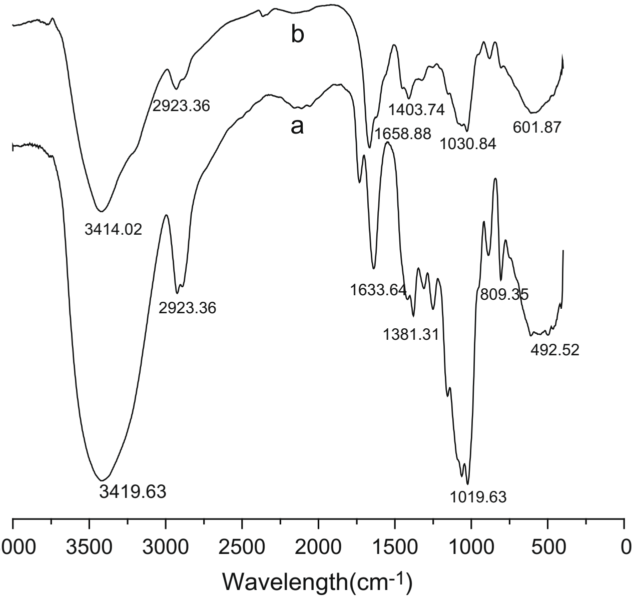

Fig. 1. FTIR spectra of: (a) KGM and (b) modified KGM.

1110 cm^{-1} and 1070–1020 cm^{-1}, and 868 cm^{-1} may be attributed to xanthate unit, thus the FTIR spectra verified that the synthesis reaction has been successfully carried out (Soppirnath & Aminabhavi, 2002).

3.2. DSC analysis

The detailed thermal property data of samples was displayed in Table 1. All the samples tested showed two stages of decomposition. The first stage process was in the temperature range of 49–130 °C, attributed to the release of water molecules in the sample, and the enthalpy of which changed haphazardly with the Cu^{2+} ion removal rate. The results may be assigned to the different water content in the different samples. However, the enthalpy of the second degradation declined regularly with the increase of Cu^{2+} ion removal rate. It lead to the conclusion that the higher Cu^{2+} ion removal rate corresponding to the lower enthalpy, which was favorable for the adsorption of Cu^{2+} ions onto the flocculants.

3.3. Elemental analysis

Table 2 showed the different element content (C, H, N and S) with different adsorption ability. It can be seen that the H% and N% decrease from 6.72% and 12.31% to 5.64% and 3.02%, respectively, when the S% increase from 3.84% to 8.21%. The removal rate of Cu^{2+} ion increased gradually with the decrease of H% from 6.72% to 5.73%, N% from 12.31% to 4.35%, and S% from 3.84% to 8.19%, and declined with the further decrease or increase. The decrease of H% may be due to the substitution of various reactions, including crosslinking, grafting and xanthation, which contributed to the adsorption property. The Cu^{2+} ion removal rate may have some relations to the proportion of N% and S%. When the N% was too high (12.31%), it induced too high a molecular weight of polymer and segmental overlapping of some grafted chains, reversely the S% was too low, there were not enough xanthate groups, both of which were not favorable for the adsorption. But when the N% was too low (3.02%) and S% too high (8.21%), the Cu^{2+} ion removal rate neither demonstrate the optimal effect. That means there exists the equilibrium between the two, only in this best condition (N: 4.35% and S: 8.19%) can the Cu^{2+} ion removal rate exhibit the maximum.

Table 1
Thermal properties of samples with different Cu^{2+} removal rate.

Sample	Decomposition stage	Temperature range (°C)	Enthalpy (J/g)	Hr%
1	1	49.3–118.5	134	67.3
	2	193.5–373.1	−3619	
2	1	52.4–125.4	89	78.2
	2	194.2–369.2	−3541	
3	1	50.3–130.2	183	87.4
	2	189.6–366.4	−3506	
4	1	53.3–123.5	189	95.7
	2	198.7–371.4	−3485	

3.4. Effect of cation concentration on removal of Cu^{2+} ions

Different concentration of NaCl, KCl, CaCl$_2$, MgCl$_2$, AlCl$_3$ and same dosage of flocculant was added in the testing solution, respectively. The concentration of the original Cu^{2+} ion solution was 50 mg/L, and the solution was tested at room temperature and pH of 5. The Cu^{2+} ion removal rate increased gradually with the increase of most of the cations and leveled off with further increase, just as shown in Fig. 2. The figures lead to the observation that the K$^+$, Ca^{2+}, Mg^{2+}, Al^{3+} cations can accelerate the Cu^{2+} ions removal, and this effect was more obvious with increases of electric charge number of cations, but Na$^+$ almost had no effect on Cu^{2+} ions removal. The explanation was as follows:

