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Preparation of mercaptoacetyl chitosan and its removal performance of copper ion and turbidity

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ABSTRACT

In order to extend the application range of natural polymer flocculants chitosan (CTS), the macromolecule flocculant-mercapto-acetyl chitosan (MAC) which traps heavy metals was prepared by amidization reaction with CTS and L-cysteine. The optimum preparation conditions of the MAC were investigated through orthogonal experiment and its performances on removing copper ion and turbidity at different conditions were tested. The experimental results show that: (1) The optimal preparation conditions of MAC are as follows: the mass ratio of m(chitosan):m(mercaptoacetic acid) is 1:2, pH value is 4.5 and the reaction time is 2.5 h. (2) Compared with CTS, MAC has better water solubility and higher efficiency for removing copper ions and turbidity. The removal rate of Cu^{2+} is promoted by the presence of coexisting cations. (3) With pH value increasing the removal efficiency of Cu^{2+} by MAC is enhanced. However, the influence of the pH value to turbidity is not significant. (4) The removal efficiencies of heavy mental ions and the turbidity are greatly promoted by the cooperation effects for the water sample containing heavy metal ions and turbidity causing substances. The maximum removal rate of turbidity is up to 100%.

Keywords: Flocculant; Chitosan; Mercaptoacetic acid; Heavy metal; Turbidity

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1. Introduction

The fresh water is the essential material for survival of all living things on earth. Unfortunately, water resources are almost depleted due to the growing water pollution caused by the development of the industry. In the last few years, the heavy metal ions coming from electroplating, tannery operations, metal finishing, etc. became one of the great and serious contaminant in wastewaters. Therefore, it is important to remove heavy metal ions from wastewater.

Flocculation is one of the most important methods for water treatment. Most of the current flocculants, such as polyacrylamide (PAM), polyaluminium chloride, polyethyleneimine, are very efficient for removal of turbidity from wastewater. However, it is impracticable for the present flocculants to remove the soluble substances including soluble heavy metal ions very well from the water and wastewater. So, novel flocculants are expected to remove soluble heavy metal ions from the water and wastewater, which

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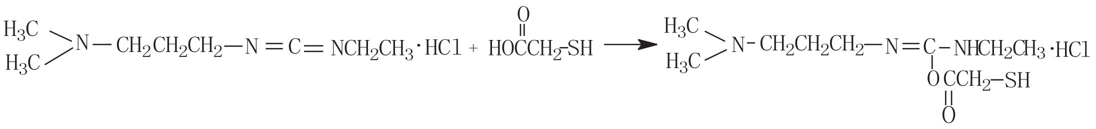
motivates many research groups to improve the ordinary flocculants by theoretical and experimental methods. In order to remove both soluble heavy metal species and insoluble substances efficiently by flocculation, some research groups tried to graft some strong ligands for heavy metals ions, such as thioglycolic acid or its salt group, to the current macromolecular flocculant such as starch [1], polyethylenimine [2], PAM [3], etc. These new flocculants are not only able to remove turbidity from water by electrical neutralization and bridge effect between particles, but also able to remove soluble heavy metal ions from water by coordination and chelation.

As a natural polymer flocculant, the chitosan (CTS) draws more and more attention due to its advantages: high yield, biodegradability, non-toxic, and non-producing secondary pollution [4]. Furthermore, dissolved CTS has the ability to bind heavy metal ions by coordination through the dentates, such as $-NH_2$ and $-OH$ on their long molecular chain [5]. Unfortunately, the direct application of CTS is limited because CTS has poor water solubility and small relative molecular mass. Then, investigating new method of modifying CTS has become a new hot research [6,7]. Through amidation reaction between CTS and mercaptoacetic acid (TGA), our group has obtained a new kind of flocculant mercapto-acetyl chitosan (MAC) [8]. The MAC has the ability to remove the copper ions and turbidity. In the present paper, we have made a deep investigation on the preparation conditions for the MAC through orthogonal experiment. The effects of the initial pH values of the solution and various coexisting inorganic ions on its flocculating performance were investigated.

