

Synthesis and Trapping Properties of Dithiocarbamate Macromolecule Heavy-Metal Flocculants

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ABSTRACT: The synthesis and trapping properties of dithiocarbamate macromolecule heavy-metal flocculants (DMHMFs) were studied. DMHMFs were synthesized through the reaction of polyimine with carbon disulfide under alkaline conditions. The dosage of sodium hydroxide, carbon disulfide, and polyimine and the reaction temperature and time were studied in detail. The flocculants were detected and characterized with IR spectroscopy, ultraviolet-visible spectroscopy, and solubility measurements. The trapping and removal properties of DMHMFs with respect to some heavy-metal ions were also studied. The results showed that a proposed trapping agent had

good trapping and removal properties with respect to some heavy-metal ions in a wide pH range. The removal rates of copper(II) and lead(II) were up to 99.44 and 98.74%, respectively. In comparison with traditional inorganic chemical precipitation agents, the formation and precipitation of the flocs were quicker, and the dosage of the trapping agent was lower. In addition, in the precipitation processes, other flocculants did not need to be added, so the treatment process was simple. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2461–2466, 2008

Key words: heavy metal ions; polyamines; synthesis

INTRODUCTION

The method of flocculation plays an important role in water treatment.¹ The flocculating effect is determined mainly by the qualities and species of flocculants. Organic macromolecule flocculants emerged in the 1950s and were gradually used in environmental protection in the 1960s. Their advantages are as follows: large molecular weights, strong adsorption and bridging abilities, multifunctional groups, good flocculating effects, easily filtered flocs, lower dosages, little and easily treated sludge, freedom from pH and temperature, and so on.² According to the characteristics of wastewater, they can be synthesized selectively through changes in the function and the electric charge of the function and through

control of the molecular weight. Therefore, organic macromolecule flocculants have recently been widely used in wastewater treatment.³

Water pollution due to toxic heavy metals is a serious environmental and public health issue.^{4,5} The removal of heavy metals from mine drainage and industrial effluents has become important for maintaining water quality standards that are suitable for environmental and human health.^{6–8} Macromolecule heavy-metal flocculants (MHMFs), which have the ability to trap and remove heavy-metal ions, can be obtained by the introduction of a strong dentate of a heavy metal into organic macromolecule flocculants. Aminodithioformic groups contain some coordination atoms, such as sulfur and nitrogen. The chelating compounds are formed steadily by aminodithioformic groups chelating with some heavy-metal ions.^{9,10} Dithiocarbamate macromolecule heavy-metal flocculants (DMHMFs) can be obtained by the introduction of aminodithioformic acid groups into organic macromolecule flocculants. These flocculants not only have the advantages of organic macromolecule flocculants but also have a good ability to trap and remove heavy-metal ions in wastewater efficiently and steadily. Therefore, they could potentially be used widely in water pollution control.^{11,12} In comparison with traditional inorganic chemical precipitation agents, MHMFs have many advantages: lower dosages, freedom from pH

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adjustments, simple operation, and no secondary pollution. The use of DMHMFs could lead to new methods and technologies for heavy-metal pollution control.

In this study, DMHMFs were synthesized through the reaction of polymine with carbon sulfide under alkaline conditions. The active hydrogen of the imine group in polymine was substituted by carbon disulfide. The new flocculants (DMHMFs) had the ability to trap and remove heavy metals. Moreover, polymine is cheap as a raw material. The specific synthesis procedures of DMHMFs with polymine and carbon sulfide have not been reported previously.

In the treatment process of traditional chemical precipitation methods,¹³ such as hydroxide precipitation method and sulfide precipitation,¹⁴ after traditional inorganic reagents are added to wastewater containing heavy metals, the particles that form are so minute that they cannot precipitate. The very tiny particles that form can be precipitated only by the addition of another flocculant. However, the DMHMFs synthesized in this study could both trap heavy-metal ions and flocculate and precipitate the particles. After these trapping agents were added to wastewater containing heavy-metal ions, the formation and precipitation of the flocs were quicker, and the dosage of the proposed trapping agents was lower. In addition, in the precipitation processes, other flocculants did not need to be added, so the treatment process was simple.

