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Removal of Cu^{2+} and turbidity from wastewater by mercaptoacetyl chitosan

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ABSTRACT

A macromolecule heavy metal flocculant mercaptoacetyl chitosan (MAC) was prepared by reacting chitosan with mercaptoacetic acid. In preliminary experiments, the flocculation performance of MAC was evaluated by using wastewater containing Cu^{2+} or/and turbidity. Some factors which affect the removal of Cu^{2+} and turbidity were also studied. The experimental results showed that: (1) MAC can remove both Cu^{2+} and turbidity from wastewater. The removal efficiency of Cu^{2+} by using MAC combined with hydrolyzed polyacrylamide is higher than that by only using MAC, the removal efficiency of Cu^{2+} reaches above 98%; (2) when water sample containing not only Cu^{2+} but also turbidity-causing substance, the removal efficiency of both Cu^{2+} and turbidity will be promoted by the cooperation effect of each other, the residual concentration of Cu^{2+} reaches below 0.5 mg L^{-1} and the turbidity reaches below 3 NTU, Cu^{2+} is more easily removed by MAC when turbidity is higher; (3) the removal efficiency of Cu^{2+} increases with the increase in pH value, contrarily removal efficiency of turbidity decreases with the increase in pH value.

1. Introduction

Flocculation is one of the most important methods for water treatment. Today many kinds of flocculants including inorganic and organic flocculants are widely used in the treatment of water and wastewater. The typical flocculants in common use are polyaluminum chloride (PAC), polyferric sulfate (PFS) and polyacrylamide (PAM). All of them are very efficient for the removal of turbidity from water and wastewater [1]. It is well known that the main objects of flocculation are the hydrophobic colloid and suspended particle which consist of insoluble substances. Although there have been many kinds of flocculants today, it is nearly impracticable to remove the soluble substances very well from water and wastewater directly by these current flocculants.

The soluble heavy metal ions in water are permanent pollutants. They can be adsorbed onto particles, or become particles by hydrolysis. Therefore, the heavy metal content of water can be reduced to some extent by flocculation. However, there are still a large number of heavy metals that are soluble in water after flocculation. They are mainly metal complexing species with different ligands. Therefore, the flocculation unit must be followed by other treatment units, for example, chemical precipitation, adsorption, ion exchange and membrane filtration.

Macromolecule heavy metal flocculants is a new kind of flocculant [2–6]. They 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 species from water by coordination and chelation. Because macromolecule heavy metal flocculants have such two functions, it is possible to omit some treatment units that follow the flocculation unit to remove heavy metals or reduce the operating load of them. In this way, the water treatment system could be greatly simplified. To develop this new kind of flocculant which can scavenge heavy metal ions in polluted water, some strong ligands for heavy metals, such as dithioic acid or its salt group, were grafted to starch, and phosphonate group was grafted to macromolecular flocculant [2–6].

Dissolved chitosan is a good flocculant, and has the ability to bind heavy metals by coordination. But the produced complex compounds cannot precipitate very well. For this reason, mercapto-group was introduced to chitosan by reacting chitosan with mercaptoacetic acid (TGA) in our work. The product was named as mercaptoacetyl chitosan (MAC). Because mercapto-group is a strong ligand for heavy metals, and the solubility product values (K_{sp}) of heavy metal thiolate is usually very small, MAC can form the insoluble chelate and complex with heavy metal species in wastewater. In this paper the preparation of MAC is introduced and its performances are evaluated by using the wastewater containing turbidity and/or copper ions as the target.

2. Principle

2.1. Synthesis

Chitosan can be amidated by TGA in the presence of 1-ethyl-3-3 (dimethylamino-propyl) carbodiimide hydrochloride (EDC·HCl) as the activating agent. The reactions are as follows:

