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Research Article

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Coagulation and adsorption of cadmium from aqueous solution using chitosan

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ABSTRACT

The removal of Cd(II) from aqueous solution by chitosan(CTS) were investigated. In this research, the CTS were used as flocculant and adsorbent, respectively. First, the IR spectra analyzed the structure of CTS. Then the effect of flocculation conditions such as dosage of the CTS, the pH value, the stirring time at the second stage and the settling time in the coagulation test were investigated in details. When the Cd(II) initial concentration in aqueous solution was 3.0mg/L, the maximum removal rate could reach 99.7% when the pH value was 7.0 and the dosage was 4.0mg/L. Then the adsorption test using CTS also researched, including CTS dosage as adsorbent, initial concentration of Cd(II), oscillation time and the pH value were investigated in the adsorption test.

Key words: Flocculant, Adsorption, Chitosan, Removal efficiency

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INTRODUCTION

Cadmium pollution is one of the greatest pollution in the world, and with the development of science and technology, the pollution would become worse[1-2]. If the concentration more than 4.0 mg/L in the irrigation water, it would effect the growth of rice and other crops, and if the concentration more than 0.1 mg/L in the water, the fish and other marine organisms would be die[3-6]. Therefore, the presence of cadmium in water resource is an urgent problem. At present, several techniques have been developed in the scope of water treatment, such as: physical chemical remediation, phytoremediation, bioremediation. Flocculation is one kind of essential and the cheapest process for the water treatment and widely used. Polymerization of chitosan is one of the typical kind nature organic flocculants and has become most widely used in the field of electroplating industrial wastewater treatment[7].

Chitosan(CTS), the main derivative of chitin, a copolymer that is primarily composed of β(1-4) linked 2-amino-2-deoxy-d-glucopyranose units and residual 2-acetamido-2-deoxy-d-glucopyranose units, is a chemical derivative obtained by alkaline deacetylation of chitin and is also found naturally in some fungal cell walls. It has been used for removal substances from drinking water, treatment of wastewater from distilleries, removal of heavy metal from waste waters, treatment of food processing wastes, lignin removal as well as other applications[8].

In the present study, CTS was used for the removal of Cd(II) from aqueous solutions. Firstly, the CTS using as flocculant, and it could achieve the great removal rate. The effects of variables such as dosage, stirring time, pH value and the settling time were studied[9-10]. Secondly, it used as adsorbent in removing Cd(II) from aqueous solutions. The effects of variables such as adsorbent dosage, initial concentration of Cd(II), oscillation time and the pH value were studied.

EXPERIMENTAL SECTION

2.1 Material and instruments
Cadmium nitrate, Sodium hydroxide, Hydrochloric acid, Xylenol orange and Hexamethylenetetramine were purchased from Tianjin Kermel Chemical Reagent Co., Ltd; CTS was purchased from Henan Jianye Chemical Co., Ltd.

● Fourier Transformed Infra Red (FT-IR) Spectrophotometer (Niclet 6700, Niclet instrument Company, USA)
● Jar Tester (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd. China)
● UV-Vis spectrophotometer (TU-1910, Beijing Purkinje General Instrument Co., Ltd, China)

2.2 Wastewater sample
Take 1.37g Cadmium nitrate with the electronic balance, dissolved in 100mL beaker and transferred the solution into a 500mL volumetric flask. The flask was filled up to 500 mL with distilled water to reached 1000 mg/L. Then placed in the refrigerator for save.

2.3 CTS solution
Take 10.0g CTS with the electronic balance, dissolved in 500mL beaker and transferred the solution into a 1000mL volumetric flask. The flask was filled up to 1000 mL with distilled water to reached 10.0g/L. Then placed in the refrigerator for save.

2.4 Preparation of stain: Aqueous solution of xylenol orange（0.1%）
Take 1.00 g xylenol orange with the electronic balance, dissolved in 250mL beaker and transferred the solution into a 1000mL volumetric flask. When the dosage of xylenol orange（0.1%）was 4.0 mL, the complex have a maximum absorbance, so the dosage of xylenol orange was 4.0 mL in the experiment.