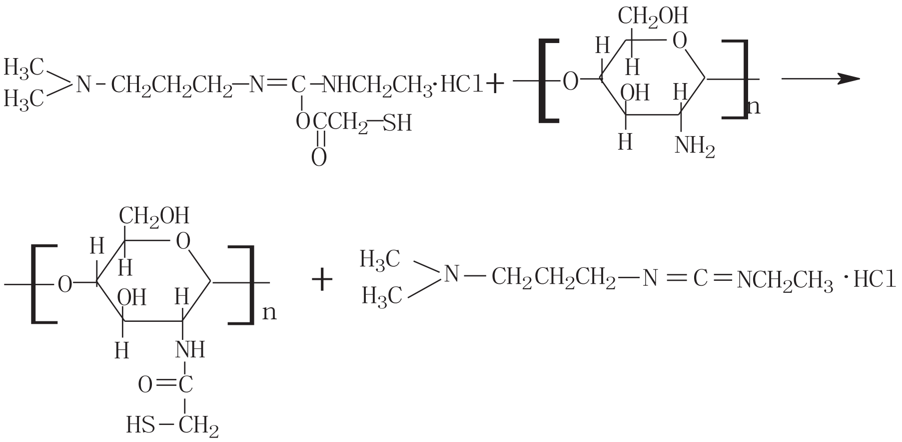
2. Principle

2.1. Synthesis

Under the effect of activator, CTS, and thioglycolic acid can produce amidation reaction. In this reaction, 1-ethyl-3-(3-dimethyllaminopropyl) carbodiimide hydrochloride (EDC·HCl) was selected as the activating agent [7,8]. The chemical reactions are as follows [8]:



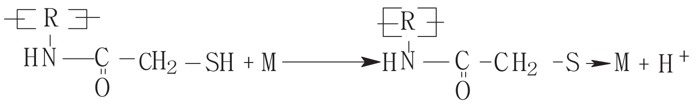
(1)



(2)

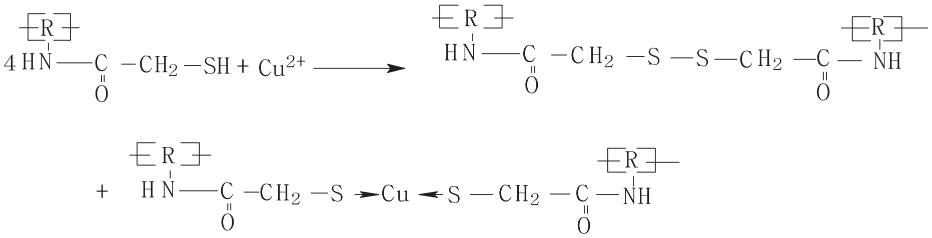
2.2. Removal of heavy metal ions

After MAC is added to wastewater containing heavy metal ions such as Cu^{2+}, Pb^{2+}, Cd^{2+} and Ni^{2+}, etc., ion exchange and coordination/chelation reactions between mercapto-group (–SH) on MAC and the heavy metal ions mentioned above could occur and this could form stable hydrophobic chelates. This reaction is shown in Eq. (3).



$$\overset{\text{-}[\mathrm{R}]\text{-}}{\mathrm{HN}}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-\mathrm{CH_2}-\mathrm{SH}+\mathrm{M}\longrightarrow\overset{\text{-}[\mathrm{R}]\text{-}}{\mathrm{HN}}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-\mathrm{CH_2}-\mathrm{S}\rightarrow\mathrm{M}+\mathrm{H^+}\tag{3}$$

(3)

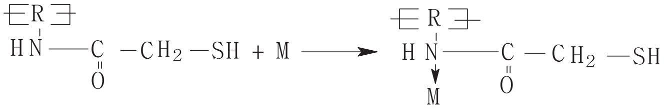


$$4\,\overset{\text{-}[\mathrm{R}]\text{-}}{\mathrm{HN}}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-\mathrm{CH_2}-\mathrm{SH}+\mathrm{Cu^{2+}}\longrightarrow\overset{\text{-}[\mathrm{R}]\text{-}}{\mathrm{HN}}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-\mathrm{CH_2}-\mathrm{S}-\mathrm{S}-\mathrm{CH_2}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-\overset{\text{-}[\mathrm{R}]\text{-}}{\mathrm{NH}}$$
$$+\ \overset{\text{-}[\mathrm{R}]\text{-}}{\mathrm{HN}}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-\mathrm{CH_2}-\mathrm{S}\rightarrow\mathrm{Cu}\leftarrow\mathrm{S}-\mathrm{CH_2}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-\overset{\text{-}[\mathrm{R}]\text{-}}{\mathrm{NH}}\tag{4}$$

