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Cellulose derived from corn straw for the efficient adsorption of Cd(II) from water

Bangwei Li[a,b,†], Zhonglei Xie[c,d,†], Mengying Guo[a,b], Tianya Chen[a,b], Xiulan Ma[a,b], Yujun Wang[a,b,*], Chang Peng[e,*]

[a] *College of Resources and Environment, Jilin Agricultural University, Changchun 130118, China, emails: yujunw@jlau.edu.cn (Y. Wang), 1103800573@qq.com (B. Li), 2848853715@qq.com (Z. Xie), 2388401068@qq.com (M. Guo), 834912713@qq.com (T. Chen), 1012199068@qq.com (X. Ma)*
[b] *Jilin Provincial Key Laboratory of Soil Resource Sustainable Utilization for Commodity Grain Bases, Jilin Agricultural University, Changchun 130118, China*
[c] *College of Plant Science, Jilin University, Changchun, 130062, China*
[d] *College of Construction Engineering, Changchun Sci-Tech University, Changchun, 130600, China*
[e] *Institute of Agricultural Resources and Environment, Jilin Academy of Agricultural Sciences (Northeast Agricultural Research Center of China), Changchun 130033, China, Tel. +86 17549634245; Fax: +86 13500419456; email: wyj0431@126.com (C. Peng)*

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ABSTRACT

In order to study the adsorption performance of modified cellulose on Cd(II) in wastewater, cellulose was extracted from corn straw by the extraction method of nitric acid-ethanol, and three modified cellulose materials, that is, chitosan-cellulose (Cell-CS), citric acid-cellulose (Cell-CA) and chitosan/citric acid-cellulose (Cell-CA-CS) were prepared by single and compound modification of chitosan and citric acid. The adsorption properties of modified cellulose materials for Cd(II) in water were studied by laboratory simulation. The results from the structure characterization with Fourier-transform infrared spectroscopy, scanning electron microscopy and energy-dispersive X-ray spectroscopy showed that the group of C=O occurred on the surface of Cell-CA, chitosan particles were attached to the surface of Cell-CS; Cell-CA-CS was being of the structural characteristics of both of Cell-CS and Cell-CA. The results from the adsorption test showed that the adsorption kinetic characteristics of Cd(II) in water can be described by pseudo-second-order kinetic model, and the adsorption thermodynamic characteristics can be described by Langmuir equation. The adsorption capacity of cellulose materials for Cd(II) in water was in the order of Cell-CA-CS > Cell-CS > Cell-CA > Cell. The result from the five times of adsorption-regeneration showed that Cell-CA-CS still had a large adsorption capacity for Cd(II) in water and consequently had great potential for the treatment of Cd(II) containing wastewater.

Keywords: Corn straw cellulose; Cellulose-modified; Water treatment; Cd(II); Adsorption characteristics

1. Introduction

Water pollution of heavy metals has become one of the environmental issues of general concern in the world today. The heavy metal cadmium (Cd), as a commonly used metal in industrial production, has the characteristics of strong migration, carcinogenicity and high toxicity in water bodies. Cadmium(II)-containing wastewater discharged from industry is highly toxic and non-degradable [1]. Cadmium is difficult to be digested and decomposed after taken up

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* Corresponding authors.

† These authors contributed equally to this work.

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by the human body through the food chain, and enriched in the liver and kidneys, leading to cancer or other diseases [2]. Comparing with other heavy metals, the Cd(II) in the system of water-soil-plant is easier to be uptake by crops such as rice [3], and easily cause the "itai-itai disease" if eating rice with high Cd content for a long time. The International Agency for Research on Cancer had listed Cd as the first category of carcinogens [4]. In recent years, there was many traditional methods for the treatment of wastewater containing Cd(II), such as chemical precipitation, ion exchange, electric repair and adsorption method [5–8]. However, these methods had the different disadvantages, for example, the method of chemical precipitation is difficult to be used to treat wastewater with low-concentration Cd(II), the method of ion exchange is restricted by environmental factors and treatment conditions, and difficult to be used in large-scale wastewater treatment [9], the method of electric repair consume more energy and costs.

