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Removal of micro complex copper in aqueous solution with a dithiocarbamate compound

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ABSTRACT

In this article, DTC-S, a kind of heavy metal capturing agent, was chosen to evaluate the removal effects of complex copper solutions. The complex copper was 5.0 mg/l. The Cu(II)-NH_3 was easily removed due to its similarity of free Cu^{2+} in aqueous solution, and the suitable conditions were initial pH 9.0, 20 mg/l DTC-S and one hour's precipitation. The Cu(II)-EDTA and Cu(II)-Cit were more stable due to their ligands. To reach the standard, the optimal dosage of DTC-S was doubled, and the initial pH was adjusted between 9.5–11.5. The removal rate slightly decreased when external metal ions existed in Cu(II)-EDTA solution. Infrared spectra and SEM micrographs showed the DTC-S was a dithiocarbamate compound, whose functional groups could chelate copper ions in copper complexations.

Keywords: Cu(II)-NH3; Cu(II)-EDTA; Cu(II)-Cit; Removal rate; Micro complex copper; Heavy metal capturing agent; DTC-S

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1. Introduction

The world is suffering from heavy metal wastewater that is hazardous to human being. The industrial activities such as mining, smelting and electroplating industries represent important pollutant sources. The removal of toxic heavy metals or decreasing their concentrations to permitted discharge levels is a serious problem facing numerous industries [1,2]. The specific gravities of heavy metals are greater than 5.0 and copper is one of these. Copper is an essential trace element for living things, but it is potentially toxic if its amount is in excess. Copper has been identified as a pollutant of concern by the U.S. Environmental Protection Agency (EPA) because of its widespread occurrence and toxic impact in the environment [3]. And for human copper will cause stomach upset and ulcer, mental retardance, liver and brain damage, and so on [4]. Copper has been used with capturing agents in the most case, such as ammonia (NH_3), ethylenediaminetetraacetic acid (EDTA), citric acid (Cit). For industrial uses, the copper ion is chelated by these capturing agents because it is more stable. The complex copper leave behind in the wastewater, which are Cu(II)-NH_3, Cu(II)-EDTA, Cu(II)-Cit respectively according to the different ligands.

The heavy metals are not biodegradable and tend to accumulate in living organisms [5]. The methods of heavy metal removal from wastewater have been performed by chemical precipitation, adsorption, cementation, electrolysis, ion exchange, membrane filtration,

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coagulation and flocculation, electrochemical treatment [4,6–8]. The chemical precipitation is regard as a most common method in industry practical application, which is to transform dissolve metal ions into insoluble compounds, including neutralizing precipitation and sulfide precipitation. However, the removal efficiency would not be noticeable when complex compounds exist or the metal concentration is low. Heavy metal capturing agents (HMCA) are developed as advanced chemical to remove heavy metal in aqueous solution because of the complex precipitation.

Matlock et al. designed and synthesized a new thiol-containing compound, which could effectively precipitate toxic metal such as iron in the leachate solution [9]. A new dithiocarbamate-type capturing agent, sodium 1,3,5-hexahydrotriazinedithiocarbamate, prepared by Fu et al. was used to remove complex copper from wastewater [10]. It could effectively precipitate copper to less than 0.5 mg/l from both synthetic and actual industrial wastewater containing Cu-EDTA in the range of pH 3–9. The group team also perform a coordination polymerization HMCA, N,N′-bis-(dithiocarboxy)piperazine to compared with a widely used HMCA diethyldithiocarbamate, through the treatment of three kinds of nickel-containing wastewaters [11]. Fu's group indicated the promising future of dithiocarbamate-type HMCA. Usually one of the materials, carbon bisulfide (CS_2), has a toxic effect on living things. Therefore, certain agricultural products were investigated to synthesize HMCA. Although these HMCA were less efficient, the process was more environmentally friendly. Chang et al. used two kinds of agricultural xanthates (IPX and ISX) to treat copper-containing wastewater to meet the Taiwan EPA's effluent standard (3 mg/l) [12]. Although agricultural xanthates were regarded as adsorption material, the heavy metal cheated by adsorbent partially.

Adsorption is now recognized as an effective method and is reported scores of times. Eren et al. tested to adsorb Cu(II) from aqueous solution by raw sepiolite, manganese oxide-coated sepiolite and base activated sepiolite samples [13]. The adsorption capacities of them were 5.55, 6.70 and 13.46 mg/g, respectively. Talhi et al. and Zhang et al. also treated copper with *Acacia raddiana*, and fungus *Flammulina velutipes* as their biosorbents [14,15]. Other methods were also reported to treat with the metal containing wastewater. Juang removed Cu-EDTA by membrane filtration [16].

