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Study on the flocculating properties of quaternized carboxymethyl chitosan

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Summary

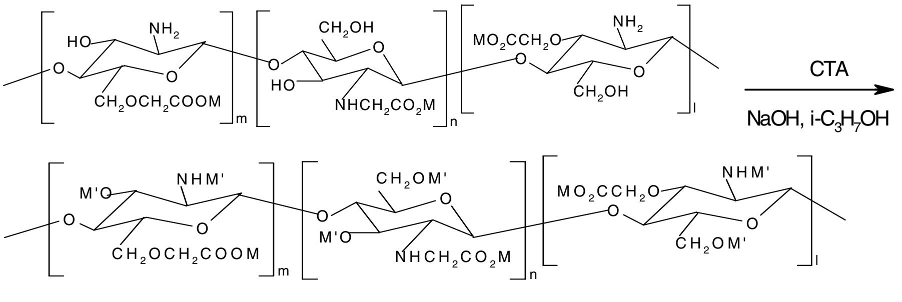
Quaternized carboxymethyl chitosan (QCMC) was prepared through the grafting reaction of carboxymethyl chitosan (CMC) with 3-chloro-2-hydroxypropyl trimethylammonium chloride (CTA) as a quaternizing agent in 2-propanol medium under basic condition. The synthetic conditions for QCMC were as follows: 40.0% of NaOH aqueous solution as catalyst; reaction temperature, 60.0°C and reaction time, 10.0 h; NaOH/CMC, 0.50; CTA/CMC, 1.50 (mass ratio). The characterization by FT-IR and ^{1}H NMR demonstrated that QCMC was a typical amphoteric chitosan derivative in which the carboxymethyl group and the quaternary ammonium group were both introduced into the chitosan molecular chain. QCMC was applied to flocculate a simulated wastewater containing 40.15mg/L Cd(II) or 15.62mg/L Cr(VI) respectively. The results indicated that the appropriate pH value for removal of Cd(II) and Cr(VI) were *ca* 8.5 and 5.0, and the appropriate corresponding mass concentrations of QCMC was 140*mg/L* and 120.0*mg/L*, respectively. Under these conditions, the removal ratio of Cd(II) and Cr(VI) may reach *99.7%* and *94.4%*, respectively.

Introduction

Chitosan(CTS), the most abundant natural amino polysaccharide, is produced by the deacetylation of chitin, which is one of the key constituents of the shells of crustaceans and is a by-product of the fishing industry[1,2]. Chitosan is a natural nontoxic biopolymer consisting of β-(1,4)-2-acetamido-2-deoxy-D-glucose and β-(1,4)-2-amino-2-deoxy-D-glucose units[3,4]. Chitosan is of commercial interest due to its high percentage of nitrogen compared with synthetically substituted cellulose[1]. This makes chitosan could be regarded as a useful chelating agent[5]. As most of the present-day polymers are synthetic materials, their biocompatibility and biodegradability are much more limited than those of natural polymers such as cellulose, chitin, chitosan and their derivatives[1]. In this respect, chitosan is recommended as suitable functional materials, because this natural polymer has excellent properties such as biocompatibility, biodegradability, non-toxicity, adsorption properties, etc[6-8]. However, chitosan also has its defect. It can not be dissolved in aqueous solution when pH is higher than 6.0, this has brought some negative influences on its application, such as flocculation property and improving viscosity etc[9]. In order to overcome this disadvantage, some methods, such as carboxymethylation, sulfating modification and hydroxyethylation etc, have been applied for chitosan[10-14].