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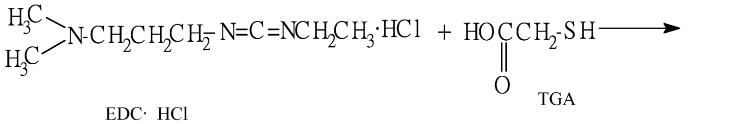
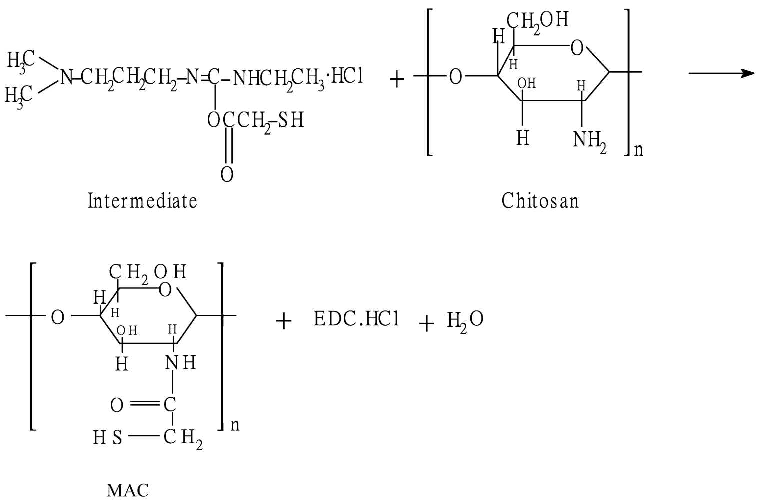


(1)



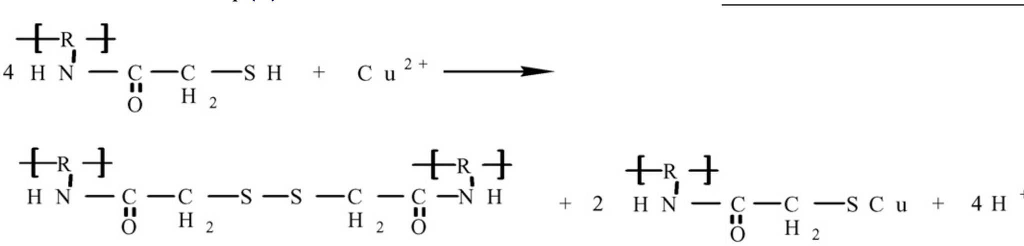
(2)

First EDC·HCl reacts with TGA to form the intermediate, thus activating the carboxylic group on TGA molecule. Secondly the intermediate reacts with chitosan to form the MAC.

2.2. Removal of Cu^{2+}

2.2.1. Redox and coordination/chelation between –SH and Cu^{2+} ions

After MAC is added to wastewater containing Cu^{2+} ions, both the redox and coordination/chelation reactions between –SH on MAC molecule and Cu^{2+} ions in the solution probably take place, as a result, insoluble cuprous complex/chelate and disulfide form. This reaction is shown in Eq. (3):

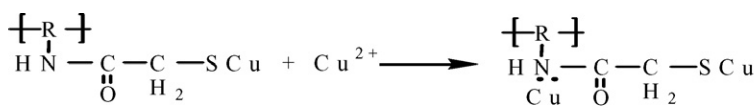


(3)

It was reported that mercapto-group can be oxidized by some oxidant [7]. As we know bivalent copper ions are oxidant, therefore MAC is oxidized by copper ions to disulfide and the copper ions themselves are reduced at the same time by mercapto-groups on MAC molecule to cuprous ion, which forms an insoluble complex/chelate with the remaining mercapto-groups on MAC molecules. According to soft hard acid base principle, mercapto-group on MAC is a soft base and cuprous ion is a soft acid, therefore they could easily react to form a stable metal-complex [8–11], in addition, because the solubility product of –SCu is very small, copper ions are well precipitated by MAC.

2.2.2. Coordination between –NH– and Cu^{2+}

When the above reaction takes place, the coordination between –NH– on MAC molecule and Cu^{2+} in the solution also takes place at the same time. This reaction is shown in Eq. (4):



As a result, some of copper ions are coprecipitated with above comlpex/chelate produced in Eq. (3), therefore the removal will be strengthened.

Because the coordinate groups which combine with one heavy metal ion may come from different MAPEI molecules, the above products would form the flocs with network structure, leading the “sweep” effect for colloid materials in wastewater.