Compared with the above treatment methods, the adsorption method has the advantages of simple, effective and inexpensive [10–12]. Corn straw is the primary agricultural waste produced by cultivation in Northeast China. According to statistics, China's corn planting area reached 41.28 million ha in 2019, furthermore, the amount of corn straw will increase with the increasing corn yield [13]. Up to present, many scholars were concerned with the exploring of the efficient adsorbents using corn straw or biochar made from high-temperature carbonized of corn straw to treat heavy metals in wastewater. Owing to corn straw containing a large amount of soluble organic substances, chemical oxygen demand will increase or organic pollutants will leache out in the water if corn straw directly added to wastewater [14]. The process of preparing corn straw biochar has the disadvantages of high energy consumption and poor recovery after wastewater treatment. Therefore, it is necessary for the development of new strategies to further utilize corn straw and improve the adsorption performance of corn straw. That making full use of the natural ingredients of corn straw itself and extracting cellulose from corn straw for wastewater treatment will provide a new research direction for utilization of corn straw.

Cellulose, a biodegradable and renewable natural polymer [15], have a three-network space structure and containing multiple active groups, such as hydroxyl and carboxyl groups [16]. For the limitation of the adsorption performance of unmodified cellulose, it will increase the adsorption capacity of straw cellulose through modification with chemical methods due to some active groups introduced onto the corn straw, which can make the cellulose-based adsorbent capture more polluting metal ions [17]. Nowadays, many scholars have used cellulose as raw material to prepare new adsorbents with excellent adsorption performance on heavy metal ions in wastewater using graft copolymerization [18–20], esterification modification [21,22] and oxidation modification [23]. Chitosan is a natural polymer material with rich resources and wide distribution in nature. Because its molecular chain contains multiple hydroxyl, amino and other active groups, chitosan can effectively chelate and adsorb heavy metal ions and has excellent compatibility and degradability. Nevertheless, chitosan has poor adsorption performance and selectivity for low concentration heavy metal ions in wastewater, as well as the disadvantage of difficult solid–liquid separation after wastewater treatment. If chitosan is combined with cellulose, it can not only effectively improve the adsorption effect of cellulose, but also broaden the application scope of chitosan in wastewater treatment, increase the unit mass of cellulose, avoid cellulose being too light to recovery in water, and achieve a good effect of solid–liquid separation.

In this paper, cellulose (Cell) was extracted from corn straw and three modified cellulose materials, that is, chitosan-cellulose (Cell-CS), citric acid-cellulose (Cell-CA) and chitosan/citric acid-cellulose (Cell-CA-CS), were prepared by single and compound modification of chitosan, citric acid and chitosan-citric acid, respectively. The adsorption characteristics of Cell, Cell-CS, Cell-CA and Cell-CA-CS for Cd(II) in wastewater were discussed under the different conditions including adsorption time, temperature, solution pH and dosage of modified cellulose. Further, the mechanism of adsorption of modified-cellulose for Cd(II) in wastewater was also discussed according to the structure characterization of modified cellulose. It will provide theoretical basis and technical reference for the efficient removal of Cd(II) from wastewater by natural cellulose materials.

2. Materials and methods

2.1. Test materials and chemical reagents

Corn straw, taken from the experimental field of Jilin Agricultural University, Changchun, China, was washed and dried at 105°C for 10 h, cut into 1~2 cm pieces, crushed and passed 60 mesh sieve, dried at 65°C to constant weight and set aside.

Chemical reagents, including absolute ethanol, nitric acid, acetic acid, sodium hydroxide, citric acid, and cadmium chloride, are all analytical, chitosan (degree of deacetylation ≥90%), purchased from Sinopharm Chemical Reagent Co., Ltd. The test water was deionized.

The mixture of nitrate and ethanol: uniformly mixing concentrated nitric acid and absolute ethanol with a volume ratio of 4:1.

Acetic acid solution of chitosan: put 1.0 g of chitosan into 200 mL of 5% acetic acid solution and fully stirred and dissolved.

The solution of Cd(II) with 1,000 mg L^{-1}: put 2.0311 g $CdCl_2$ into a 500 mL beaker, dissolved in a small amount of water, moved to 1,000 mL volumetric flask and volume, shook well for use. The lower concentrations of Cd(II) solutions were prepared by diluted the Cd(II) solution of 1,000 mg L^{-1} with deionized water.

2.2. Methods of cellulose preparation and modification

Method for preparation of cellulose (Cell): extracted from corn straw by nitric acid-ethanol method as the procedure [24]: both of 5 g of corn straw and 125 mL of nitric acid-ethanol mixture were added in a dry Erlenmeyer flask, conical bottle mouth is equipped with a condensation return pipe, heat it in a boiling water bath for 1 h, filter to remove the solvent after cooled, repeated the above operation three to five times until the fiber turns white, the residue was washed with nitric acid-ethanol mixture, washed