Carboxymethyl chitosan (CMC) is a chitosan derivative obtained by the carboxymethylation of chitosan. CMC has three types: O-Carboxymethyl chitosan, N-Carboxymethyl chitosan and N,O-Carboxymethyl chitosan[1,14]. Compared with chitosan, the solubility of CMC in aqueous solution is improved remarkably because of the introduction of carboxymethyl group. Hjerde reported that the CMC could be dissolved in acidic, neutral or basic aqueous solution when the substituting degree of carboxymethylation for chitosan is more than 0.60[15]. The existence of carboxymethyl group ($-CH_2COOH$) in the molecular structure conferred the CMC with better properties in becoming membrane, increasing viscosity, improving retentive moisture, flocculating properties and chelating properties. For these reasons, CMC has found itself more important and extensive applications in many other fields, such as industry, agriculture, biochemical industry, medicine and health, etc [1,16]. As to the flocculating of some toxic metal ions, CMC still has some defects. For example, the chelating ability of CMC to Cr(VI) and some negative colloidal particles or ions is not high enough, which impedes its application in flocculating. The reason for these defects is that CMC is the derivative of chitosan only through the modification of carboxymethylation, which would lead to the increasing of negative electricity for chitosan but no obvious influence on its positive electricity.

Quaternary modification is usually regarded as an efficient way to improve positive electricity, and many methods have been reported for the quaternary modification of chitosan [17-19]. There exist some reactive H atoms in the molecular structure of CMC and chitosan, which make it possible to prepare quaternized carboxymethyl chitosan (QCMC) that carboxymethyl and quaternary ammonium group may be simultaneously introduced into the chitosan molecule chain. We herein report a method for the quaternary modification of CMC with 3-chloro-2-hydroxypropyl trimethylammonium chloride (CTA) as grafting agent (Scheme 1). The flocculating properties of the quaternary CMC for Cr(VI) and Cd(II) were studied in detail.



Scheme 1 Synthesis of quaternized carboxymethyl chitosan (QCMC), M=H or Na or Negative ion; M′=H or $-CH_2CH(OH)CH_2N^+(CH_3)_3Cl^-$

Experimental

Materials

Chitosan was purchased from Shanghai Lanji Sci.-Tech. Lt. Co. and its degree of deacetylation was determined to be 91.4% by potentiometric titration or 93% by ^{1}H NMR. The viscosity molecular weight (Mv) of chitosan is 2.96×10^5. CMC-1 and CMC-2 were prepared in our laboratories as described elsewhere[20-23]. The substitution degree of carboxymethylation for CMC-1 and CMC-2 were 85.6 % (N-substitution, 29.4%; O-substitution, 56.2%) and 67.1% (N-substitution, 21.3%; O-substitution, 45.8%) determined by elemental analysis and ^{1}H NMR, respectively. Their molecular weight (Mw) was determined by GPC analysis to be 2.48×10^5 and 2.51×10^5, respectively. The aqueous solution of 3-chloro-2-hydroxylpropyl trimethyl ammonium chloride (CTA) was prepared in our laboratory as described elsewhere [24-26]. The mass concentration of the obtained CTA was measured by potential titration to be 497g/L. Sodium hydroxide was purchased from the third factory of chemical reagent in Tianjin, excellent grade. All other chemicals were of reagent grade and were used without purification as received.

Quaternization of CMC with CTA as modifying agents

Dried CMC-1 or CMC-2 (8.0g) was weighted accurately and added into a four-neck bottle. Then, 75.0 mL of 2-propanol and 10g of NaOH aqueous solution (mass concentration, 40.0%) were added. The mixture was heated to 45.0°C in water bath under stirring and alkalized for 1.0 h until the solution became a thick liquid material. CTA (24.0 mL) was added into the bottle dropwise in case the temperature was higher than 60.0°C. When the CTA was added completely, the temperature was elevated to 60.0°C and the reaction was stayed at this temperature for 10.0 h under stirring. Then the pH value of the solution was adjusted to *ca* 7.0 with HCl solution (mass concentration, 10.0%) and filtered. The resultant dreg was washed by 60.0 mL CH_3OH aqueous solution (mass concentration, 85.0%) for three times, then by 50.0 mL ethanol for three times and filtered. The solid was dried below 80°C by infrared drier until its mass quantity was constant. Then the product-QCMC-1 or QCMC-2 that resulted from the quaternization of CMC-1 or CMC-2 with CTA as grafting agent was obtained respectively. They were put into vacuum drier for use later.