(4)

Meanwhile, the mercapto-group on MAC is a reduced group. It can be oxidized by the bivalent copper ions when MAC is added to wastewater containing Cu^{2+} [9]. Therefore, MAC can be oxidized by copper ions to form a disulfide and the copper ions themselves are reduced to cuprous ion simultaneously. According to the soft hard acid base principle, the mercapto-group on MAC is a soft base and the cuprous ion is a soft acid; the cuprous ion could easily react to form a stable and insoluble complex/chelate with the remaining mercapto-groups on MAC molecules [10]. The reaction is shown in Eq. (4).

When the above reaction takes place, the coordination between –NH– on MAC molecule and the heavy metal ions mentioned above in the solution also takes place at the same time. The corresponding reaction equation is given in Eq. (5).



$$\overset{\text{-}[\mathrm{R}]\text{-}}{\mathrm{HN}}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-\mathrm{CH_2}-\mathrm{SH}+\mathrm{M}\longrightarrow\overset{\text{-}[\mathrm{R}]\text{-}}{\underset{\overset{\downarrow}{\mathrm{M}}}{\mathrm{HN}}}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-\mathrm{CH_2}-\mathrm{SH}\tag{5}$$

(5)

2.3. Removal of turbidity

MAC is a long-chain polymer. It has some active groups, such as –NH–, –OH, etc. on its long molecular chain. On one hand, the –NH– combines with H^+ and becomes $-NH_2^+-$ in the solution, then a high charge density cationic polyelectrolyte forms, and the macromolecule can neutralize the negative charges of the turbidity substances. On the other hand, the long macromolecule chain plays a bridge effect between turbidity substances at the same time. In addition, the polymer chain has a "sweep" function for the colloids. For these three mechanisms, the turbidity can be removed eventually.

3. Experiments

3.1. Materials

Thioglycolic acid and CTS (deacetylation 90%, MW 2–4 × 10^5) were supplied by Shanghai Chemical Reagent Corp., Shanghai, China; EDC·HCl was supplied by Shanghai Sanpu Chemical Engineering Corp. Ltd., Shanghai, China; sodium nitrate and other compounds were supplied by Tianjin Chemical Reagent Factory, Tianjin, China.

Jar test instrument (Model J6-1A) was purchased from Beijing West City Instrument Factory, China; Spectrophotometer (Model 723) was provided by Beijing Rayleigh Analytical Instrument Corp. Ltd., China; Infrared spectrophotometer (Digilab FTS3000) was purchased from Varian Corp., America; Elementar Analysensysteme GmbH was purchased from VarioEL Corp., Germany.

3.2. Preparation of MAC

In the preparation of MAC, there are some factors which affect the flocculation performance of the MAC, such as pH, temperature, the dosage of activating agent (EDC·HCl), etc. [7,8,11,12]. In order to obtain the optimum preparation conditions of the MAC, five factors and four-level orthogonal experiments were designed; the orthogonal table is shown in Table 1. In the orthogonal experiments, evaluation index was the removal rate of copper ions by MAC. The pH of the reaction solution was adjusted by using 0.1 mol L^{-1} HCl/NaOH solution, the temperature of reaction solution was kept at 25℃.

3.3. Flocculation test

Stock solutions of Cu^{2+} (10 g/L) were prepared from analytical copper nitrate, and flocculation experiments were conducted at room temperature using beaker test on a six-joint-stirrer. Four-hundred milliliters of working Cu^{2+} solution prepared by diluting stock solution with tap water or/and some of kaolin suspension were added to a 500 mL beaker. The pH values of water samples in the beakers were adjusted to the desired values. The required doses of MAC were added to the beakers by rapid stirring. The Cu^{2+} solution was stirred at a uniform speed of 120 rpm for 3 min, followed by the slow stirring at 40 rpm for 10 min, and then settled for 15 min. Samples were taken from the supernatants. Concentrations of heavy mental ions and/or the turbidity were measured by 220 FS atomic absorption spectrometer (Corp., Varian, USA) and/or the turbidity meter (Hanna Instruments, Italy), respectively [13].