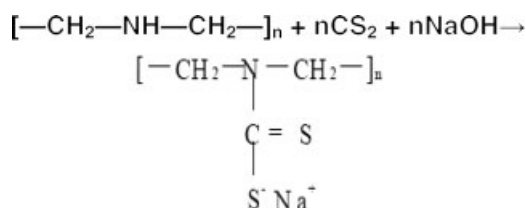
EXPERIMENTAL

Materials

Polymine (molecular weight = 10,000) was obtained from Liyi Assistant Co. (Guangxi, China). Carbon disulfide and sodium hydroxide were provided by Chengdu Chemical Agent Factory (Chengdu City, China), and the two reagents and all metal-ion salts were analytical-grade. All aqueous solutions and standard solutions were prepared with distilled water. The pH of the heavy-metal-ion solution was adjusted with a sodium hydroxide solution or a hydrochloric acid solution.

Main synthesis route of DMHMFs

Under certain conditions, DMHMFs were synthesized by the reaction of polymine with carbon sulfide and sodium hydroxide. The main synthesis route was as follows:



Synthesis procedure of DMHMFs

A three-necked, round-bottom flask (500 mL) was used as the reaction vessel. A given mass of a polymine solution (30%) and sodium hydroxide were added to the flask in a cold-water bath. After cooling to room temperature, carbon disulfide was added at the speed of two drops per minute. The reaction vessel was moved into a fixed-temperature water bath after the carbon disulfide was completely added. Under certain temperature, as the reaction continued, the reaction solution color changed from milky to nacreous. All procedures were carried out with stirring.

Purification of the product

The synthesized DMHMF was a sodium salt and thus could dissolve easily in water; this led to some difficulties for product purification. The research results showed the product did not dissolve in ethyl alcohol, and ethyl alcohol could dissolve in water. Therefore, ethyl alcohol was used as the dehydrant of the product solution. Then, the solid DMHMF product was obtained.

Experiments with the trapping and removal of heavy-metal ions with DMHMFs

A ZR 4-6 stirring machine (Shenzhen Zhongran Water Industry Technology Development Co. Ltd., Shenzhen, China) with six stirrers was used in this experiment. Under different conditions, a DMHMF solution was added to a wastewater analogue (200 mL) containing Cu^{2+} (100 mg/L) or Pb^{2+} (100 mg/L). The mixture solution was stirred for 3 min at 100 rpm min after 2 min at 300 rpm. Then, the solution was filtered after some minutes of sedimentation. The concentration of Cu^{2+} or Pb^{2+} was assayed by ultraviolet-visible (UV-vis) spectrophotometry.

RESULTS AND DISCUSSION

Synthetic conditions

Effect of the sodium hydroxide dosage on the production rate

The effect of the sodium hydroxide dosage on the production rate was studied through changes in the sodium hydroxide dosage from 2.0 to 5.0 g. The research results are given in Figure 1. Figure 1 shows that when the dosage of sodium hydroxide was between 2.0 and 2.5 g, the production rate increased quickly. When the dosage was between 2.5 and 3.5 g, the production rate evidently did not increase, and when the dosage was 4.0 g, the production rate was highest. Therefore, 4.0 g was selected as

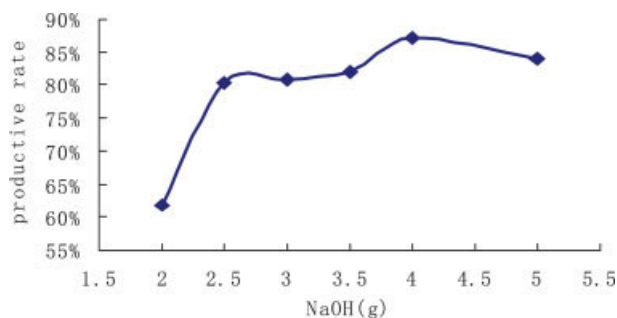


Figure 1 Effect of the sodium hydroxide dosage on the production rate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the optimal dosage of sodium hydroxide. The reaction conditions were as follows: polymine, 19.3 g; carbon disulfide, 6 mL; reaction time, 3 h; and water bath temperature, 30°C. The reaction had to be performed under alkaline conditions. The given dosage of sodium hydroxide ensured that the reaction solution would be alkaline all the time and that the product would exist in the sodium salt form.