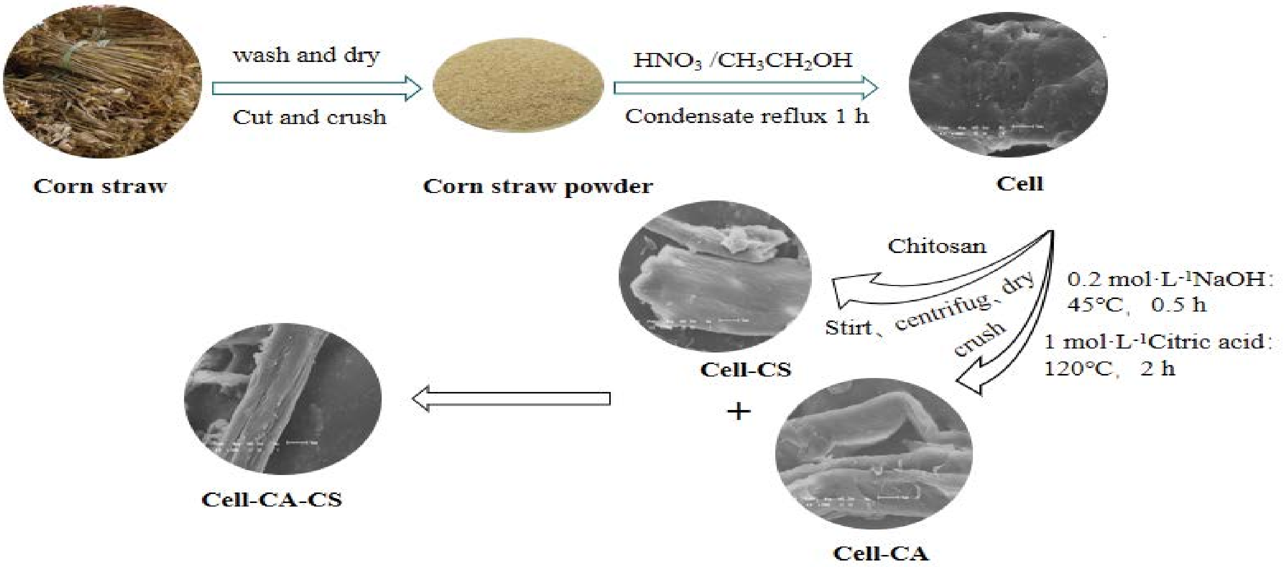


Fig. 1. Schematic presentation of the preparation and modification of cellulose materials.

with hot water to neutrality, finally, washed the sample with absolute ethanol twice, suction filtered, dried at 65°C to obtain a solid Cell, which was ground through a 100-mesh sieve for reserve.

Method for preparation of chitosan-cellulose (Cell-CS): added both of 5.00 g of Cell and 100 mL of chitosan into acetic acid solution, placed on a magnetic stirrer and stirred for 1 h, stood at room temperature for 3 h, centrifuge and dried at 65°C to obtain a solid Cell-CS, ground through a 100-mesh sieve for reserve.

Method for preparation of citric acid-cellulose (Cell-CA): added both of 5.00 g of Cell and 100 mL of NaOH solution with a concentration of 0.2 mol L^{-1} into a dry beaker, treated at 40°C for 0.5 h, filtered with suction, washed to neutrality, dried at 65°C to obtain the alkalized Cell pretreated with NaOH, and then added both of 5 g of alkalized Cell and 60 mL of citric acid solution with a concentration of 1 mol L^{-1} into a dry beaker, placed on a magnetic stirrer and stirred for 2 h at 120°C, drained and washed until neutral, centrifuge and dried at 65°C to obtain a solid Cell-CA, ground through a 100-mesh sieve for reserve.

Method for preparation of chitosan/citric acid-cellulose (Cell-CA-CS): added both of 5.00 g of Cell-CA and 100 mL chitosan acetic acid solution into a dry beaker, placed on a magnetic stirrer and stirred for 1 h, stood at room temperature for 3 h, centrifuged and dried at 65°C to obtain a solid Cell-CA-CS, ground through a 100-mesh sieve for reserve. Schematic presentation of the preparation and modification of cellulose materials as shown in Fig. 1.

2.3. Batch adsorption experiments

Adsorption kinetics experiments. Added 1.00 g of Cell or Cell-modified into 400 mL of Cd(II) solution with 100 mg L^{-1}, adjusted the solution pH to 5.0, covered the beaker with plastic wrap, stirred thoroughly in a magnetic stirrer at 298 K, centrifuged, filtered and diluted the adsorption solution sample taken at different time points within 0, 1, 2, 5, 10, 20, 30, 60, 120 and 240 min, determined the concentrations of Cd(II) in solution by atomic absorption spectrophotometry. Each treatment repeated three times.