4. Results and discussion

4.1. The results of orthogonal experiment

The removal rates of Cu^{2+} of 16 times orthogonal experiments in Table 1 are 80.64, 81.45, 83.66, 83.42, 76.63, 84.56, 79.33, 87.42, 84.15, 87.5, 87.25, 80.96, 91.01, 91,5, 90.93, and 86.6, respectively. Through orthogonal test and extreme difference analysis, the optimum technological conditions were determined as following: the mass ratio m(CTS):m(TGA) is 1:2, the pH value is 4.5, and the reaction time is 2.5 h. In 120 mL reaction solution, the dosage of EDC·HCl is 0.30 g and the amount of TGA is 1.3 mL.

4.2. Characterization

To confirm the fact that thiol has been successfully grafted to CTS, FTIR spectra and elemental analysis were employed.

The FTIR spectra of both CTS and MAC are shown in Fig. 1. From Fig. 1, it can be seen that new absorptions appear in the adsorption spectra of MAC. The adsorption at 2,567 cm^{-1} belongs to mercapto-group. The adsorption at 3,392 and 1,689 cm^{-1} belongs to amide group. The adsorption at 1,523 cm^{-1} belongs to imino. These absorptions illustrate that TGA is successfully grafted to CTS [14].

Table 1
The table of orthogonal experimental design ($L_{16}(4^5)$)

Factors	m(CTS): m(TGA)	pH value	TGA (mL)	EDC·HCl (g)	Time (h)
Level	3:2	4	0.9	0.25	2.5
	1:1	4.5	1.1	0.3	3
	2:3	5	1.3	0.35	3.5
	1:2	5.5	1.5	0.4	4

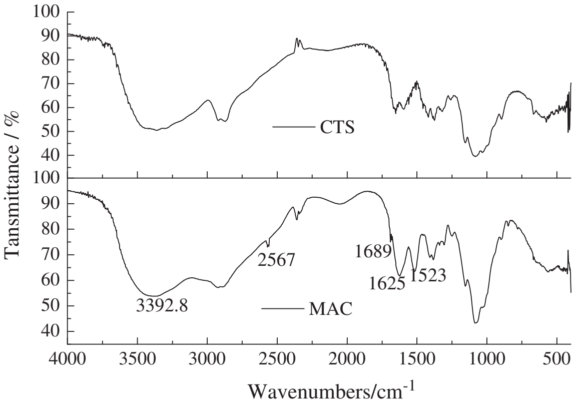


Fig. 1. FTIR spectra of MAC and CTS.

The elemental analysis showed that the sulfur content in MAC sample was from 2.30 to 2.55%, which also determined that TGA was successfully grafted to CTS macromolecule.

4.3. Comparison of water solubilities between MAC and CTS

Firstly, MAC and CTS were dried at 40℃ under a vacuum at the same time and then, a certain amount of the same were taken and put into solutions of different pH values. It is shown that CTS is soluble in dilute aqueous solution of hydrochloric acid, acetic acid, etc. But it is not soluble in neutral water solution. However, MAC is still soluble in aqueous solution when it's pH value is increased up to 11.

4.4. The performance of removing Cu^{2+} by MAC

4.4.1. Comparison of MAC and CTS and TGA on the removal of Cu^{2+}

The removal efficiency of Cu^{2+} by MAC, CTS, and TGA is shown in Fig. 2. It is clear from this figure that the removal efficiency of Cu^{2+} by MAC is the highest and the removal rate of Cu^{2+} by CTS is the lowest. It has nearly no efficiency for removing copper ions when CTS alone is added to wastewater, it has the same conclusion with Gamage, etc. [5]. These results could be explained as follows: CTS reacts with copper ions through coordination between $–NH_2$ and Cu^{2+}; it is observed that this product is a very fine particle, which settled slowly and was difficult to separate from water solution. Compared with CTS and TGA, MAC reacts with copper not only through coordination between –NH$_2$ and Cu^{2+}, but also through coordination or chelation between mercapto-group and Cu^{2+}, these products are water insoluble. As a macromolecular flocculant, MAC is leading the bridge effect between particles, the flocs produced by MAC are sufficiently large, settles rapidly, and is easily separated.