2.5 The system of Hexamethylenetetramine-KNO_3-HNO_3
Take 100.00 g hexamethylenetetramine with the electronic balance, dissolved in 250mL de-ionized water, adjust the pH value to 6.36 with 6.0mol/L HNO_3, then added 3.0 g KNO_3, and transferred the solution into a 1000mL volumetric flask and constant the volume.

2.6 Flocculation test
A ZR 4-6 stirring machine (Shenzhen Zhongran Water Industry Technology Development Co., Ltd., Shenzhen, China) with six stirrers was used in this experiment. 200 mL of wastewater was transferred into a beaker. Flocculants were dosed under medium stirring speed of 250 r/min for 4 min, and then changed to the speed of 80 r/min for 10 minutes. After, quiescent settling of 30 minutes, samples were collected from 2 cm below the surface for measurement using UV-Vis. Translated into concentration to calculate the removal rate.

2.7 Adsorption test
A water bath oscillator THZ—82 (Jintan Ronghua Instrument Co., Ltd.) was used in this experiment. 100 mL of wastewater with 3.0 mg/L was transferred into erlenmeyer flask (250 mL) and adding CTS solution into the Cd(II) solution, placed it into water bath oscillator at room temperature, then adding 4.0mL of 0.1% xylenol orange solution and 5.0mL of hexamethylenetetramine buffer solution for color reaction, settling 20min after shaking.

2.8 IR spectra characterization
IR spectra of CTS was analyzed in the range of 4000-500 cm^{-1} with KBr as dispersant. The characteristic absorption frequency was listed in table 1. It was evident that the absorption peak at 3400 cm^{-1} and 2918 cm^{-1} was –OH and C-H stretching vibration absorption peak, respectively. The characteristic peak at 1657cm^{-1} was -$CONH_2$ absorption peak, the 1422 cm^{-1} correspond to =CH_2 was bending vibration absorption peak.

Table 1. Infrared spectra (cm^{-1}) analysis of chitosan

Absorption peak	3400	2918	1657	1422
Groups	-OH	C-H	-CONH-	=CH_2

RESULTS AND DISCUSSION

3.1 Single influential factor analysis
3.1.1 Effect of the dosage on Cd(II) removal rate
In this experiment, the effect of flocculants dosage on the Cd(II) removal efficiency was investigated with an initial

Cd(II) concentration at 3.0 mg/L and the dosage of CTS range from 1.0 mg/L to 5.0 mg/L and not adjust the pH value.

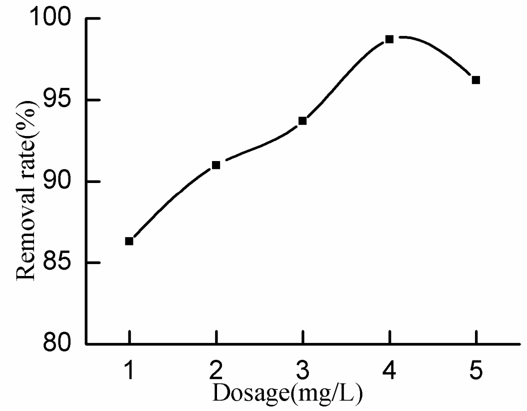

Figure 1 The effect of dosage on the removal rate

Fig. 1 shows that the removal efficiency of Cd(II) by CTS had the better removal efficiency and the removal efficiency was increased from 86.3% at 1.0mg/L to 98.7% at 4.0mg/L as the increased of CTS dosage. As the CTS dosage further increased, the removal efficiency decreased. The reason was that when CTS was over dosage, the positive charge of flocs increased, furthermore, repulsion interaction among flocs was enhanced and so flocs were restabilized and dispersed in treated samples.

3.1.2 Effect of pH value on Cd(II) *removal rate*

In this experiment, the effect of pH value on the Cd(II) removal efficiency was investigated with an initial Cd(II) concentration of 3.0 mg/L, the dosage of CTS was 4.0 mg/L and the pH range from 5.0 to 9.0.