Adsorption isotherm experiments. Added 0.05 g of Cell or Cell-modified into a batch of centrifuge tubes containing 20.00 mL solutions with different initial Cd(II) concentrations of 25, 50, 75, 100, 125, 150, 175, 200 mg L^{-1}, adjusted the solution pH to 5.0, oscillated for 240 min at the temperatures of 288, 298 and 308 K, respectively, centrifuged, filtered and diluted the supernatants, determined the concentrations of Cd(II) in solution by atomic absorption spectrophotometry. Each treatment repeated three times.

Adsorption experiments under the different adsorbent dosage. Added 20.00 mL of Cd(II) solution with 100 mg L^{-1} into a batch of 50 mL centrifuge tubes, then added 0.05, 0.10, 0.15, 0.20 and 0.25 g of Cell or Cell-modified, respectively, adjusted the solution pH to 5.0, oscillated on a constant temperature water bath at 298 K for 240 min, centrifuged, filtered and diluted the supernatants, determined the concentrations of Cd(II) in solution by atomic absorption spectrophotometry. Each treatment repeated three times.

Adsorption experiments under the different solution pH. Added 20.00 mL of Cd(II) solution with 100 mg L^{-1} into a batch of 50 mL centrifuge tubes, then added 0.05 g of Cell or Cell-modified, respectively, adjusted the pH to 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 with dilute HNO_3 and NaOH solution, oscillated on a constant temperature water bath at 298 K for 240 min, centrifuged, filtered and diluted the supernatants, determined the concentrations of Cd(II) in solution by atomic absorption spectrophotometry. Each treatment repeated three times.

Desorption and regeneration test of cellulosic material of the adsorption of cellulosic materials for Cd(II) in the water was conducted at the initial concentration of Cd(II) 100 mg L^{-1}, the dosage of cellulosic materials 12.5 g L^{-1}, the temperature 298 K and the pH 5.0 of the adsorption solution, after the adsorption equilibrium reached, filtered and separated the cellulosic materials from the adsorption solution, and then the separated cellulosic materials was mixed with 20 mL HNO_3 1 mg L^{-1} to desorb Cd(II) from the cellulosic materials at room temperature for 2 h. The concentration of Cd(II) in the desorption solution was measured. The cellulose material was washed with ultrapure water and dried. The above procedure was repeated five times in order to assess regeneration capability of the cellulose materials.

2.4. Methods of characterization and determination

The functional groups of cellulose materials were characterized by infrared spectroscopy (Irtracer-100 infrared spectrometer), the surface morphology characteristics of cellulose materials were observed by scanning electron microscope (SS-550 SEM), the elements of cellulose materials were analyzed by energy spectrum analysis (Horiba 7021-H2 X-ray energy spectrometer), and the specific surface area and particle size of cellulose materials were analyzed by the specific surface area and pore size determined (3H-2000P specific surface area analyzer). The concentration of Cd(II) in solution was determined by flame atomic absorption spectrophotometry. Adjusted the acetylene pressure to 0.05 MPa, the air pressure to 0.2 MPa, the measurement wavelength was 228.8 nm, the lamp current was 0.2 mA. By draw a standard curve from the measured absorbance to the concentration, the linear correlation coefficient was 0.998.

2.5. Adsorption models

The amount adsorbed per unit mass of the adsorbent q_t (mg g^{-1}) and the removal percentage R_t (%) was calculated based on the following equations:

$$R_t = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

$$q_t = \frac{\left(C_0 - C_t\right)V}{m} \tag{2}$$

where C_0 and C_t represent the Cd(II) concentration (mg L^{-1}) at the initial time of the solution and *t*, respectively, *V* represent the total volume of the solution (L), *m* represent the mass of adsorbent added (g).

The pseudo-first-order model, pseudo-second-order model and intra-particle diffusion equations used in adsorption kinetics were as follows:

$$q_t = Q_{e,1}\left(1 - e^{-k_1 t}\right) \tag{3}$$

$$q_t = \frac{Q_{e,2}^2 k_2 t}{1 + Q_{e,2} k_2 t} \tag{4}$$

$$q_t = k_p \cdot t^{0.5} + S \tag{5}$$

where $Q_{e,1}$ and $Q_{e,2}$ represent the equilibrium adsorption capacity (mg g^{-1}) of the pseudo-first-order model equation and the pseudo-second-order model equation, respectively. k_1 and k_2 represent the adsorption rate constants of pseudo-first-order and pseudo-second-order model equations, respectively. k_p and *S* represent the intra-particle diffusion rate constant (mg g^{-1} $min^{-0.5}$) and constant (mg g^{-1}).