4.4.2. Effect of pH value

The effect of solution pH value on the removal efficiency of Cu^{2+} is presented in Fig. 3. It is clear from Fig. 3 that the removal efficiency of Cu^{2+} is dependent on the pH value. This result can be explained as follows: when the pH value is decreased, the H$^+$ concentration increases; H$^+$ has free tracks and it is easy to accept lone pair electrons of –S on the polymer, and the coordination between H$^+$ and the –S on polymer is enhanced. At the same time, when H$^+$ concentration increases (NH– changes to $-\mathrm{NH}_2^+$), due to the repulsion of the same charge, the removal rate of Cu^{2+} is decreased. When H$^+$ concentration increases, the electrode potential of the Cu^{2+}/Cu$^+$ is receded [15]. Then, the oxidation–reduction reaction ability of Cu^{2+} and MAC is decreased and the concentration of Cu$^+$ is diminished relatively. According to the soft hard acid base principle, mercapto-group could easily react with Cu$^+$ than with Cu^{2+}.

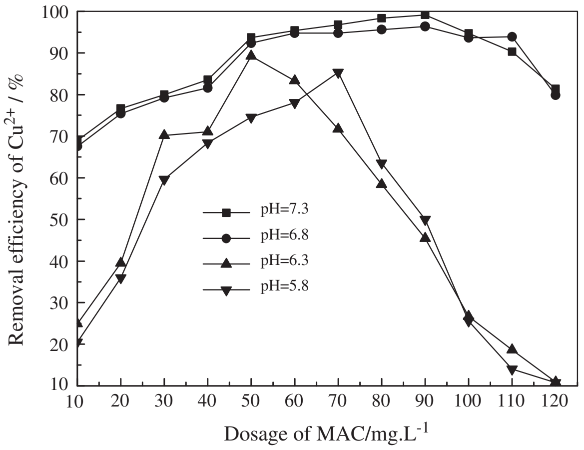


Fig. 3. Effect of pH on removal rate of Cu^{2+} by MAC.

4.4.3. Effect of turbidity

Generally speaking, wastewater containing Cu^{2+} is turbid due to the presence of substances which cause turbidity. Therefore, the influence of turbidity on removal of Cu^{2+} was investigated. The pH values of working solutions containing 25 mg.L^{-1} Cu^{2+} were 6.3. The result is shown in Fig. 4.

Fig. 4 shows that the removal rate of Cu^{2+} increased with the increase in turbidity, the higher the turbidity of the water sample, the higher the rate of removal, and the maximum removal rate of Cu^{2+} was 96.73%. It means that the turbidity can promote the removal efficiency of heavy metal ions. The reason is that MAC cannot only rely on the redox and chelation of MAC for removal of dissolved copper ions in waste water, but also use "adsorption bridging" role to link substances causing turbidity into flocs. When turbidity is increased, the quantity of flocs is also increased, which has the "sweep" function for the insoluble colloidal compound of copper with MAC and the weak adsorption function for the soluble copper ions.

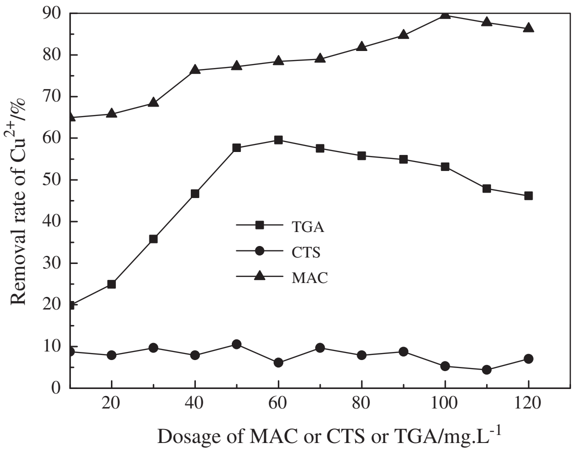


Fig. 2. Removal efficiency of Cu^{2+} by MAC or CTS or TGA.