The flocculant was anionic, with large negative charges in the solution. Besides charges in reacting with Cu^{2+} ions, there still existed some negative charges in the resultant, which can generate static exclusion force, but it will accelerate the flocculating process in the presence of cations, in respect that the electric charge layer was compressed by the neutralization between cations and the resultant mentioned above, which lowered electric potential (ζ), and increased the flocculating process. Moreover, the more cation charge numbers, the more effective is the performance (Song, 1990). So Ca^{2+}, Mg^{2+}, and Al^{3+} were more effective than Na$^+$ and K$^+$ in the contribution to Cu^{2+} ions removal. However, the effect of Mg^{2+} ions on Cu^{2+} ions removal was more obvious than that of Ca^{2+}, due to more charge numbers available in Mg^{2+}. As a fact, the assistance to Cu^{2+} ions removal was as follows: Al^{3+} > Mg^{2+} > Ca^{2+} > Na$^+$ > K$^+$.

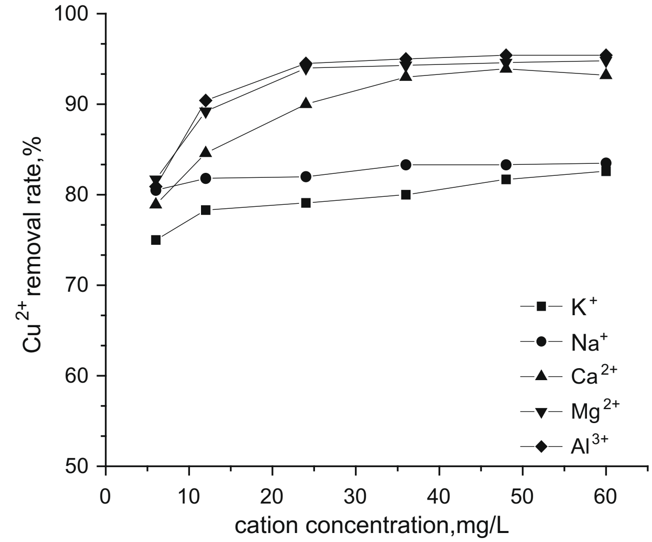

Fig. 2. Effect of cation concentration on removal of Cu^{2+} ions.

Table 2
The elemental analysis of different samples.

Sample	ECH (mol/L)	CAN (mol/L)	NaOH (mol/L)	CS$_2$ (mol/L)	M_{KGM}: M_{AM}	Elemental analysis (%)				Hr%
						C	H	N	S	
1	4.9×10^{-3}	4.0×10^{-3}	0.05	47×10^{-3}	1:3	42.83	6.72	12.31	3.84	67.3
2	8.3×10^{-3}	4.0×10^{-3}	0.1	71×10^{-3}	1:1.5	40.17	6.29	7.86	5.75	78.2
3	4.9×10^{-3}	4.5×10^{-3}	0.1	35×10^{-3}	1:2.5	37.92	5.92	5.24	7.81	87.4
4	4.9×10^{-3}	4.0×10^{-3}	0.1	59×10^{-3}	1:3	37.56	5.73	4.35	8.19	95.7
5	11.4×10^{-3}	3.0×10^{-3}	0.1	35×10^{-3}	1:2.5	37.15	5.64	3.02	8.21	90.5

M_{KGM} and M_{AM} are the weight ratio of KGM and AM.

3.5. Effect of anion concentration on removal of Cu^{2+} ions

Different concentration of NaCl, $NaNO_3$, Na_2SO_4, Na_2–EDTA and same dosage of flocculant was added in the testing solution, respectively. The original concentration of the Cu^{2+} ion solution was 50 mg/L, and the solution was tested at room temperature and pH of 5. The results were displayed in Fig. 3. The experimental data lead to the fact that the effect of Cl^- and NO_3^- on Cu^{2+} ions removal was slight with the increase of anion concentration, and the Cu^{2+} ions removal rate decreased gradually with the increasing concentration of Na_2SO_4 and Na_2–EDTA. The similar phenomenon was also observed by several other researchers (Chen, Liu, & Wang, 2007; Kumar & Verma, 2007), which could be interpreted as follows:

In the aqueous solution, there exists competitions of anions for coordination with Cu^{2+} ions in the solutions, and the stability of coordinated compound was decided by coordination constant (Hu & Huang, 2001), the order of which is as follows: $EDTA > SO_4^{2-} > Cl^- > NO_3^-$. The coordination constant of NO_3^- ion was lowest among these anions, so the ability of preventing flocculants and copper ions from chelating was weakest, in correspondence with the higher removal rate of copper ions. In contrast, EDTA anions have the strongest coordination constant, so it decreased the chelation of flocculants with Cu^{2+} ions most, assigned to lowest the removal rate of copper ions. This result implies that the flocculant has a higher ability of competition for copper ions than NO_3^-, Cl^- ions, but lower ability of competition for copper ions than SO_4^{2-} and EDTA.