Study on the flocculating properties of QCMC to Cd(II)

0.506 g of QCMC-1 was dissolved in 99.5 mL of distilled water, giving rise to an aqueous solution of QCMC-1 with mass concentration of 5.062 g/L. 900 mL of simulated waste water containing 40.15 mg/L Cd(II) was divided equally into nine conical bottles. An appropriate aliquot of QCMC-1 solution was added into every bottle. The pH value of wastewater in each conical bottle was adjusted to 3.0, 4.0, 5.0, 6.0, 7.0, 7.5, 8.0, 8.5 and 9.0 with 0.100 mol/L HCl or NaOH aqueous solution, respectively. Then, the bottles were put into an oscillator (SHZ-type, Jingcheng Guosheng experimental instrument factory in Jintian) and shook for 30 min. After staying for 5.0 h, some of the upper liquid was taken out and the mass concentration of Cd(II) was determined according to literature [27]. The removal ratio of Cd(II) by QCMC-1 was determined by the change of its quantity in wastewater as follows.

$$Cd^{2+} \text{ removal ratio\%} = (C_0V_0 - C_1V_1)/C_0V_0 \times 100 \qquad (\mathbf{1})$$

Where C_0 and C_1 were the mass concentration of Cd(II) in wastewater before and after processing; V_0 and V_1 were the volume of the wastewater before and after processing, respectively.

Study on the properties of QCMC to flocculate Cr(VI)

To each of the nine conical bottles was added 100 mL of the simulated wastewater containing 15.62 mg/L of Cr(VI) (mass concentration), respectively. Then, the calculated QCMC-1 solution was added and the pH value of the solution in each bottle was adjusted to 2.0, 3.0, 4.0, 4.5, 5.0, 5.5, 6.0, 7.0 and 8.0 with 0.100 mol/L of HCl or NaOH solution, respectively. The bottles were shook and stayed according to the method presented above. Some of the upper liquid was taken out and the mass concentration of Cr(VI) in wastewater was determined by the reported method [28]. The removal ratio of Cr(VI) by QCMC-1 was determined by the equation as follows.

$$Cr(VI) \text{ removal ratio\%} = (C_0'V_0' - C_1'V_1')/C_0'V_0' \times 100 \qquad (\mathbf{2})$$

Where C_0' and C_1' were the mass concentration of Cr(VI) in wastewater, and V_0' and V_1' were the volume of wastewater before and after processing, respectively.
The studies on the flocculating properties of QCMC-2, CMC-1 and CMC-2 to Cd(II) and Cr(VI) were similar to that of QCMC-1.

Infrared spectrum

Fourier transform infrared (FT-IR) spectra were recorded with KBr pellets on a Nicolet Nexux FT-IR 670 spectrometer. Sixteen scans at a resolution of 4 cm^{-1} were averaged and referenced against air.

^1H NMR spectrum

^1H NMR spectra were obtained with Bruker DRX-500 spectrometer that equipped with a tri-nuclei inverse probe with a Z gradient at 500.13 MHz at 25°C ± 0.5°C. All the ^1H NMR spectra were measured in D_2O solution and the sample was dissolved in a 5 mm diameter tube at a concentration of about 20 mg/mL.

Results and Discussion

Identification of resonance in the spectra

The FT-IR spectra of CTS, CMC-1 and QCMC-1 were presented in **Fig. 1**. The absorption bands at 1655.32, 1594.87, 1323, 1381 cm^{-1} in the spectrum of CTS was assigned to primary, secondary and tertiary amides, and $-CH_3$ bend vibration. Both characteristic peaks for CTS at 3359 and 1070.32 cm^{-1} could be attributed to the O-H and C-O vibration, respectively [29]. Two strong peaks at 1592.94 and 1413.59 cm^{-1} in CMC-1 spectrum and 1592.89 and 1405.83 cm^{-1} in QCMC-1 spectrum were