This article mainly focuses on a capturing agent, named DTC-S, which was selected to investigate the removal of micro complex copper. Three sorts of complex copper, Cu(II)-NH_3, Cu(II)-EDTA and Cu(II)-Cit were chosen as target pollutants to evaluate the effects of DTC-S. The concentrations of copper were approximately 5 mg/l before treatment and were determinated by an atomic absorption spectrophotometer (AAS) afterwards. The means could obtain concentrations accurately before and after treatment to calculate the removal efficiencies [17,18].

2. Experiments and methods

2.1. Materials and reagents

Copper sulfate pentahydrate ($CuSO_4$ $5H_2O \geq 99\%$), Nitric acid (HNO_3, 65%–68%), Ferric chloride pentahydrate ($FeCl_3$ $6H_2O \geq 99\%$), and Calcium chloride ($CaCl_2 \geq 96\%$) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Ammonia solution (NH_3, 25%), trisodium citrate dihydrate ($C_6H_5Na_3O_7$ $2H_2O$, Cit-3Na ≥ 99.0%) and EDTA-2Na (99.0%) were all of analytical grade. DTC-S was selected and obtained from Xizhang Environmental Protection Medicament Company (Wuxi, Jiangsu, China), as well as Polyaluminium chloride (PAC) and Polyacrylamide (PAM). Deionized water was used to prepare all solutions in this study.

2.2. Preparation of Cu(II)-NH_3, Cu(II)-EDTA and Cu(II)-Cit

The preparation of Cu(II)-NH_3 solution with a copper content of 500 mg/l was approximately carried out as follows: 0.9766 g $CuSO_4$ $5H_2O$ was dissolved and NH_3 was added with stirring until the newly generated deposition dissolved again. The copper reaction in this solution was defined by Eq. (1), (2). Finally, the mixture was determined to 500 ml in a volumetric flask.

$$Cu^{2+} + nNH_3 \rightarrow Cu(NH_3)_n{}^{2+} \quad (1)$$

$$NH_3 + H_3O^+ \rightarrow NH_4{}^+ + H_2O \quad (2)$$

The Cu(II)-EDTA and Cu(II)-Cit solution was prepared in the same way. Equimolar $CuSO_4$ $5H_2O$ and ligand agent was measured, then dissolved in a flask and determined in a volume flask by distilled water to ensure the copper concentration was 500 mg/l approximately. All the solutions above were stocked at 4°C in the refrigerator.

2.3. Batch experimental procedures

Batch experiments were performed to evaluate the removal efficiency of copper complexation. 100 ml of diluted stock solution was diluted 100 times to get the copper concentration around 5.0 mg/l. The obtained solution was poured into a flask. The pH value was adjusted by H_2SO_4 or NaOH, and then the solution was stirred by a magnetic agitator at constant temperatures.

Firstly, certain DTC-S was added in the flask and stirred at 300 rpm for 20 min. After that, 0.25 ml PAM (3 mg/l) and PAC (1.5%, wt) solutions were added and the speed of stirring reduced to 60 rpm for 10 min. After an hour of precipitation time, the 30 ml supernatant fluid of the solution was shifted to another flask and acidified by HNO_3 to guarantee the low pH circumstance of the sample. All the samples were filtered through a 0.45 µm membrane filters before being analyzed.

2.4. Analytic methods

Copper concentrations were analyzed by an AAS using Shimadzu (Kyoto, Japan) AA6300 before and after the treatment to calculate the removal rates of complexation copper.

Infrared (IR) spectra were obtained in the range of 2000 to 400 cm^{-1}, using a Thermo Nicolet Nexus 670 FT-IR spectrometer (Madison, WI, USA). The sample was mixed with 20 times of KBr, then grinded and compressed into thin slices.

The SEM micrographs of samples were obtained with different amplified times, using a FEI (Eindhoven, The Netherlands) SIRION-100 Field Emission Scanning Electron Microscope (FSEM), after the gold sputtering treated.

3. Results and discussion

3.1. Effect of dosage of DTC-S

Different dosages of DTC-S were investigated to illustrate the relationship between the dosage and the removal rates of Cu(II)-NH_3, Cu(II)-EDTA and Cu(II)-Cit, and the results are shown in Fig. 1. The complex copper removal rate reached 95% when the dosage of DTC-S was 25 mg/l, 35 mg/l, 35 mg/l in Cu(II)-NH_3, Cu(II)-EDTA and Cu(II)-Cit solution, respectively. Compared with each curve, Cu(II)-NH_3 was easier to be removed, Cu(II)-Cit came next. The removal rates increased with the dosage. However, the complex copper could not be removed completely according to the data. The highest removal rate was about 97%. Because the removal rate not only depended on the dosage of DTC-S, but also the precipitate time. How the factor of precipitate time affected the results would be discussed in the chapter 3.3. Under this rate, the residential complex copper concentration was 0.15 mg/l, which had reached the newly published standard of 0.5 mg/l. To evaluate other factors, we chose 20 mg/l dosage of DTC-S to conduct further experiments on the three solutions.