3.6. Effect of pH on removal of Cu^{2+} ions

The original concentration of the Cu^{2+} ion solution was 50 mg/L; the solution was tested at room temperature. In order to avoid the natural removal by hydroxide precipitation, the pH values were adjusted to different values from 3.0 to 5.0 by HCl. Fig. 4 shows that Cu^{2+} removal rate varies with the flocculant doses. As it can be appreciated, the higher pH values and flocculant doses enhanced the Cu^{2+} ions removal rate. At a higher pH value, more xanthogenic acid groups of flocculant were ionized to negative xanthogenic acid radical groups, and accordingly more chelating between the two. Therefore a gradual increase of Cu^{2+} ions removal was displayed.

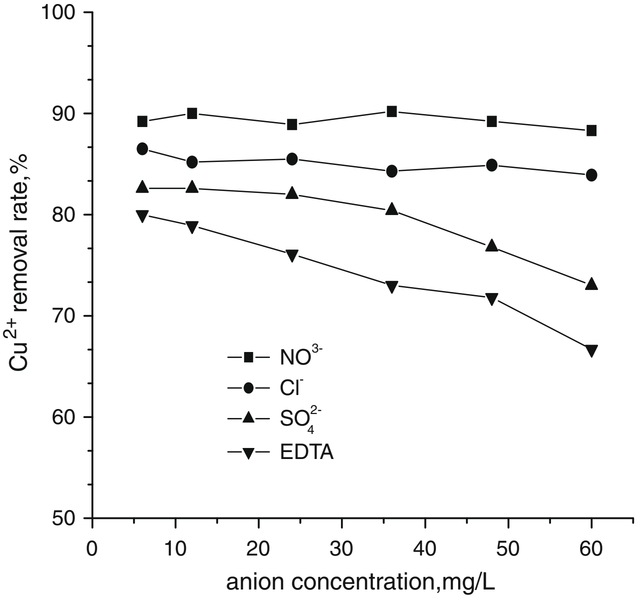

Fig. 3. Effect of anion concentration on removal of Cu^{2+} ions.

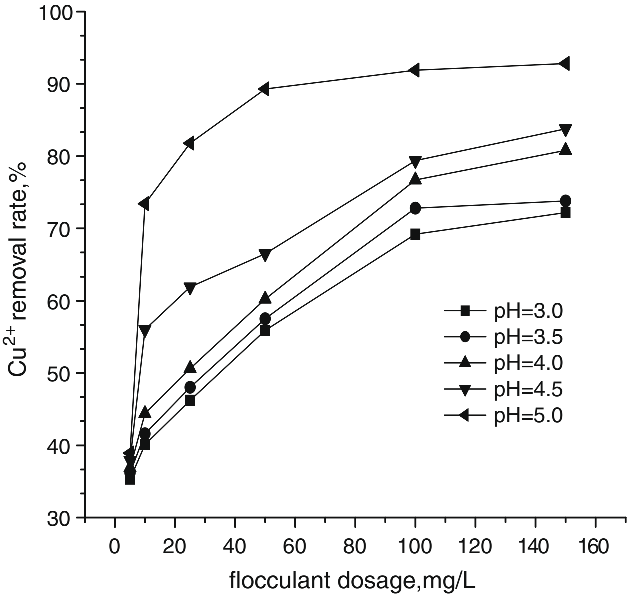

Fig. 4. Effect of pH on removal of Cu^{2+} ions.