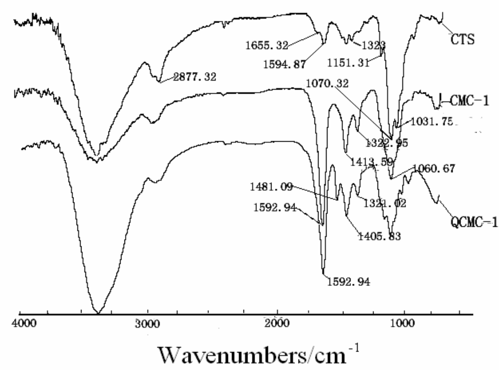


Fig. 1 FT-IR spectra of CTS, CMC-1 and QCMC-1

ascribed to the asymmetrical and symmetrical stretching of $-COO^-$ group[30]. In the spectrum of CMC-1, the C-O stretching band at 1031.75 cm^{-1} corresponding to the primary hydroxyl group of CTS disappears, which confirmed a high carboxymethylation of OH-6. The characteristic peak of second hydroxyl group at 1070.32 cm^{-1} of chitosan had shifted to 1060.67 cm^{-1} for CMC-1. In contrast, a new peak appears at 1481.09 cm^{-1} for QCMC-1, which indicated that the methyl of the quaternary ammonium group has been introduced into CMC-1[31-32].

The 500MHz ^{1}H NMR spectra of CMC-1 and QCMC-1 were shown in **Fig. 2** and **Fig. 3**. The resonance of 6-substituted and 3-substituted carboxymethyl-protons ($-OCH_2COOD$) in chitosan appeared in the spectral region of 4.2-4.6x10^{-6} and 4.6-4.7x10^{-6}, respectively[15]. The resonance of 2-substituted carboxymethyl-protons ($-NCH_2COOD$) of chitosan occurred in the spectral region of 3.2-3.4x10^{-6}[15,33]. Compared with CMC-1, these resonances also occurred in the ^{1}H NMR spectrum of QCMC-1. There were some new resonances for QCMC-1. A stronger resonance appeared in 3.2049x10^{-6}, which could be attributed to the methyl-protons of quaternary ammonium group. Three new resonances appeared in the 2.7628x10^{-6}, 4.2927x10^{-6}, 3.3023x10^{-6}, which could be attributed to the C_1, C_2 and C_3 protons of quaternary ammonium group introduced into CMC-1.

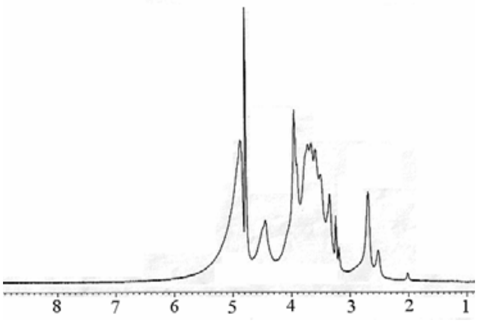


Fig. 2 ^{1}HNMR spectrum of CMC-1

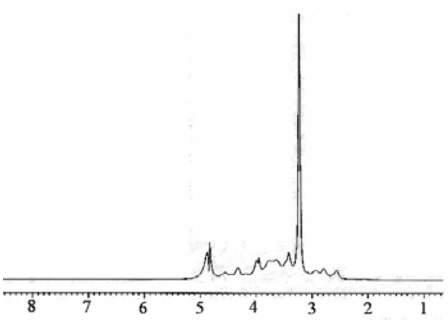


Fig. 3 ^{1}HNMR spectrum of QCMC-1

Properties of QCMC to flocculate Cd(II)

The influence of pH of wastewater on the properties of QCMC-1 to flocculate Cd(II) was shown in **Fig. 4**. The removal ratio of Cd(II) by QCMC-1 increased rapidly with the increase of pH at the beginning. When the pH value is up to 8.5, the removal ratio of Cd(II) reached the maximum (*ca* 99%) and thereafter high pH did not favor flocculation of Cd(II). The reason for this tendency may be due to the existence of different form of QCMC-1 at different pH. In acidic solution, the carboxyl in the QCMC-1 molecular chain existed in the form of -COOH, and thus the ability of QCMC-1 to remove Cd(II) mainly depended on the ability of -COOH, -OH, $-NH_2$ and -NH- to combine Cd(II). When the pH value is higher, the carboxyl existed in the form of $-COO^-$, which exerted a stronger electronic-static attraction for Cd(II). Accordingly, QCMC-1 showed a higher removal of Cd(II) under alkalescent condition. But when the pH value is much higher, the removal ratio of Cd(II) by QCMC-1 decreased. The reason that result in this trend was concerned with the Cd(II) in strong basic condition is transferred readily to $Cd(OH)_2$, which is unfavorable for QCMC-1 to combine. Furthermore, the excessive OH^- would facilitate Cd(II) to form hydration complex, which is also unfavorable for QCMC-1 to remove Cd(II).