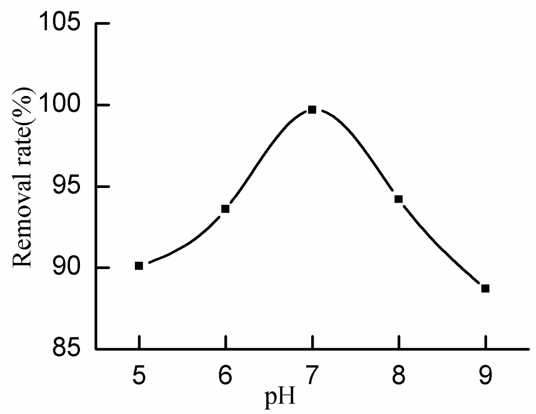

Figure 2 The effect of pH on the removal rate

Fig. 2 shows that the pH value is an important factor affecting the flocculation. As the increasment of the pH value, the Cd(II) removal rate increased first and then decreased as the increased of the pH value range from 7 to 9. When the pH value was 7.0, the flocculants had the best effect and the removal rate could reached 99.7%. This related to the form of CTS and Cd(II) structure in the aqueous solution, the active -NH_2 of CTS can be formed as a cationic polyelectrolyte with H^+ in the solution, and the degree of electric charge depend on the pH value of the solution.

3.1.3 Effect of stirring time on Cd(II) *removal rate*

In this experiment, the effect of stirring time at the second stage on the Cd(II) removal efficiency was investigated with an Cd(II)concentration of 3.0 mg/L and the stirring time range from 2.0 min to 10.0 min, not adjust the pH value.

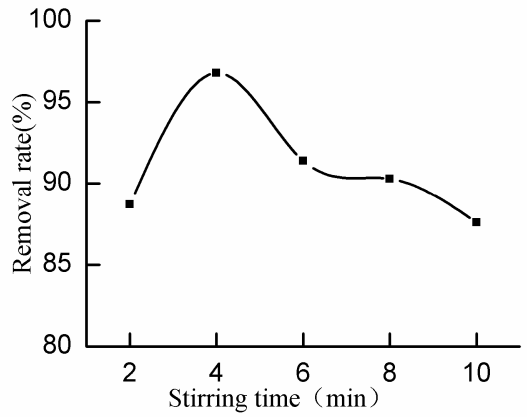

Figure 3 The stirring time on the removal rate

Fig. 3 shows that the determination of optimum stirring time for Cd(II) removal rate was carried out at 2.0～10.0 min. It was known that stirring time influenced the removal rate, when the stirring time was 4.0 min at the second stage, the removal rate could reach its maximum at 96.8%. When treating Cd(II) wastewater, CTS flocculants showed both charge neutralization and adsorption bridging functions. When the stirring time was too short, it made the flocculants and the Cd(II) molecules in insufficient contact with each other, and could not play the charge neutralization and adsorption bridging functions very well. But when the stirring time was too long, it could decrease the adsorption bridging functions of CTS flocculants and the absorbed small flocs of the Cd(II) molecule was broken, which lead the Cd(II) molecules in flocs released into the water again, so the removal efficiency decreased.

3.1.4 Effect of settling time on Cd(II) *removal rate*

In this experiment, the effect of settling time at the second stage on the Cd(II) removal efficiency was investigated with an Cd(II) concentration of 3.0 mg/L and the settling time range from 5.0 min to 25.0 min, not adjust the pH value.