Effect of the polymine dosage on the production rate

When the other reaction variables were fixed, the effect of the polymine dosage on the production rate was studied. The research results are given in Figure 2. Figure 2 shows that the production rate decreased when the polymine dosage increased. Therefore, 17.0 g was selected as the optimal dosage of the polymine. The polymine (30%) was viscous, and the reaction solution viscosity increased with the polymine dosage increasing. Therefore, sodium hydroxide and carbon disulfide could not react with the polymine adequately, and the production rate decreased. In addition, the surplus polymine remaining in the reaction solution led to more difficulties for the purification experiments.

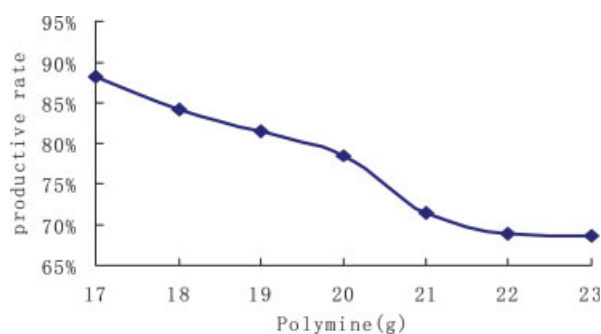


Figure 2 Effect of the polymine dosage on the production rate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

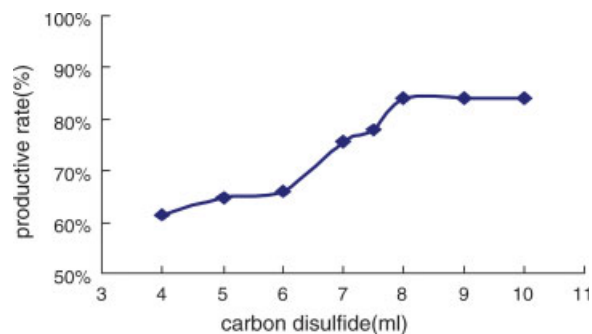


Figure 3 Effect of the carbon disulfide dosage on the production rate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Effect of the carbon disulfide dosage on the production rate

When the other reaction variables were fixed, the effect of the carbon disulfide dosage on the production rate was studied. The research results are given in Figure 3. Figure 3 shows that when the dosage of carbon disulfide was between 4.0 and 6.0 mL, the production rate evidently did not increase. When the dosage of the carbon disulfide was between 6.0 and 8.0 mL, the production rate increased quickly, and when the dosage was more than 8.0 mL, the production rate was invariable. Therefore, 8.0 mL was selected as the optimal dosage of carbon disulfide. Because carbon disulfide has a lower boiling point and volatilizes easily, vitalization is inevitable in procedures of dropping, moving, and reacting. The polymine could react sufficiently when the amount of carbon disulfide was excessive.

Effect of the reaction temperature on the production rate

Because carbon disulfide has a lower boiling point and volatilizes easily, the reaction temperature was controlled at a lower temperature. However, the reaction speed was slow when the temperature was too low. The system temperature increased because the reaction heat was released after sodium

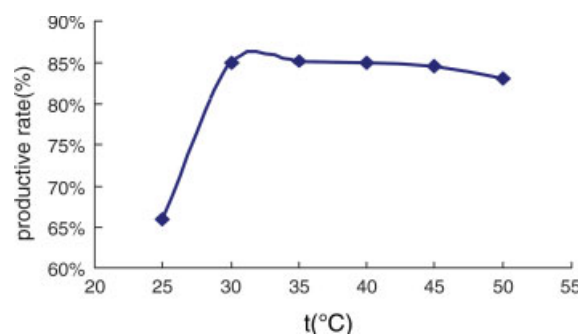


Figure 4 Effect of the reaction temperature on the production rate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