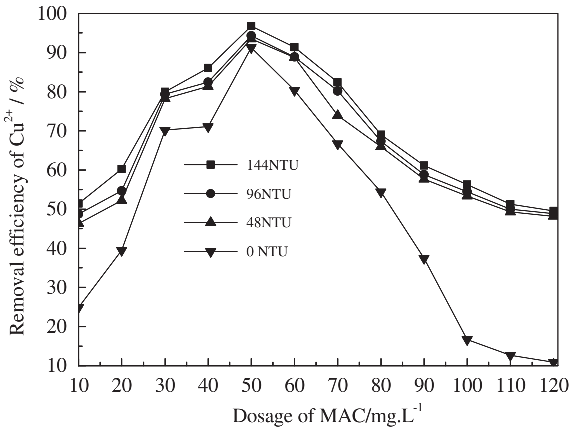


Fig. 4. Influence of turbidity on removal rate of Cu^{2+}.

Therefore, the removal of copper is increased when water samples have turbidity.

4.4.4. Effect of inorganic ions

Heavy metal wastewater always contains various inorganic ions such as Na^+, Ca^{2+}, F^-, Cl^-, etc. [16]. The presence of the inorganic ions coexisting with Cu^{2+} may affect the removal of Cu^{2+}. It is important to investigate the influence of inorganic ions coexisting with Cu^{2+}. Therefore, the solution of sodium nitrate ($NaNO_3$), potassium nitrate (KNO_3), calcium nitrate ($Ca(NO_3)_2$), magnesium nitrate ($Mg(NO_3)_2$), sodium chloride (NaCl), sodium fluoride (NaF), or sodium sulfate (Na_2SO_4) was added into water samples containing Cu^{2+}. The equivalent concentration of inorganic salt is 0.120 equivalent·L^{-1}, respectively. The constant initial Cu^{2+} concentration is 25 mg. L^{-1} and flocculation experiments were carried out for these samples with different dosages of MAC. The results can be seen from Fig. 5.

It is shown in Fig. 5(a) that the removal of Cu^{2+} was enhanced in the presence of these coexisting cations. Moreover, the order of promotion was that $Ca^{2+} \approx Mg^{2+} > K^+ \approx Na^+$ for the same initial cation equivalent concentrations. From Fig. 5(b), it can be found that the effect of anions on Cu^{2+} removal was similar.

The colloidal particles possess the structure of diffused double layer. The presence of monovalent and divalent cations can cause the diffuse layer to be compressed and the zeta potential to be decreased. As a result, these colloidal particles easily form greater flocs and settle rapidly.

However, the coexisting anions can hinder the electrostatic attraction between Cu^{2+} and MAC because they can be attracted to the chain surface of MAC by electrostatic interaction, but the coexisting Na^+ can weaken the effect. Consequently, the removal rate of Cu^{2+} was promoted by the presence of these coexisting ions.

4.5. The performance of removing turbidity by MAC

4.5.1. Comparison on the removal of turbidity by MAC, CTS, and TGA

The initial turbidity of the working solution is 252 NTU prepared by Kaolin suspension. The pH value of working solution is 7.7. The flocculation experiments were carried out when different amounts of MAC or CTS or TGA were added into working solution. The results are shown in Fig. 6.

Fig. 6 shows that the removal efficiency of turbidity by MAC is little higher than that by CTS and the highest removal efficiency reaches to 74%. This result may be explained as follows: on one hand, MAC is obtained by amidation reaction between the CTS and the thioglycolic acid, its molecular weight has a significant increase, which makes the ability of adsorption bridging improved substantially; on the other hand, the effect of carbonyl group reduces the alkalinity of –NH, thus decreases the combination between –NH and H^+, therefore the ability of electrical neutralization becomes weaker.