The removal capacities for Cu(II)-NH_3, Cu(II)-EDTA and Cu(II)-Cit are respectively 190, 136 and 136 mg/g. Referred to prior researchers' work, the adsorption capacity for Cu is below 80 mg/g [19–22]. Therefore, in our experiment, the chemical effects were important and the adsorption effects did not exist or could be ignored even though the adsorption existed.

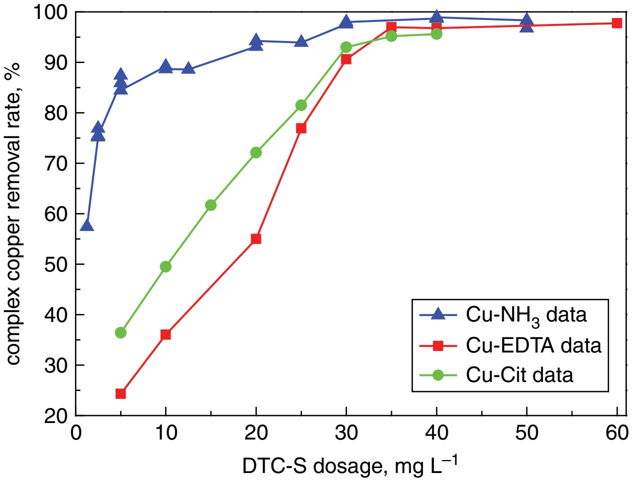


Fig. 1. Effect of DTC-S dosage on the complex copper removal rate, $T = 25°C$, $pH_{in} = 9.0$, $C_{Cu(II)} = 5.0$ mg/l.

3.2. Effect of initial pH

The effect of initial pH of the reaction solution was investigated over pH values ranging from 3.0–12.5. After 30 min reaction at the 30°C and 60 min of precipitation, the complex copper removal rates by 20 mg DTC-S in 100 ml aqueous solution are shown in Fig. 2. The fitting curve on Cu(II)-NH_3 indicated a sharp increase of the Cu(II)-NH_3 removal rate as the pH ranged from 5.5 to 8.0, and more Cu(II)-NH_3 were removed with the increasing of pH until it reached 10.8. Nevertheless, the removal rate decreased gradually when pH value was above 10.8. The pH value

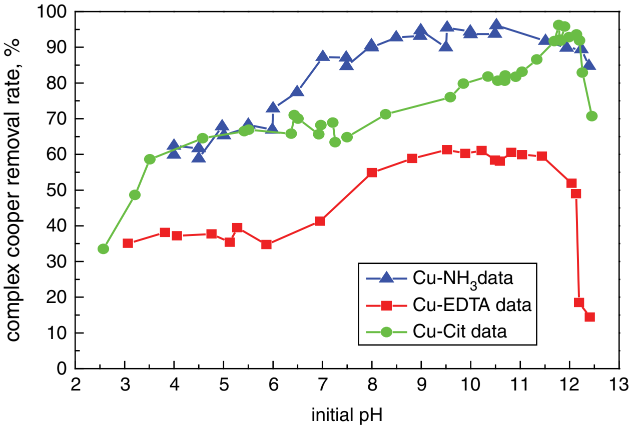


Fig. 2. Effect of initial pH on the complex copper removal rate, $T = 25°C$, $pH_{in} = 3.0–12.5$, $C_{Cu(II)} = 5.0$ mg/l.

Table 1
The stability constants of various species in Cu(II)-NH_3 system solution

Order	Species	Stability constant ($\lg\beta_n$)
1	$Cu(NH_3)^{2+}$	4.31
2	$Cu(NH_3)_2^{2+}$	7.98
3	$Cu(NH_3)_3^{2+}$	11.02
4	$Cu(NH_3)_4^{2+}$	13.32
5	$Cu(NH_3)_5^{2+}$	12.86

affected the reaction in two different ways. One was the constitution of the Cu(II)-NH_3 solution system; another was the property of DTC-S. The stability constants of various species in the Cu(II)-NH_3 system are shown in Table 1. The total copper (C_T) included $Cu(NH_3)^{2+}$, $Cu(NH_3)_2^{2+}$, $Cu(NH_3)_3^{2+}$, $Cu(NH_3)_4^{2+}$, $Cu(NH_3)_5^{2+}$ and Cu^{2+}. Therefore, the occupancies of species were as follows.