3. Experiments

3.1. Materials

Polyacrylamide (MW 25×10^6, hydrolysis 24.01%,) was purchased from Baiying Chemical Reagent Factory, Baiying, China; TGA (AR) and chitosan (AR, deacetylation 90%, MW $2–4 \times 10^5$) were purchased from Shanghai Chemical Reagent Corp., Shanghai, China; EDC·HCl (CP) and Kaolin (CP) and other compounds (AR) were purchased from Shanghai Sanpu Chemical Engineering Corp. LTD., Shanghai, China.

Jar test instrument (Model J6–1A) was purchased from Beijing West City Instrument Factory, China; Spectrophotometer (Model 721) was provided by Shanghai Precise Science Corp. LTD, China; Infrared spectrophotometer (Digilab FTS3 000) was purchased from Varian Corp., America; Elementar Analysensysteme GmbH was purchased from VarioEL Corp., Germany.

3.2. Preparation of MAC

First, 1 g of Chitosan was dissolved in 8 ml of HCl solution (1 mol L^{-1}), and then a little amount of distilled water was added to this solution. After chitosan was completely dissolved, 1.5 ml of TGA and 0.31 g of EDC·HCl were added dropwise to this solution in sequence under strong stirring until the system was completely mixed. Thereafter, the pH of the solution was adjusted to 5.0 by using HCl solution (1 mol L^{-1}), and distilled water was added until the volume of solution reaches to 120 ml. The solution was kept at 20 °C in a water bath and continued by constantly stirring for 3.5 h. Thus the MAC product was obtained. These optimum conditions were experimentally determined by using the method of orthogonal experiment.

3.3. Flocculation test

5% suspension of kaolin and 10 g/L solution of $CuSO_4$ were prepared as stock solutions. 400 ml of tap water and 1 ml of above $CuSO_4$ solution or/and 5 ml of above kaolin suspension were added to a 500 ml jar. The pH values of water samples in the jars were adjusted to the desired values respectively. Such six jars were placed on a six-joint-stirrer, and MAC solutions were added in different dosages of 0, 4, 5, 6, 7, and 8 ml, respectively to different jars, which were stirred by stirring blades at the uniform speed of 140 rpm for 2 min, followed by the slow stirring at 40 rpm for 10 min. Later, 10 min of settling time was required. After these procedures, the supernatants were drawn, and the turbidity and/or concentrations of copper ions were measured by the turbidity meter (Hanna instruments, Italy) and/or 220FS atomic absorption spectrometer (Corp., Varian, USA), respectively [12].

4. Results and discussion

4.1. Characterization

The product was put into acetone liquid and deposited from it, then dried at 40 °C under a vacuum. Thus the pure product was obtained and identified by infrared and elemental analysis.

The FTIR spectra of both chitosan and MAC were recorded with KBr dispersion method for comparison. These two FTIR spectra are shown in Figs. 1 and 2, respectively.

Comparing these two figures, it can be seen that new absorptions appear in the absorption spectrum when chitosan was changed to MAC. The weak absorption at 2562.96 cm^{-1} belongs to mercapto-group; four absorptions including the strong absorption at 1574.42 cm^{-1}, the weak absorption at 3266.67 cm^{-1}, the weak absorption at 1634.18 cm^{-1} and the weak absorption at 1523.33 cm^{-1} belong to second amide. These absorptions show that the new macromolecule has mercapto-groups and secondary amide groups [13].

The elemental analysis shows that the sulfur content in MAC sample reaches to 2.5%.

Therefore it was determined that the TGA was successfully grafted to chitosan macromolecule.

4.2. Comparison of the removal of Cu^{2+} by MAC with other chemicals

After the pH values of water samples containing Cu^{2+} were adjusted to 5.3, jar tests were carried out in different conditions, respectively as following: (1) chitosan was added only; (2) TGA was added only; (3) MAC was added only; (4) MAC was added combined with 0.01% hydrolyzed polyacrylamide (HPAM); (5) MAC was added in the presence of 86 NTU turbidity in water sample. The results of the removal efficiency of Cu^{2+} are shown in Fig. 3.