4.5.2. Effect of pH value

Fig. 7 shows the effects of pH value on the turbidity removal rate by MAC. The initial turbidity of working solution is 105 NTU. It is clear that the best turbidity removal can be obtained when the pH value of the solution is 6, the pH value has an impact to some extent on the removal rate of turbidity by MAC, but the effect is lighter than that of the CTS [8]. This is because the level of solvation of the organic polymer

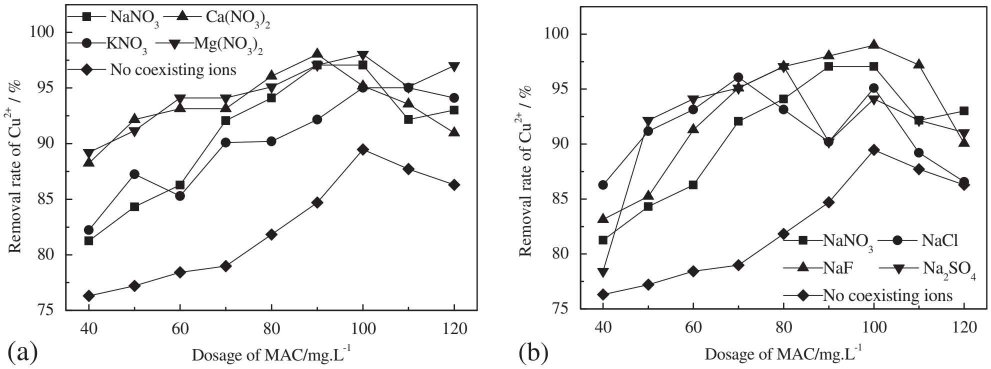


Fig. 5. Effect of cations (a) and anions and (b) on removal rate of Cu^{2+} by MAC.

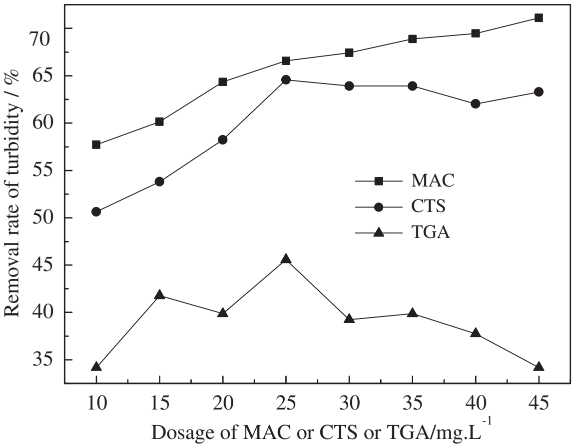


Fig. 6. Comparison of the removal of turbidity by MAC and CTS and TGA.

affects to its flocculation performance. Compared with CTS, the water solubility of the MAC is greatly enhanced because of the polar group –SH, the ability of "adsorption bridging" is also enhanced with the stretching of molecules in aqueous solution.

4.5.3. *Effect of heavy metal ions*

The water samples used in these test, which were synthesized in laboratory by copper nitrate, nickel nitrate, cadmium nitrate, mercury chloride, kaolin and tap water, contained both turbidity (158 NTU) and $Cu^{2+}/Ni^{2+}/Cd^{+}/Hg^{2+}$ (25 mg.L^{-1}). Flocculation experiments were carried out using different dosage of MAC at pH 7.0. The results are shown in Fig. 8. Fig. 9 shows the effects of Cu^{2+} on the turbidity removal rate with MAC at pH 5.0 and pH 7.0.

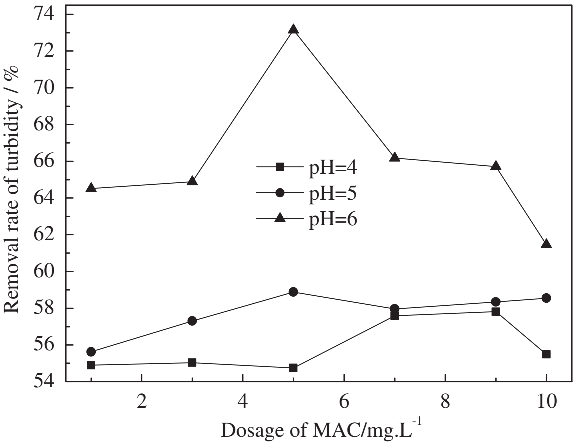


Fig. 7. Effects of pH value on the turbidity removal rate by MAC.