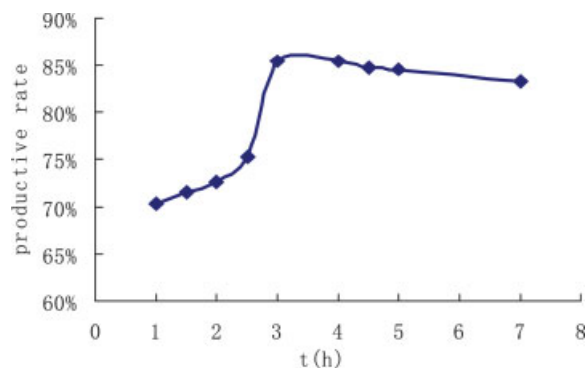


Figure 5 Effect of the reaction time on the production rate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

hydroxide dissolved, so the system had to be cooled before carbon disulfide was added.

When the other reaction variables were fixed, the effect of the reaction temperature on the production rate was studied. The research results are given in Figure 4. Figure 4 shows that when the reaction temperature was between 25 and 30°C, the production rate increased quickly. When the reaction temperature was higher than 30°C, the production rate fell because carbon disulfide volatilizes easily. Therefore, 30°C was selected as the optimal reaction temperature.

Effect of the reaction time on the production rate

When the other reaction variables were fixed, the effect of the reaction time on the production rate was studied. The research results are given in Figure 5. Figure 5 shows that the production rate evidently increased when the reaction time was within 3 h. When the reaction time was 3 h, the reaction had already been sufficient. However, the production rate fell after 3 h because of side reactions.

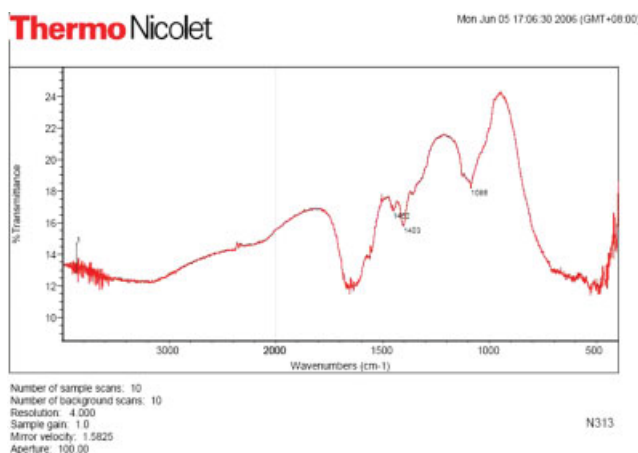


Figure 6 IR spectrogram of the polyimine. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Analysis of the IR Spectrogram of the Product

Absorption peak (cm^{-1})	Group
1452	N—C=S
1088	C=S

Therefore, 3 h was selected as the optimal reaction time.

Detection of the product structure

IR spectra

IR spectra of DMHMFs were recorded on a Magna-IR spectrometer (Thermo Nicolet Corporation Madison, WI, USA) in the range of 4000–500 cm^{-1} with KBr as the dispersant. The IR spectroscopy atlas is shown in Figure 6, and the characteristic absorption frequencies are listed in Table I. Characteristic bands of N—C=S and C=S appeared at about 1452 and 1088 cm^{-1} , respectively, confirming the presence of these main functional groups.