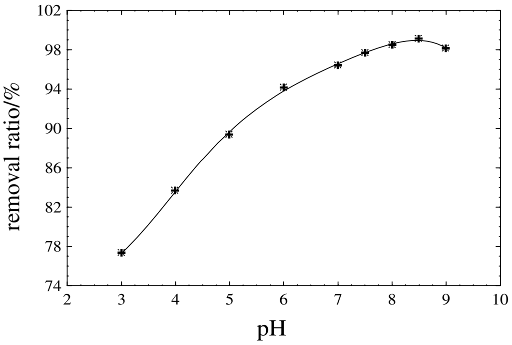


Fig. 4 Relationship between the removal ratio of Cd(II) by QCMC-1 and pH. Wastewater, 100 mL; QCMC-1 aqueous solution, 2.5 mL; flocculating temperature, 20°C.

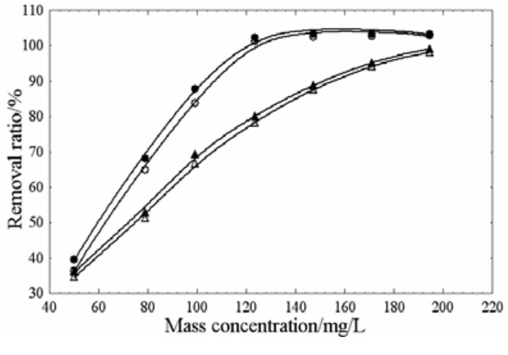


Fig. 5 The influence of the mass concentration of QCMC and CMC on their ability to flocculate Cd(II). Wastewater pH, 8.0; flocculating temperature 20°C; ○- QCMC-1, ●- CMC-1, △- QCMC-2, ▲- CMC-2.

The influence of the mass concentration of chitosan derivatives on their ability to flocculate Cd(II) were showed in **Fig. 5** and the corresponding curves fitted the Langmuir curve well. The results indicated that the removal ratio of Cd(II) by QCMC and CMC increased quickly with the increase of their mass concentration at the beginning. When the mass concentration of QCMC-1 and CMC-1 in the wastewater is about 140mg/L and 130 mg/L respectively, the increasing of their mass concentration could not result in the increase of removal ratio of Cd(II) obviously. This trend may be resulted from the effects of the concentration change of Cd(II) in the wastewater on the flocculating ability of QCMC and CMC. Lower mass concentration of QCMC and CMC would result in less Cd(II) to be flocculated. On the other hand, higher mass concentration of Cd(II) in the wastewater could offer higher impetus for QCMC and CMC to flocculate Cd(II).

The results in Fig 5 also revealed that QCMC-1 and CMC-1 had higher Cd(II) flocculating ability than QCMC-2 and CMC-2, which suggested that a high substitution degree of carboxymethylation may facilitate the Cd(II) flocculation and Cd(II) was mainly bond to -COO$^-$ group.

The properties of QCMC to flocculate Cr(VI)

The ability of QCMC-1 to flocculate Cr(VI) was further investigated. **Fig. 6** showed the influence of pH on the flocculation of Cr(VI) by QCMC-1. It could be seen that the pH value of solution exerted a great influence on the flocculation of Cr(VI). The relationship between the removal ratio of Cr(VI) and pH exhibited a typical Bell-shaped curve. Under higher and lower pH, the removal ratio of Cr(VI) by QCMC-1 was low. When the pH was *ca* 5.0, the removal ratio could get to the highest value (*ca* 94%). The reason that resulted in this trend may concerned with both the QCMC-1 and Cr(VI) had different forms in different pH, respectively. As for Cr(VI), there is a chemical equilibrium in water as follow.