$$\alpha_{Cu^{2+}} = \frac{[Cu^{2+}]}{C_T} = (1 + \beta_1[NH_3] + \beta_2[NH_3]^2 + \beta_3[NH_3]^3 + \beta_4[NH_3]^4 + \beta_5[NH_3]^5)^{-1} \quad (3)$$

$$\alpha_{Cu(NH_3)^{2+}} = \frac{[Cu(NH_3)^{2+}]}{C_T} = (\frac{1}{\beta_1[NH_3]} + 1 + \frac{\beta_2}{\beta_1}[NH_3] + \frac{\beta_3}{\beta_1}[NH_3]^2 + \frac{\beta_4}{\beta_1}[NH_3]^3 + \frac{\beta_5}{\beta_1}[NH_3]^4)^{-1} \quad (4)$$

$$\alpha_{Cu(NH_3)_2^{2+}} = \frac{[Cu(NH_3)_2^{2+}]}{C_T} = (\frac{1}{\beta_2[NH_3]^2} + \frac{\beta_1}{\beta_2[NH_3]} + 1 + \frac{\beta_3}{\beta_2}[NH_3] + \frac{\beta_4}{\beta_2}[NH_3]^2 + \frac{\beta_5}{\beta_2}[NH_3]^3)^{-1} \quad (5)$$

$$\alpha_{Cu(NH_3)_3^{2+}} = \frac{[Cu(NH_3)_3^{2+}]}{C_T} = (\frac{1}{\beta_3[NH_3]^3} + \frac{\beta_1}{\beta_3[NH_3]^2} + \frac{\beta_2}{\beta_3[NH_3]} + 1 + \frac{\beta_4}{\beta_3}[NH_3] + \frac{\beta_5}{\beta_3}[NH_3]^2)^{-1} \quad (6)$$

$$\alpha_{Cu(NH_3)_4^{2+}} = \frac{[Cu(NH_3)_4^{2+}]}{C_T} = (\frac{1}{\beta_4[NH_3]^4} + \frac{\beta_1}{\beta_4[NH_3]^3} + 1 + \frac{\beta_2}{\beta_4[NH_3]^2} + \frac{\beta_3}{\beta_4[NH_3]} + 1 + \frac{\beta_5}{\beta_4}[NH_3])^{-1} \quad (7)$$

$$\alpha_{Cu(NH_3)_5^{2+}} = \frac{[Cu(NH_3)_5^{2+}]}{C_T} = (\frac{1}{\beta_5[NH_3]^5} + \frac{\beta_1}{\beta_5[NH_3]^4} + \frac{\beta_2}{\beta_5[NH_3]^3} + \frac{\beta_3}{\beta_5[NH_3]^2} + \frac{\beta_4}{\beta_5[NH_3]} + 1)^{-1} \quad (8)$$

where $[NH_3]$ is the concentration of free ammonia in the Cu(II)-NH_3 solution system. The species distribution diagram was obtained by the equations above (from 3 to 8), and shown in Fig. 3. The weak base ammonia would be replaced easily when pH was high. When the pH value was adjusted, OH^- was introduced and free NH_3 increased to keep the hydrolytic equilibrium of $NH_3 H_2O$. The total quantity of ammonia was constant. Therefore, the part of ammonia chelated with Cu^{2+} decreased, and the complex copper was removed more efficient. In fact, the curve fit the analysis when pH was not high. When pH was over 10.8, the rates declined slowly. Here, perhaps the high pH affected the structure of DTC-S, which was closely linked with removal efficiency.

The fitting curve of Cu(II)-EDTA which was different with the first one, also implied that the pH played an important role. Under acidic environment, the removal rate was less than 40%, and increased with pH value not significantly. The removal rate did not increase markedly until the initial pH reached 7.0. The trend of complex copper removal was similar with Cu(II)-NH_3 system. When pH exceeds 12.0, the rate drastically

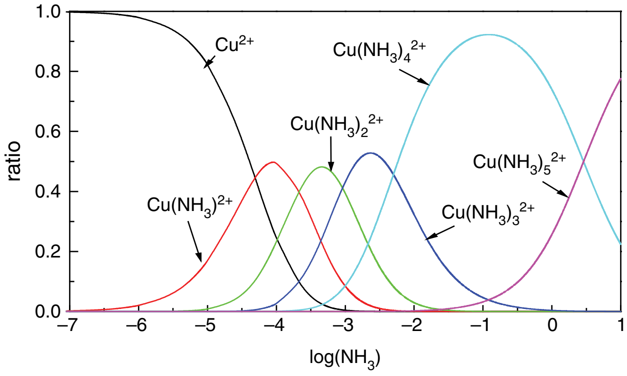


Fig. 3. Distribution diagram for Cu(II)-NH_3 system.