It can be seen that there is nearly no efficiency for removing copper ions when chitosan is added, and the highest removal rate of copper ions only reaches to 59.26% when TGA is added. But when MAC is added, the highest removal rate of copper ions reaches to

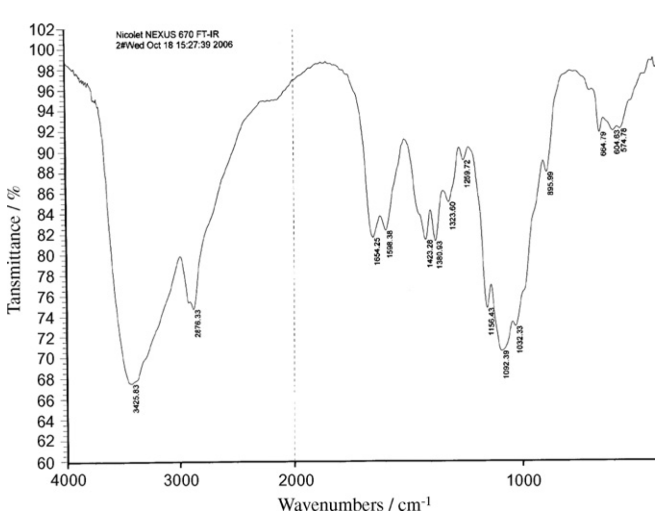


Fig. 1. IR spectrum of chitosan.

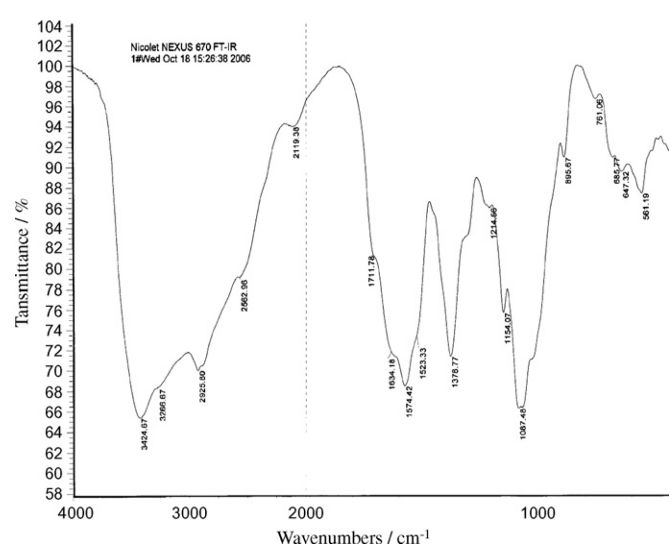


Fig. 2. IR spectrum of MAC.

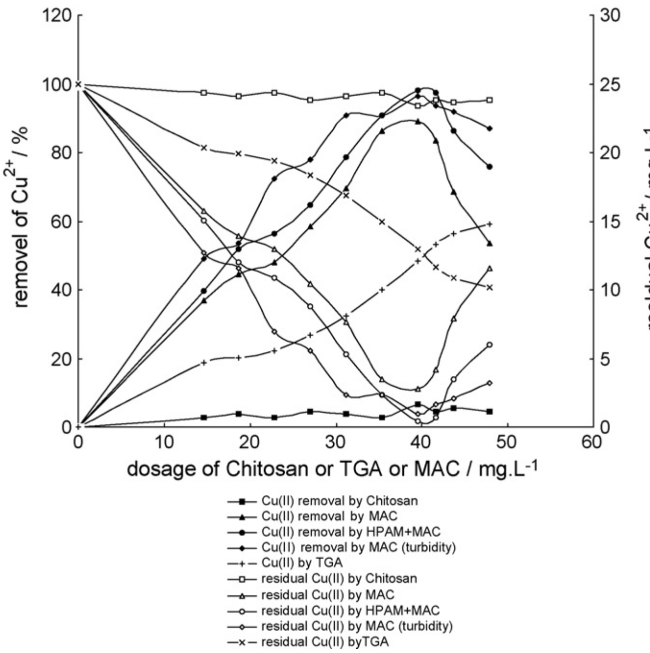


Fig. 3. Comparison of the efficiencies for removing Cu^{2+} in different conditions.