3.7. Effect of turbidity on removal of Cu^{2+} ions

The original concentration of the Cu^{2+} ion solution was 50 mg/L; the solution was tested at room temperature and pH of 5. Different dosage of flocculant and kaolin suspension was added in the testing solution, forming different turbidities of 0NTU, 50NTU, 100NTU. It was favorable for the Cu^{2+} ions removal in the presence of kaolin suspension, and the effect was improved evidently with the increase of flocculant and turbidity, as indicated in Fig. 5. Since kaolin is a kind of mineral, containing aqueous aluminosilicate. There is also a large amount of —OH groups on its surface. In view of the great characteristics mentioned above, it is not difficult to find its super absorbent ability. Moreover, the particle–polymer–particle complex was served as a bridge intermedium in the present of kaolin, when a polymer comes into contact with a colloidal

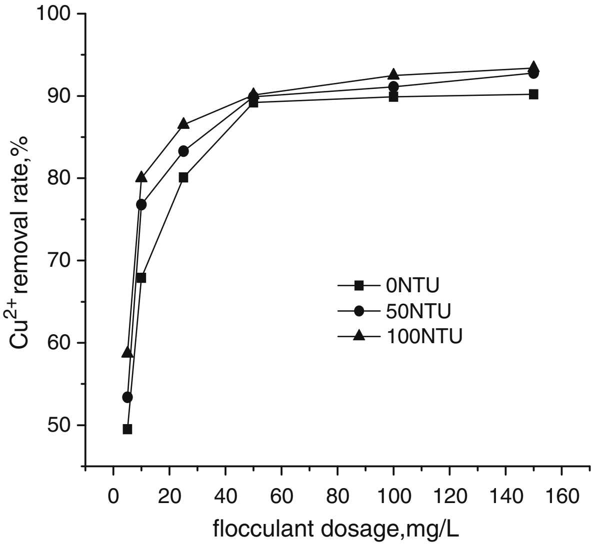

Fig. 5. Effect of turbidity on removal of Cu^{2+} ions.

particle, some of its groups adsorb at the particle surface, leaving the remainder of the molecule extending out into the solution and if a second particle with some vacant adsorption sites contacts these extended segments, adsorption can occur, which forms a bridge (Tian & Xie, 2008). With the increase of flocculant and turbidity, suspended particulates were occluded by PAM chains on the polymer, and the solution was re-stabilized.

3.8. Effect of Cu^{2+} concentration on removal of turbidity

Different dosage of Cu^{2+} ions and flocculant was added in the testing solution, respectively. The original turbidity of the Cu^{2+} ion solution was 50NTU, and the solution was tested at room temperature and pH of 5. The turbidity removal rate increased significantly with the increase of flocculant and Cu^{2+} ions, as displayed in Fig. 6. Just like description in Section 3.6, it was favorable for the Cu^{2+} ions removal in the presence of kaolin suspension, in the same way, it was helpful for turbidity removal in the present of Cu^{2+} ions. The more Cu^{2+} ions were adsorbed onto kaolin particulates and flocculants, the more is the sediment formed at the bottom of beaker, and accordingly the higher is the turbidity removal rate. At the same time, the positive copper ions not only neutralize the negative charges of xanthogenic acid groups of the flocculant because of chelation, but also neutralize the negative charges of substances causing turbidity, thus reduce the repulsion of xanthogenic acid groups and particles consequently greatly enhancing the flocculation (Chang, Hao, & Duan, 2008).

4. Performance of the novel flocculant in plating wastewater treatment

The original parameters of the plating wastewater were as follows: the pH value was 2.9, turbidity 773NTU (Nephelometric Turbidity Unitsl), concentration of Cu^{2+} ions 382.8 mg/L, concentration of Pb^{2+} ions 27.2 mg/L. As it can be seen in Fig. 7, the removal rate of Pb^{2+}, Cu^{2+}, and turbidity increased significantly with the increase of flocculants, especially when the dosage was approximately 150 mg/L, the removal rate of Pb^{2+}, Cu^{2+} and turbidity was up to the maximum, however, an excess of flocculant lead to the decline of removal rate. And also the removal rate of Cu^{2+} was higher than that of Pb^{2+}, which possibly had a certain relation to the lower solubility product (K_{sp}) of Cu(II)-flocculant compared with Pb(II)-flocculant (Chang et al., 2008). Simultaneously, the comb-like structure of flocculant on the basis of crosslinked Konjac glucomannan-graft-acrylamide-co-sodium xanthate, was helpful for the formation of bridging of particle–polymer–particle correlated to the combination of network structure of flexible grafting PAM chain and semi-rigid KGM molecular chain (Tian et al., 2008), and favorable for the chelation between xanthogenic acid groups and heavy metal ions.