UV-vis spectra

UV-vis spectra of DMHMFs were recorded on a TU-1810 UV-vis spectrometer (GBC Scientific Instruments Inc., Germany) in the range of 200–1100 nm. Distilled water was used as the DMHMF solvent and also as a reference. The UV-vis spectroscopy atlas is shown in Figure 7, and the characteristic absorption frequencies are listed in Table II. The

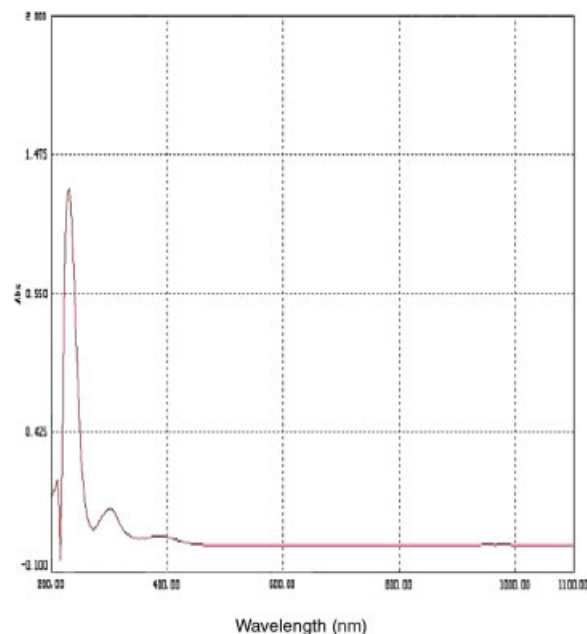


Figure 7 UV spectrogram of the polyimine. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Analysis of the UV Spectrogram of the Product

Absorption peak (nm)	Description
230	$\pi-\pi^*$ transition of N—C—S group
302	$n-\pi^*$ transition of CS ₂ group

atlas suggests that there were characteristic double-bond structures partly between carbon and nitrogen and between carbon and sulfur, and this confirmed that the main functional groups were present in the product.

Solubility detection of the product

The solubility of the product in some solvents was studied. The research results showed that the product was insoluble in acetone, carbon tetrachloride, and absolute ethyl alcohol but dissolved in water.

Heavy-metal-ion trapping and removal properties

Effect of the product dosage on the heavy-metal-ion removal rate

Heavy-metal-ion solutions (100 mg/L) and DMHMF solutions (0.0263 mg/L) were prepared. The effect of the DMHMF dosage on the heavy-metal-ion removal rate was studied in the dosage range of 0.5–5.0 mL. The research results are given in Figure 8. Figure 8 shows that the removal rate of copper(II) changed from a low value of 50.78% at 0.5 mL to its maximum of 86.09% at 3.0 mL. The lead(II) removal rate changed from a low value of 68.54% at 0.5 mL to a maximum of 97.59% at 1.5 mL. However, the removal rate of copper(II) or lead(II) decreased as the dosage increased from 4.0 to 5.0 mL or from 2.0 to 5.0 mL, respectively. The influence of the product dosage on the removal of heavy-metals can be explained on the basis of electrostatic repulsion. As the dosage of the product increased excessively, some xanthic acid groups of the product chelated

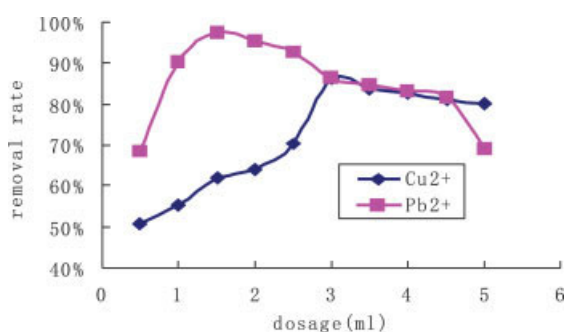


Figure 8 Effect of the product dosage on the heavy-metal-ion removal rate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