dropped, even below 15%. The unusual characteristic of EDTA solution could be used to explain this drastic reduction. There were four carboxylic groups and two nitrogen atoms in EDTA structure. Each nitrogen atom had a pair of electrons, and could be the coordination atom, as well as the oxygen atoms in carboxylic groups. The EDTA was normally a hexadentate ligand, also was a hexahydric Lewis acid. The dissociation about the equilibrium were as follows.

$$H_6Y^{2+} \leftrightarrow H_5Y^{+} \leftrightarrow H_4Y \leftrightarrow H_3Y^{-} \leftrightarrow H_2Y^{2-} \leftrightarrow HY^{3-} \leftrightarrow Y^{4-} \tag{9}$$

With the increasing of the pH value, EDTA ionized H^+ gradually until pH reached 12.0. All the EDTA species became Y^{4-}, which was also named hexahydric Lewis base. Y^{4-}, the hexadentate ligand, was the strongest ligand among all the EDTA species. It firmly combined with copper ion one by one leading to extremely low removal rates.

The fitting curve on Cu(II)-Cit was even unordinary. When pH equaled 11.8, the removal rate achieved highest, appropriately 95%. The removal rate decreased when the pH value was greater than or less than that point. A dramatic decrease of rate after pH over 12 was also observed in the Cu(II)-Cit solution, compared with the Cu(II)-EDTA.

The citric acid was an organic acid, with three carboxyl Groups and one hydroxyl. Carboxylic oxygen atoms and one hydroxyl oxygen atom could theoretically chelated with the copper ion. However, because of the steric hindrance effect, only three of the four could chelate an ion simultaneously to form a five-numbered or six-numbered ring. The citric acid was similar with EDTA, a polybasic acid, which ionized H^+ gradually with the increase of pH value. Consequently, the trend of curve appeared similar with each other. The stability constant of Cu(II)-EDTA was $10^{18.7}$ while that of Cu(II)-Cit was $10^{13.0}$ at pH = 12. That's why the removal rate of Cu(II)-Cit was higher than that of Cu(II)-EDTA.

According to the three curves we obtained, we considered the pH value was important to the DTC-S property, which was relative with the copper complex removal rates. The differences between the three curves in Fig. 2 implied the properties of three chelating agents. EDTA was much more stable, no matter how the species changed. We chose pH 9.0 for Cu(II)-NH_3 and Cu(II)-EDTA wastewater, while pH 10.0 for Cu(II)-Cit wastewater in batch experiments thereafter.

3.3. Effect of precipitation time and temperature

After 20 min of strong stirring of 20 mg/l dosage of DTC-S and 10 min of slight stirring of PAC and PAM at 30°C, the effects of different precipitation times were explored. The figures are shown in Table 2. The longer the precipitation time, the higher the removal rate is. It can be easily explained by the fact that the gravity sedimentation depends on the precipitation time. During the strong stirring step, the Cu(II)-NH_3 species or other complex copper species was chelated by DTC-S to form particulates, and then these particulates flocculated into much bigger particulates that could precipitate by gravity automatically. If the precipitation time was long enough, the copper containing particulates would sink at the bottom of the flask, so the highest removal rate can be expected. Table 2 implied that the highest removal rate could reach 95% approximately, and the complex copper removal rate increased quickly within 30 min. After 1 h, the rate almost kept constant. It indicated that the 60 min precipitation time was enough for this experiment and for engineering practice.

Table 2 also illustrated the complex copper removal rate as a function of temperature. The results were achieved under the initial pH value of 9.0 (Cu(II)-NH_3 solution) and 10.0 (Cu(II)-Cit solution) and precipitation time of 60 min. Two different solutions implied the removal rate increased slightly as the temperature rose. High temperature could accelerate the rate of the chelating reaction. However,

Table 2
The complex copper removal rate in different reaction conditions

Reaction conditions		Complex copper removal rate, %
Precipitation time Cu(II)-NH_3	180 min	94.5
	150 min	94.4
	120 min	93.8
	90 min	93.5
	60 min	93.4
	30 min	91.6
Temperature Cu(II)-NH_3/Cu(II)-Cit	20°C	89.9/73.1
	25°C	91.5/69.9
	30°C	90.4/70.1
	35°C	92.1/71.1
	40°C	94.5/70.7
	45°C	93.2/71.3
	50°C	93.9/72.3
EDTA-copper ratio Cu(II)-EDTA	4.0	59.26
	2.0	58.39
	1.0	60.49
	0.75	56.64
	0.5	59.27
	0.25	83.15

20 min stirring may already reach equilibrium. Consequently, the temperature did not affect the removal rates much. There was no need to adjust the temperature of wastewater in the engineering practice.