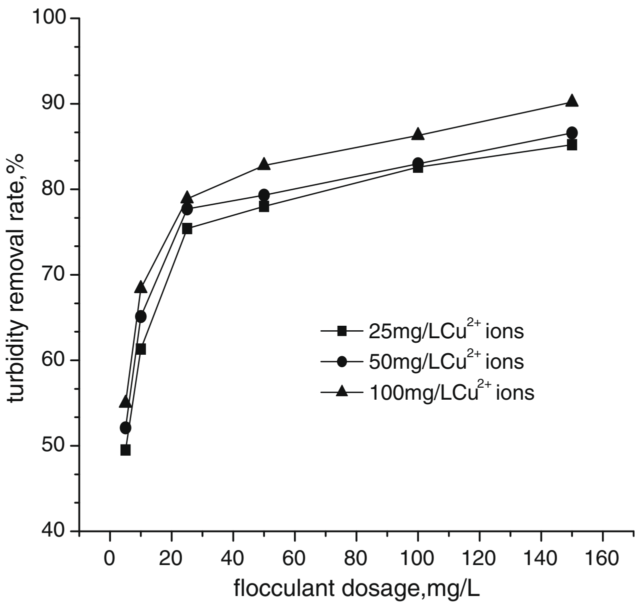

Fig. 6. Effect of Cu^{2+} concentration on removal of turbidity.

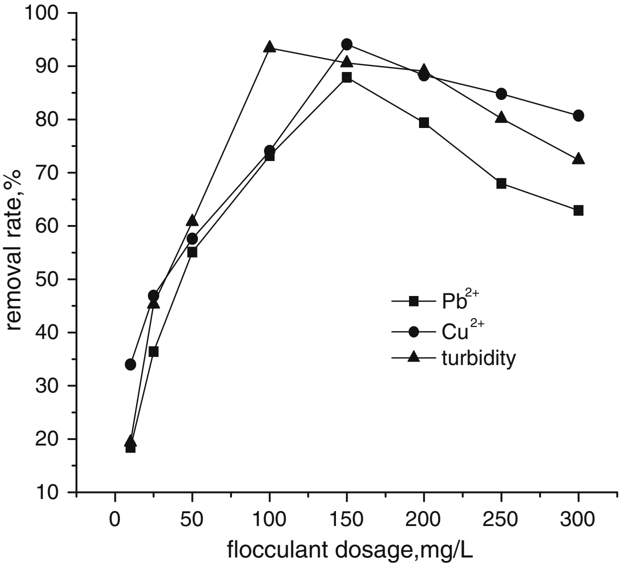

Fig. 7. Effect of flocculants on removal of Pb^{2+}, Cu^{2+}, and turbidity.

5. Conclusions

A novel flocculant on the basis of crosslinked Konjac glucomannan-graft-acrylamide-co-sodium xanthate was synthesized by crosslinking KGM, using epichlorohydrin (ECH) as crosslinker, then grafting polyacrylamide chains to crosslinked KGM by ceric ammonium nitrate(CAN) as an initiator, then semi-manufactured goods, activated by NaOH, was xanthated by reacting with carbon disulfide. The optimal synthesis conditions were as follows: KGM = 3 g, $[ECH] = 4.9 \times 10^{-3}$ mol/L at 35 °C for 2 h, then $[CAN] = 4.0 \times 10^{-3}$ mol/L, and $[AM] = 0.418$ mol/L at 45 °C for 2.5 h, and then $[NaOH] = 0.1$ mol/L, $[CS_2] = 59 \times 10^{-3}$ mol/L at 30 °C for 2 h. As a result, the final product obtained can not only remove dissociative heavy metal ions, but also reduce the component of turbidity-causing substances in water.

- Ca^{2+}, Mg^{2+} and Al^{3+} ions are more favorable than Na^{+} and K^{+} in the contribution to Cu^{2+} ions removal.
- The negative effect of various anions on Cu^{2+} ions removal is as follows: $EDTA > SO_4^{2-} > Cl^- > NO_3^-$, and EDTA, SO_4^{2-} ions are more effective than Cl^-, NO_3^- in prevention of Cu^{2+} ions removal.
- The Cu^{2+} ions removal rate increase gradually with the increase of pH value from 3 to 5.
- It is helpful for the removal of copper ions in the present of turbidity.
- With the given condition, the turbidity removal rate increase with the increase of flocculant and Cu^{2+} ions.
- Copper ions have a cooperative removal performance with turbidity in the wastewater treatment containing both copper ions and turbidity.
- The DSC data indicated that the higher Cu^{2+} ion removal rate corresponding to the lower enthalpy.

- Elemental analysis displayed that the Cu^{2+} ion removal rate exhibit the maximum when the N% and S% were 4.35% and 8.19%, respectively.

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