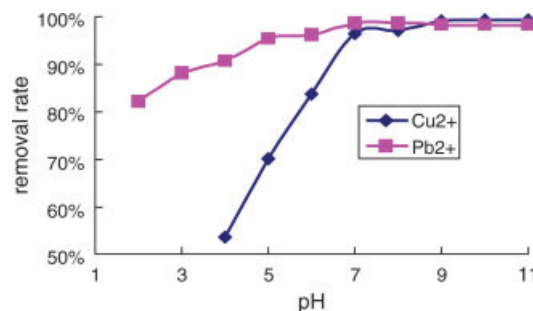


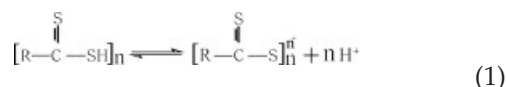
Figure 9 Effect of pH on the heavy-metal-ion removal rate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

with heavy-metal ions, but the excessive xanthic acid groups carried negative charges. There were electrostatic repulsions between these negative charges. The electrostatic repulsion between the chelate groups could result in compounds not precipitating completely. Therefore, the removal rate of heavy-metal ions decreased.

Effect of the pH on the heavy-metal-ion removal rate

Heavy-metal-ion solutions (100 mg/L) with different pHs and DMHMF solutions (0.0263 mg/L) were prepared. The effect of the pH on the heavy-metal-ion removal rate was studied in the pH range of 2.0–11.0. The research results are given in Figure 9. Figure 9 shows that the removal rate of copper(II) evidently increased when the pH changed from 4.0 to 7.0 and then stabilized when the pH increased from 7.0 to 11.0. When the pH was 7.0, the removal rate of copper(II) was up to its maximum value of 99.44%. It also can be seen that the removal rate of lead(II) increased as the pH increased from a low value of 82.18% at pH 2.0 to its maximum of 98.74% at pH 7.0. The removal rate of lead(II) was perfectly stable as the pH increased from 7.0 to 11.0. The product was a kind of organic macromolecule flocculant and had the ability to chelate the heavy-metal ions. The product proposed in this article carries some negative charges when it dissociates in water. The dissociation balance equation is shown in eq. (1). The concentration of the hydrogen ion decreases as the pH increases, and the balance equation moves to the right. Therefore, the chelating ability of xanthic acid for heavy-metal ions is strengthened as the xanthic acid ion concentration increases. As the solution pH increases, some hydroxides form because the heavy-metal ions hydrolyze. The removal rate increases because hydroxides can be flocculated by adsorption and bridging of the product. In contrast, the removal rate decreases if the pH falls. Most of the product dissociates when the pH is 7.0, and the dissociated xanthic acid ions are an

effective form for trapping the heavy-metal ions. The concentration of the effective form of xanthic acid ions does not increase as the pH increase. Therefore, the removal rate of heavy-metal ions does not change when the pH is above 7.0:



Floc precipitation

The experiments about floc precipitation were performed under the optimal pH and DMHMF dosage conditions. A heavy-metal-ion solution (100 mg/L) and DMHMF solution (0.0263 mg/L) were prepared. After the DMHMF solution was added to the heavy-metal-ion solution, the mixture was stirred for 2 min at 300 rpm and for 3 min at 100 rpm. The big flocs that appeared could precipitate in about 30 s, and the small ones took about 2 min. The results showed that the precipitation rate was very fast and that the treatment processes was simple because other flocculants did not need to be added. However, when sodium hydroxide or sodium sulfide was used as the precipitation agent to remove heavy-metal ions, the particles that formed were so minute that they could not precipitate. These very tiny particles could be precipitated only with the addition of another flocculant.

CONCLUSIONS

DMHMFs were synthesized under simple conditions, and the main synthesis conditions were studied. The structure of the DMHMFs synthesized in this study was detected and characterized with IR

and UV-vis spectra. The trapping and removal properties of the flocculating agent with respect to some heavy-metal ions were studied, and the experimental results showed that the flocculating agent had good trapping and removal properties with respect to some heavy-metal ions in a wide range of pHs. The removal rates of copper(II) and lead(II) were up to 99.44 and 98.74%, respectively. In comparison with traditional inorganic chemical precipitation agents, the formation and precipitation of flocs were quicker, and the dosage of the proposed trapping agents was lower. In addition, in the precipitation processes, other flocculants did not need to be added, so the treatment process was simple.

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