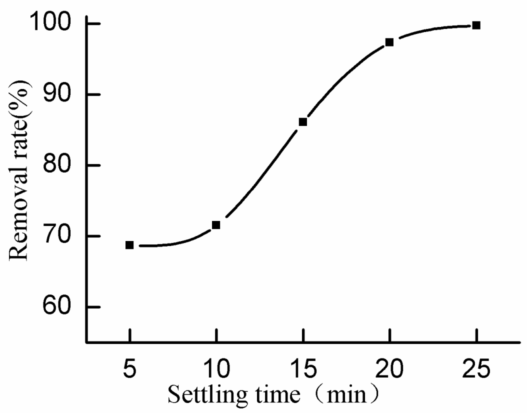

Figure 4 The settling time on the removal rate

Fig. 4 shows that the determination of optimum settling time for Cd(II) removal rate was carried out at 5.0～25.0 min. It was known that settling time influenced the removal rate, figure 4 shows that the settling time had a certain impact on the Cd(II) removal rate, as the extension of settlement time, the Cd(II) removal rate showing a first increases and then decreases, when settling time was 20 min, the CTS coagulant for water removal rate of Cd(II) maximum of 97.3%. It can be inferred that the study of the role of coagulation homeostasis process, mainly the existence of gravity of molecules and molecular thermal motion. It suggested that at the beginning period of time, the gravity played a dominant role, and as the increased of the time, the CTS flocculants and Cd(II) settled down under the action of gravity gradually at the bottom of the solution to achieve the best removal efficiency, but as the increased of time the thermal motion of molecules played the dominant role, the original settlement with the coagulant molecule in a stable period of time and then re-diffused into the solution to reach a new equilibrium, so the removal rate decreased.

3.2 Absorption property of CTS

3.2.1 Effect of CTS dosage on adsorption

In this experiment, the effect of adsorption dosage on the Cd(II) removal efficiency was investigated with an initial Cd(II) concentration at 3.0 mg/L and the dosage of CTS range from 0.5 mL to 2.5 mL and not adjust the pH value. Fig. 5 shows that the CTS had better adsorption capacity of Cd(II) and the adsorption capacity was increased as the increased of CTS dosage. The adsorption efficiency was increased from 80.3% at 0.5mL to 95.7% at 1.5mL as the increased of CTS dosage. And the adsorption efficiency was increased from 95.7.3% at 1.5mL to 99.0% at 2.0mL as the increased of CTS dosage. Considering the cost and the adsorption effect, so the optimum amount of CTS was 2.0 mL.

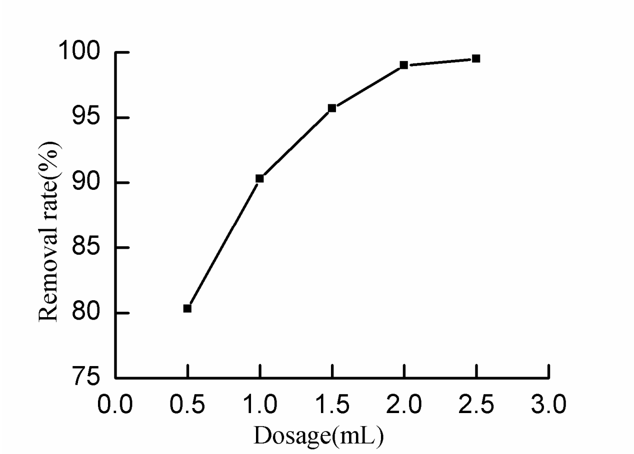

Figure 5 The CTS dosage on adsorption

3.2.2 Effect of initial concentration of Cd(II) on adsorption

In this experiment, the effect of initial concentration of Cd(II) for adsorption was investigated with the initial concentration of Cd(II) range from 1.0mg/L to 5.0mg/L, the dosage of CTS was 2.0mL, not adjust the pH value. Fig. 6 shows that the initial concentration of Cd(II) was an important parameter that determines the adsorption effect. When fixed the adsorbent dosage of CTS, the adsorption efficiency was decreased as the increased of Cd(II) initial concentration. When the dosage of CTS was 2.0 mL, and the Cd(II) initial concentration was lower 2.0 mg/L, the adsorption effect could reach 99.0%, when the Cd(II) initial concentration was more than 2.0 mg/L, the adsorption effect reduced sharply, so if the solution with high concentration of Cd(II), we could increase the amount of CTS to improve the adsorption effect of Cd(II).