88.89%. When MAC is added in the presence of turbidity, the highest removal rate of copper ions reaches to 96.3%. When MAC is added combined with HPAM, the highest removal rate of copper ions reaches to 98.15%. These results could be explained as follows. Chitosan reacts with copper ions through coordination between $-NH_2$ and Cu^{2+}, so that the water soluble complex forms; TGA reacts with copper ions through coordination/chelation between mercapto-groups and Cu^{2+}, as a result, water insoluble product forms, but it was observed that this product is very fine particle, settling slowly and difficult to separate from mother liquid; compared with above two chemicals, MAC reacts with copper ion through not only coordination between $-NH_2$ and Cu^{2+} but also coordination/chelation between mercapto-group and Cu^{2+}, because these products are water insoluble and MAC is a macromolecular flocculant which leads bridge effect between particles, the flocs produced by MAC are sufficient large to allow for rapid settling and subsequent separation, thus leading better removal. When MAC is added in the presence of turbidity in water sample, the quantity of flocs was increased because of flocculation of substances causing turbidity, this leading the "sweep" function for the insoluble colloidal compound of copper with MAC and the weak adsorption function for the soluble copper ions, therefore, the removal of copper is increased. Because HPAM is very efficient flocculant, the quantity of flocs are increased greatly when MAC is added combined with HPAM, thus "sweep" function and adsorption function are also strengthened.

4.3. Comparison of the removal of turbidity by MAC with other chemicals

After the pH values of water sample containing 86 NTU of turbidity were adjusted to 5.3, jar tests were carried out in different conditions, respectively as following: (1) chitosan was added only; (2) MAC was added only; (3) MAC was added in the presence of $25\,mg\,L^{-1}$ of Cu^{2+} in water sample. The removal efficiencies of turbidity are shown in Fig. 4.

It can be seen that chitosan is the most efficient for removing turbidity, and the highest reaches to 95%, which may be attributed to the $-NH_2$ on the macromolecule and the long molecular chain. On the one hand, the $-NH_2$ combines with H^+ in the solution becoming

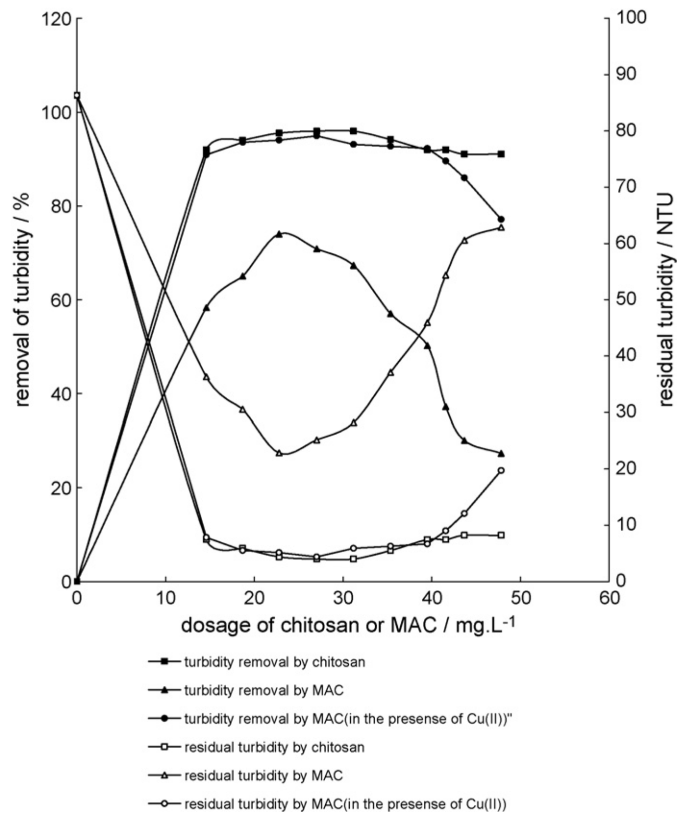


Fig. 4. Comparison of the efficiencies for removing turbidity in different conditions.