3.4. Effect of the molar ratio of EDTA to copper

EDTA is an efficient capturing agent. The stability constant of Cu(II)-EDTA is $10^{18.7}$. One mole copper could be just chelated by one mole EDTA absolutely. In this experiment, a series ratio of EDTA to copper was carried out, with the fixed condition of 20 mg/l dosage of DTC-S, initial pH 9.0, surrounding temperature 30°C, and the results are shown in Table 2.

When the mole ratio was over 0.5, the removal rate kept constant about 60%. However, when the ratio equaled 0.25, the removal efficiency achieved highes. We supposed that if an EDTA molecule combined with a Cu^{2+} ion, the exceed Cu^{2+} ions were active, and could be chelated by the EDTA that had already combined with Cu^{2+} ion. If an EDTA molecule combined with two or more Cu^{2+} ions, although the newly formed structure was large, it was not stable enough and could be easily destroyed. The Fig. 4 shows the conjecture of the complex compounds. Fig. 4 (a) describes the Cu^{2+} ion chelated by EDTA one by one, while the Fig. 4 (b) and (c) are two and three Cu^{2+} ions chelated by one EDTA molecule, respectively. In the solution system, the more EDTA contained, the less removal rate achieved.

3.5. Effect of external heavy metal ions

To investigate how the external heavy metal ions' affect removal rate, Fe^{3+} and Ca^{2+} was added to the reaction solutions. In the experiment, Cu(II)-EDTA solutions were prepared, whose copper concentration was 5.0 mg/l. Equimolar Fe^{3+} and Ca^{2+} were added into in it. All experiments were carried out at 30°C, with different dosages of DTC-S, and the results are shown in Fig. 5.

Obviously, when DTC-S is over 10 mg/l the solution only contained Cu ions achieved the highest removal rate, that is to say, the external metal ions played negative roles during the reaction process. Compared with mole ratio of Ca:Cu = 1:1 and Fe:Cu = 1:1, 35 mg/l dosage of DTC-S was a demarcation point. The curve added Ca^{2+} was better than the one added Fe^{3+} when the dosage was more than 35 mg/l. The situation was opposite while the dosage was less than 35 mg/l. Besides, we noticed that the presence of Fe^{3+} ion showed a slight promotional effect when DTC-S dosage was less than 10 mg/l.

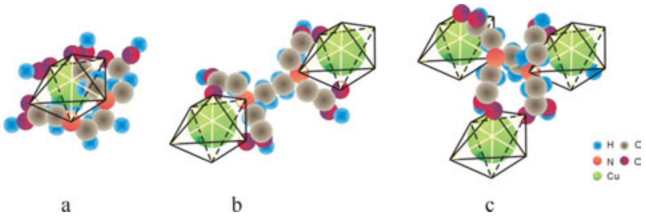


Fig. 4. The imaginary structural formulas of one EDTA molecule chelated one copper ion(a), two copper ions(b) and three copper ions(c).

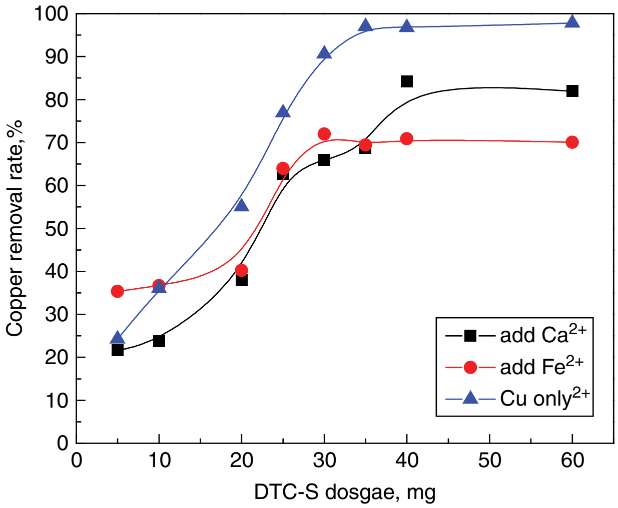


Fig. 5. The Cu(II)-EDTA removal rate when the Fe^{3+}, Ca^{2+} existed, $T = 30°C$, $pH_{in} = 9.0$, $C_{Cu(II)} = 5$ mg/l, $C_{EDTA} = 2.91$ mg/l (mole ratio of EDTA:Cu = 1:1).