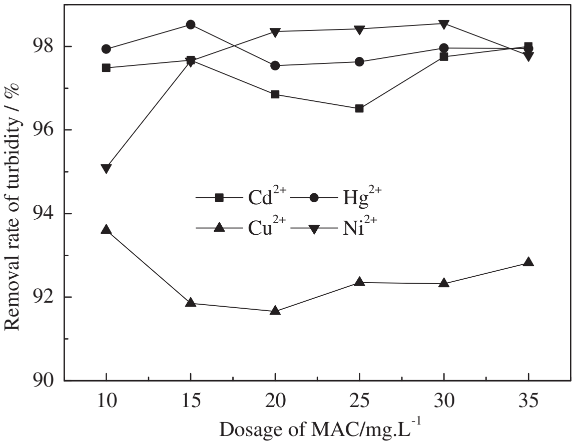


Fig. 8. Effects of different heavy mental ions on the turbidity removal rate with MAC.

It can be seen from Figs. 8 and 9 that the turbidity removal performance of the MAC has been improved in varying degrees because of the presence of different heavy metals. Fig. 8 also shows that the turbidity removal efficiency reaches to 100% when the dosage of MAC is 15 mg/L at pH 5. This may be explained as follows. When MAC is added in water sample in the presence of Cu^{2+}, Cu^{2+}, H^{+}, and Cu^{+} produced from the above redox reactions (Eq. (4)) played the electrical neutralization for turbidity substances, thus the removal efficiency was increased greatly. Furthermore, oxidation–reduction reaction ability of Cu^{2+} and MAC is higher at low pH values, so the removal efficiency was higher at lower pH values. At the same time, the heavy metal ions of Ni^{2+}, Cu^{2+}, Cd^{2+}, and Hg^{2+} with the MAC can form large flocs through coordination or chelation reaction, it sinks rapidly.

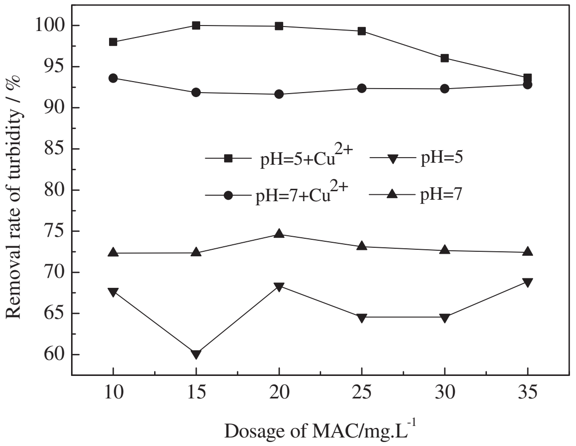


Fig. 9. Effects of Cu^{2+} on the turbidity removal rate with MAC in different pH value.

5. Conclusions

1. The optimal preparation conditions of MAC are determined as follows: m(CTS):m(TGA) is 1:2, pH value is 4.5, reaction time is 2.5 h, the dosage of EDC·HCl is 0.30 g, and the amount of TGA is 1.3 mL, respectively, for 120 mL reaction solution.
2. Compared with CTS, MAC has better water solubility and higher efficiency for removing copper ions and turbidity.
3. With the increasing pH value, the removal efficiency of Cu^{2+} by MAC was enhanced. However, the influence of the pH value to turbidity is not significant.
4. The presence of coexisting ions in the solution can significantly influence the removal of Cu^{2+} by the MAC. The removal rate of Cu^{2+} was promoted by the presence of these coexisting cations.
5. The removal efficiency of turbidity by MAC is little higher than that of CTS. The pH value of the water has impact on the removal efficiency of turbidity to some extent. When water sample contains not only heavy metal ions but also substances causing turbidity, the removal efficiency of both heavy metal ions and the turbidity are promoted by the cooperation effects of each other.

Acknowledgment

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