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+ \qquad (\mathbf{3})$$

At lower pH, the form of Cr(VI) in water is mainly $HCrO_4^-$, but at higher pH, it is mainly CrO_4^{2-}. When pH is clear to 5.0, $Cr_2O_7^{2-}$ is dominant. Partly because of the difference of the charge density and the Cr(VI) content among the forms of Cr(VI), the CrO_4^{2-} or $HCrO_4^-$ form is not favorable for the removal of Cr(VI). On the other hand,

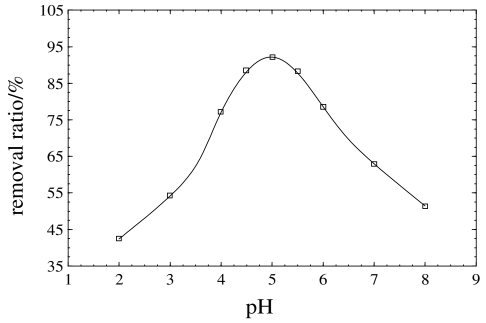


Fig. 6 The influence of pH on the property of QCMC-1 to flocculate Cr(VI). Wastewater, 100 mL; QCMC-1 aqueous solution, 2.0 mL; flocculating temperature, 20°C.

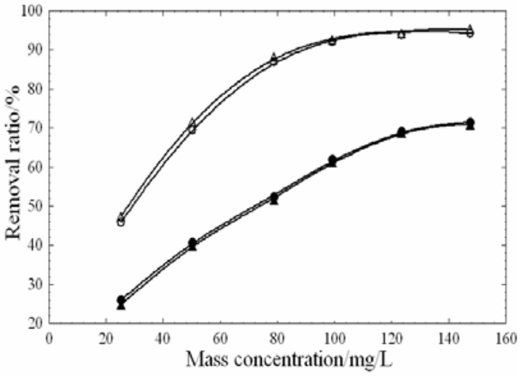


Fig. 7 Influence of the mass concentration of QCMC and CMC on their ability to flocculate Cr(VI). Flocculating condition: Wastewater pH, 5.0; flocculating temperature was 20°C; ○- QCMC-1, ●- CMC-1, △- QCMC-2, ▲- CMC-2.

when the pH is higher, the -NH_2 and -NH- groups in QCMC-1 molecule could not combine H^+ efficiently, and the carboxyl existed in the form of -COO^-, which resulted in the low ability of QCMC-1 to combine Cr(VI). When pH is too low, the protonation of the -NH_2 and -NH- groups of QCMC-1 leads to too high solubility of QCMC-1 in water, which is not favorable for the Cr(VI) floccules to form and subside.

The trend of Cr(VI) flocculation by QCMC and CMC is similar to that of Cd(II) by chitosan derivative. The relationship of the mass concentration of QCMC with the removal ratio of Cr(VI) was showed in **Fig. 7**. The fitted Langmuir curve for QCMC indicated that the removal ratio of Cr(VI) increased quickly with the increase of the mass concentration of QCMC at the beginning. When the mass concentration of QCMC in the wastewater reached 120 mg/L, the increasing of QCMC concentration could not result in the increasing of Cr(VI) removal ratio obviously. This trend was concerned with the influence of the change of Cr(VI) mass concentration in the waste water on the ability of QCMC to flocculate Cr(VI). Lower mass concentration of QCMC would result in less Cr(VI) to be flocculated. On the other hand, higher mass concentration of Cr(VI) in the wastewater could offer higher impetus for QCMC to flocculate Cr(VI).

It could also be seen that QCMC had a higher ability to flocculate Cr(VI) than that by CMC and the removal ratio of Cr(VI) by QCMC-2 is slightly higher than that of QCMC-1. These indicated that the existence of quaternary ammonium group in chitosan derivative promotes the flocculation of Cr(VI), and that Cr(VI) is mainly combined with positively-charged molecule.