EDTA may chelate the external metal ions. Therefore, less copper was expected to combine with EDTA. It was positive to the removal of copper by DTC-S. The stability constants of Cu(II)-EDTA was larger than Ca(II)-EDTA's and smaller than Fe(III)-EDTA's. According to the hypothesis, adding Fe^{3+} should enhance the removal efficiency more than adding Ca^{2+}. However, this was verified only when DTC-S dosage was below 10 mg/l. Meanwhile, the external metal ions could contest for DTC-S with original ion. This competition could reduce the removal of Cu because of the less impactful dosage of DTC-S. The extra ions not only compete for EDTA but for DTC-S. Whether the extra ions played a negative or positive role depend on the overall result. On the other hand, with the introduction of external metal, the simple Cu(II)-EDTA system was disarranged, some more complicated structure formed to affect the efficiency of DTC-S. For example, a copper atom and a ferric atom may be chelated together by one EDTA molecule at the same time. These special species may be difficult to be removed due to their complicated structures.

3.6. IR and SEM analysis

Fig. 6(a), (b), (c) and (d) show the IR spectra of DTC-S, the sediment of DTC-S reacted with Cu(II)-NH_3, Cu(II)-EDTA and Cu(II)-Cit system, respectively, in the range of 2000 to 400 cm^{-1}.

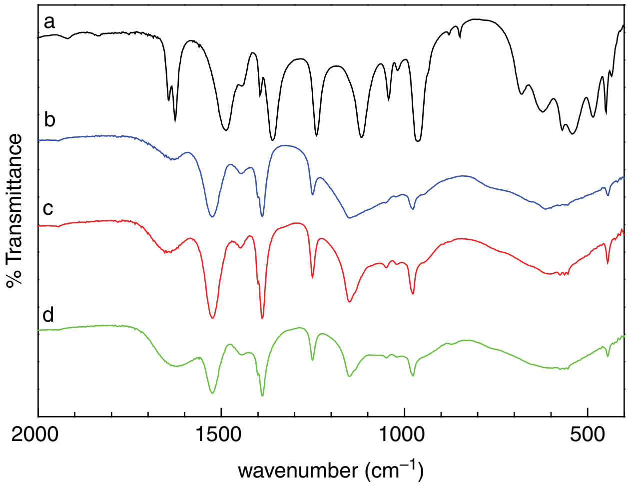
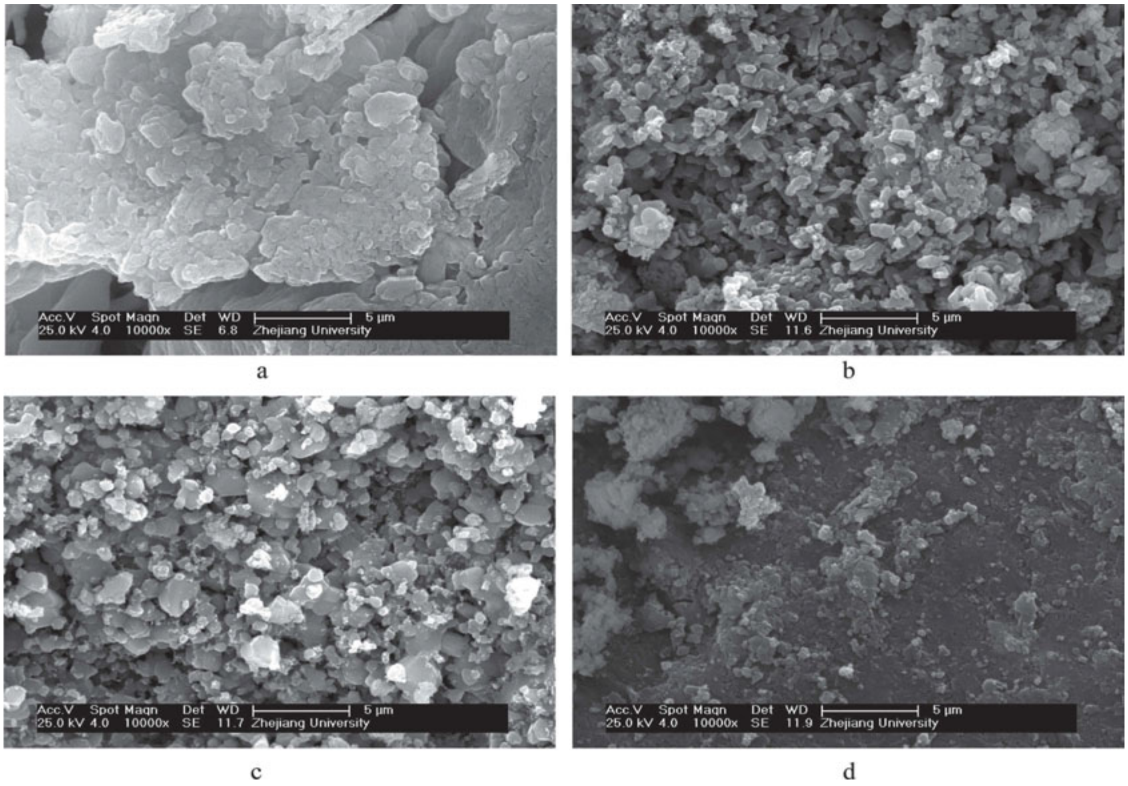