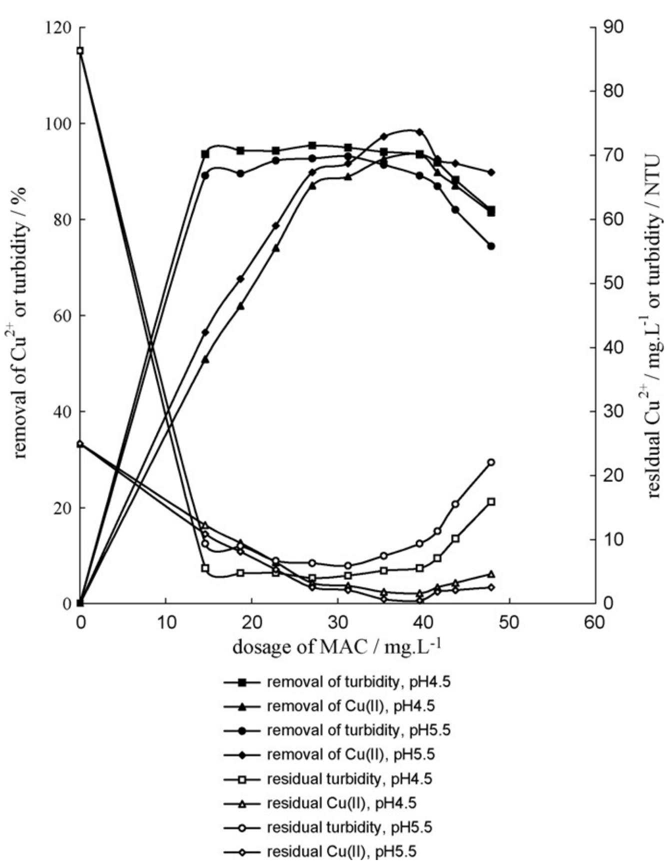


Fig. 5. Effect of pH on the removal of Cu^{2+} and turbidity by MAC.

$-NH^{3+}$, therefore the macromolecule can neutralize the negative charges of the turbidity substances. On the other hand, the long macromolecule chain plays the bridge effect between turbidity substances at the same time, thus leading a very good flocculation effect. Fig. 4 also shows that the removal efficiency of turbidity by MAC is lower than by chitosan, and the highest removal efficiency reaches to 74%. This fact may be explained by the effect of carbonyl group which reduces the alkalinity of –NH, thus decreasing the combination between –NH and H^+, leading weaker electrical neutralization for turbidity substances. But when MAC is added in the presence of Cu^{2+} in water sample, in addition to the Cu^{2+}, the Cu^+, H^+ produced from above redox and coordination/chelation reactions (Eq. (3)) play the electrical neutralization for turbidity substances, thus the removal efficiency is increased greatly, reaching to 95%.

4.4. Effect of pH on the removal of Cu^{2+} and turbidity by MAC

Fig. 5 shows that the removal efficiency of Cu^{2+} increases with the increase in pH value, on the contrary, the removal efficiency of turbidity decreases with the increase in pH value. This result can be explained as follows. When pH value is increased, the ionization of –SH on the macromolecule increases, which contribute to the coordination of –SH with the copper ions, but not favorable for the combination of –NH with H^+. Thus reducing the electrical neutralization for turbidity substances.

5. Conclusions

A novel macromolecule heavy metal flocculant MAC was prepared by reacting chitosan with mercaptoacetic acid in the presence of 1-ethyl-3-3 (dimethylamino-propyl) carbodiimide hydrochloride (EDC·HCl) as the activating agent. Detailed analysis revealed that this new flocculant could not only remove turbidity as conventional flocculants, but also remove heavy metals in wastewater. The ability of the new flocculant for copper scavenging and turbidity removal was confirmed as following:

- chitosan has nearly no efficiency for removing copper ions, and TGA is inefficient for removing copper ions, while MAC is much more efficient for removing copper ions than TGA;
- when MAC is used combined with HPAM, the removal efficiency of copper ions will be further raised;
- MAC is efficient to some extent for the removal of turbidity, but less efficient than chitosan;
- when water sample contains not only Cu^{2+} but also turbidity-causing substance, the removal efficiency of both Cu^{2+} and turbidity will be promoted by the cooperation effect of each other;
- the removal efficiency of Cu^{2+} increases with the increase in pH value, on the contrary, removal efficiency of turbidity decreases with the increase in pH value. The optimum pH value suitable for both removals should be used in treatment of wastewater containing both Cu^{2+} and turbidity.

Acknowledgments

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