Study on flocculation isotherms and kinetics of QCMC to Cd(II) and Cr(VI)

The influence of temperature on the ability of QCMC-1 to flocculate Cr(VI) and Cd(II) were presented in **Fig. 8**. It could be seen that temperature may also exert influence on the flocculation of Cr(VI) and Cd(II) by QCMC. The increase of temperature led to the increase of the removal ratio of Cr(VI) or Cd(II). The elevated temperature may play some helpful role to decrease the stability of floccules and promote them to subside in the wastewater, which accordingly facilitate the flocculation of Cr(VI) and Cd(II).

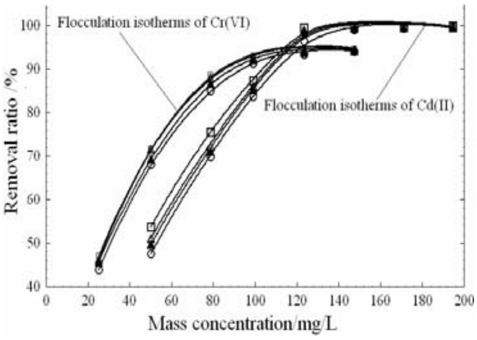


Fig. 8 The influence of temperature on the flocculation of Cr(VI) and Cd(II) by QCMC-1. Wastewater pHs, 5.0 and 8.0; flocculating temperature: ○- 10°C; ▲- 20°C; △- 30°C; □- 50°C.

Fig. 9 showed the influence of static time on the flocculation of Cr(VI) and Cd(II) by QCMC-1. The removal ratio of Cr(VI) and Cd(II) was very lower at the beginning, but the removal ratio of Cd(II) increased quickly after staying for 60 min. When the static time was 300 min, the removal ratio of Cd(II) almost reached the maximum. The effect of the static time on the removal ratio of Cr(VI) was similar to that of Cd(II), where the removal ratio of Cr(VI) increased quickly after staying for 100 min and the maximum could be obtained when the static time was 360 min.

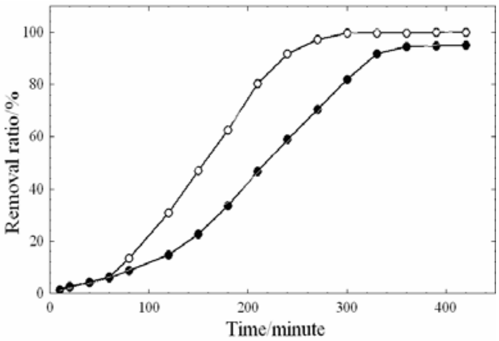


Fig. 9 The influence of staying time on the flocculation of Cr(VI) and Cd(II) by QCMC-1. Wastewater pHs, 5.0 and 8.0 for Cr(VI) and Cd(II); wastewater, 100 mL; QCMC-1 aqueous solution, 2.5mL and 2.0 mL for Cr(VI) and Cd(II), respectively; flocculating temperature 20°C; ○- Flocculation kinetics curve of Cd(II) by QCMC-1; ●- Flocculation kinetics curve of Cr(VI) by QCMC-1.

Conclusion

The quaternary ammonium group ($-CH_2CH(OH)CH_2N^+(CH_3)_3Cl^-$) was effectively introduced into the molecular structure of CMC with CTA as grafting agent. A novel derivative of chitosan, QCMC was prepared, in which the carboxymethyl group and the quaternary ammonium group existed simultaneously on the chitosan molecular chain. QCMC showed a typical amphoteric characteristic and remained the ability of CMC to combine and flocculate Cd(II). QCMC possessed higher capacity than CTS to remove Cd(II). Compared with CMC and CTS, QCMC can also combine and flocculate Cr(VI) more effectively. When the pH was 8.0 and the mass concentration of QCMC-1 in wastewater was 140 mg/L, the removal ratio of Cd(II) reached 99.7%, whereas the ratio was 99.95% and 37.8% for CMC-1 and CTS, respectively, under the same conditions. When the pH was 5.0 and the mass concentration of QCMC-1 in wastewater was 120 mg/L, the removal ratio of Cr(VI) reached 94.4%, which was far higher than that of CMC and CTS under the same conditions (68.87%, 57.36% for each).

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