Fig. 6. IR spectra of DTC-S (a), the sediment of DTC-S reacted with Cu(II)-NH_3 (b), Cu(II)-EDTA(c) and Cu(II)-Cit(d) respectively.

The spectra seemed nearly the same with each other except Fig. 6 (a). In the spectra (a), the peak at 1487 cm^{-1} was assigned to C-N stretching vibration [23,24]. The peak shifted to 1520 cm^{-1} in the other three curves, which may be caused by chelating reaction. According to Gao and Lima's work, a C–S band was reported in the region 962–989 cm^{-1} and 980–1000 cm^{-1} [23,25]. In the Fig. 6, there was a stronger band at 965 cm^{-1} in curve (a) than the three peaks nearby in curves (b) (c) (d). The adsorption band near 1100 cm^{-1} (1117 cm^{-1}) was caused by the stretching vibrations of the C = S in S–CS– structure [26]. The peaks disappeared near 1117 cm^{-1} after reaction. Therefore, DTC-S was a dithiocarbamate compound, and sulphur atoms were active groups to chelate copper ions. The peaks at 1620 cm^{-1} in all curves were relevant to the presence of water [27].

As the analysis above, we drew the conclusions as follows: The chelating position occurred in the C = S, C-S primarily. That was why CS_2 was indispensable in HMCA synthesis. The three sediments were nearly the same, and composed of DTC-S and copper, without any NH_3 or EDTA or Cit molecule. In other words, the capturing agents was taken off completely and finally taken place by DTC-S, though there may exist some intermediate steps.

Fig. 7 (a), (b), (c), (d) are the SEM photographs of the four samples, DTC-S, the sediment of DTC-S reacted with Cu(II)-NH_3, Cu(II)-EDTA and Cu(II)-Cit system, respectively. Fig. 7 (b), (c), (d) are under the same amplification. DTC-S particles had stuck together while the others' were granular. Compared with (b), (c), (d), sediment (b) had shorter diameter. Sediment (d) was



a b

c d

Fig. 7. SEM micrographs of DTC-S (a), the sediment of DTC-S reacted with Cu(II)-NH_3 (b), Cu(II)-EDTA(c) and Cu(II)-Cit(d) respectively.

quite different from the prior two. Although the three sediments shared the same IR spectra, the SEM photographs of which were totally different. The most reasonable explanation to this phenomenon was the different amount of copper in different sediments. When we dealt with Cu(II)-NH_3 solution, complex copper was removed more than other two solutions. Different copper quantities left behind in the sediment resulted in different SEM photographs that could not be detected by FTIR.

4. Conclusions

The capturing agent DTC-S was selected to investigate its micro copper complexation removal effects. The initial pH, external heavy metal ions and the ratio of copper to capturing agent were important factors for complex copper precipitation.

1. The Cu(II)-NH_3 solution achieved higher removal rate than Cu(II)-EDTA or Cu(II)-Cit system. The suitable condition for Cu(II)-NH_3 was as follows: 20 mg/l DTC-S, at 25°C, with 1 h precipitation and initial pH 9.0.
2. The optimal conditions of Cu(II)-EDTA removal are 35 mg/l DTC-S, initial pH 9.5–11.5, mole ratio of EDTA:Cu≤1:1 and without external heavy metal ions.
3. The best condition for Cu(II)-Cit removal are: 35 mg/l DTC-S, initial pH 11.5–11.8.
4. DTC-S was a dithiocarbamate compound, an effective kind of HMAC. The functional groups of C=S and C-S chelating the copper lead to the peaks change in IR spectra.

However, the existence of external heavy metal negatively affects the removal rates by creating competitions between Cu and irons for the sites of DTC-S. The temperature, another factor, did not affect the removal efficiency. In general, using DTC-S to remove micro copper complex could reach the discharge standard providing the suitable conditions. Few papers reported the removal of micro heavy metal. Further study should be conducted to find out the mechanism of the removal process and find out the more effective means using less DTC-S dosage.

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