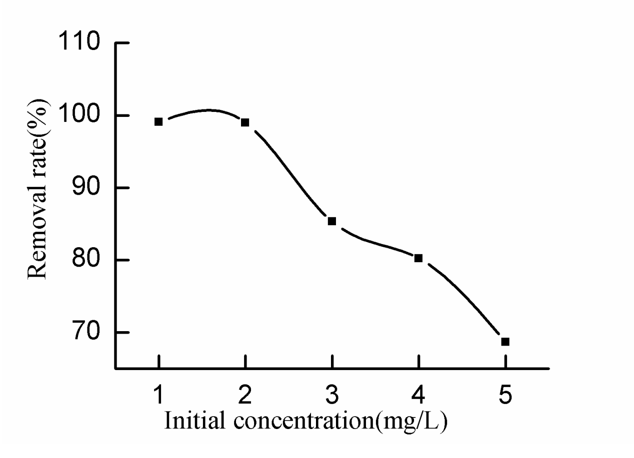

Figure 6 The initial concentration of Cd(II) on adsorption

3.2.3 Effect of oscillation time on adsorption

In this experiment, the effect of oscillation time for adsorption was investigated with the initial concentration of Cd(II) was 3.0mg/L and the dosage of CTS was 2.0mL, not adjust the pH value. The oscillation time was range from 10min to 60min. Fig. 7 shows that the oscillation time was an important parameter that determines the adsorption effect. The experimental results showed that the adsorption efficiency was increased as the increased of oscillation time. And the adsorption rate of Cd(II) in water was quick, when the oscillation time was 10min, the adsorption rate has reached more than 90.0%. The adsorption efficiency increased sharply when the oscillation time from 10 to 30 min. Adsorption equilibrium time was 50min and the removal efficiency reached more than 99.0%, so the optimum oscillation time was 50 min.

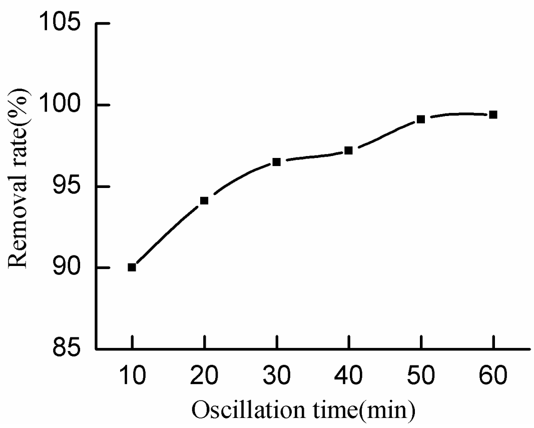

Figure 7 The oscillation time on adsorption

3.2.4 Effect of pH value on adsorption

In this experiment, the effect of pH value for adsorption was investigated with the initial concentration of Cd(II) was 3.0mg/L and the dosage of CTS was 2.0mL, and the pH range from 5.0 to 9.0. Fig. 8 shows that the pH value was an important parameter that determines the adsorption effect. The experimental results showed that the pH not only affect the degree of ionization of the substance in the solution and the surface charge of the adsorbent, but also affect the adsorbent impact dissociation of reactive functional groups. When pH <7.0, the adsorption capacity of CTS was increased with increased of pH, when the pH value was lower, the concentration of H^+ was higher, and the $-NH_2$ could be protonated easily, which could make the CTS with positive charge, and lead the adsorption performance decrease. Therefore, in order to improve the adsorption capacity, the pH should be increase appropriately, but when the pH too high, it could cause the precipitation of $Cd(OH)_2$ generated, and not conducive to the adsorption, so the optimum pH was 7.0.

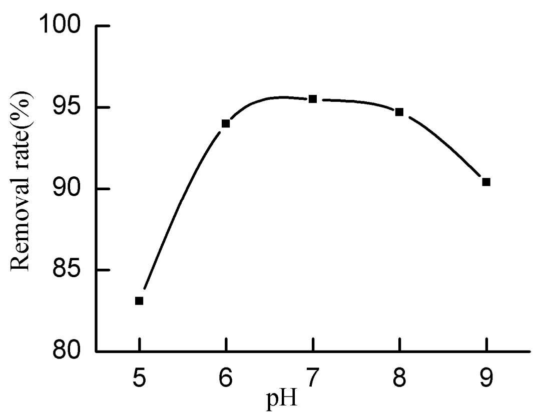

Figure 8 The pH value on adsorption

CONCLUSION

In this study, the adsorption test and coagulation test for removing Cd(II) have been researched. The single influential factor was investigated, including the dosage of the CTS, the pH value, the stirring time at the second stage and the settling time in the coagulation test. When the Cd(II) initial concentration in aqueous solution was 3.0mg/L, the maximum removal rate could reach 99.7% when the pH value was 7.0 and the dosage was 4.0mg/L. Then the adsorption test using CTS also researched, including CTS dosage as adsorbent, initial concentration of Cd(II), oscillation time and the pH value were investigated in the adsorption test.

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