The experimental data were analyzed used the adsorption isotherm models of Langmuir and Freundlich, which isotherm models are given as the following equations:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{6}$$

$$q_e = K_F C_e^n \tag{7}$$

where q_e represent the equilibrium adsorption capacity (mg g^{-1}), C_e represent the Cd(II) concentration in the filtrate after adsorption equilibrium (mg L^{-1}), q_m represent the saturated adsorption capacity (mg g^{-1}), K_L and K_F were the adsorption equilibrium constants fitted by Langmuir and Freundlich models, respectively, *n* represent the adsorption capacity constant.

The thermodynamic formula for calculating thermodynamic parameters is as follows:

$$K_D = \frac{q_e}{C_e} \tag{8}$$

$$\Delta G = -RT \ln K_D \tag{9}$$

$$\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{10}$$

where K_D represents the equilibrium distribution coefficient, q_e represents the equilibrium adsorption capacity (mg g^{-1}), C_e represents the Cd(II) concentration in the filtrate after adsorption equilibrium (mg L^{-1}), ΔG represents the Gibbs free energy (kJ mol^{-1}), *R* represents the ideal gas constant (value was about 8.314 J mol^{-1} K^{-1}), *T* represents the thermodynamic temperature (K), ΔS and ΔH represent the change in entropy (kJ mol^{-1}) and the change in enthalpy (kJ mol^{-1} K^{-1}), respectively, the values of ΔH and ΔS are calculated from the slope and intercept of the linear graph of $\ln K_D$ and $1/T$.

3. Results and discussion

3.1. Fourier-transform infrared spectroscopy analysis

Fourier-transform infrared spectroscopy (FTIR) spectrometry was used to detect the difference of functional groups between unmodified-Cell and modified-Cell (Cell-CS, Cell-CA and Cell-CS-CA) (shown in Fig. 2). The absorption peak at 897 cm^{-1} was generated by β-glycosidic bond on the surface of cellulose [25] and the peak at 2,950 cm^{-1} was the typical characteristic absorption peak of cellulose. Generally, most functional groups of the four kinds of celluloses were roughly similar, which can be explained that modified cellulose by citric acid and chitosan did not caused essential changes in the complex structure of cellulose, the modified-Cell still retains some of the characteristics of the unmodified cellulose. Compared with unmodified cellulose, the infrared spectra of different modified cellulose had also changed to varying degrees. Cell-CS and Cell-CA-CS produced N–H characteristic peaks with different intensities at 1,616 cm^{-1}. There was no obvious change in absorption peak at 2,950 cm^{-1}, which indicated the surface structure of cellulose was not damaged by chitosan and the chitosan just attached to the cellulose surface. Cell-CA and Cell-CA-CS had multiple ester C–O characteristic peaks at 1,000~1,300 cm^{-1}, which indicated that the amount of free C–O in the cellulose modified by citric acid increased to some extent. As the same time, there was an obvious characteristic peak of C=O at 1,735 cm^{-1}, which indicated that the ester functional groups were successfully introduced on the surface of cellulose after modification with citric acid. In general, after the composite modification of cellulose by chitosan and citric acid, the Cell-CA-CS was successfully introduced the functional groups both of the two modified by chitosan and citric acid separately.

3.2. SEM and energy-dispersive X-ray spectroscopy analysis

SEM was used to observe the morphology of cellulose materials, as shown in Fig. 3. The surface of unmodified Cell was compact blocks with relatively smooth and clear contour (Fig. 3a) and some flake and curled particles were attached around the surface of Cell-CS (Fig. 3b). It was indicated that after chitosan treatment, Cell-CS retained most of the function and structure of the Cell,

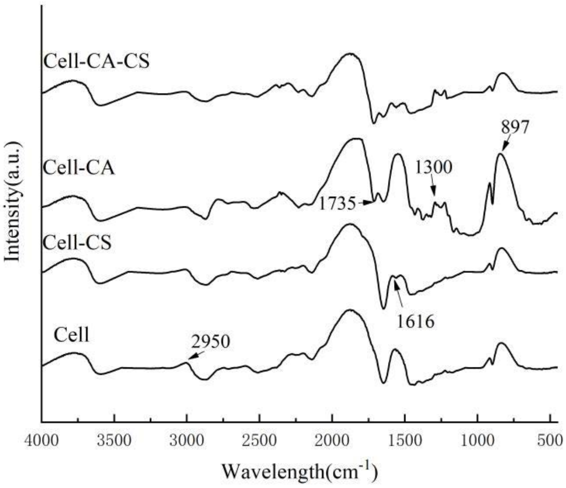
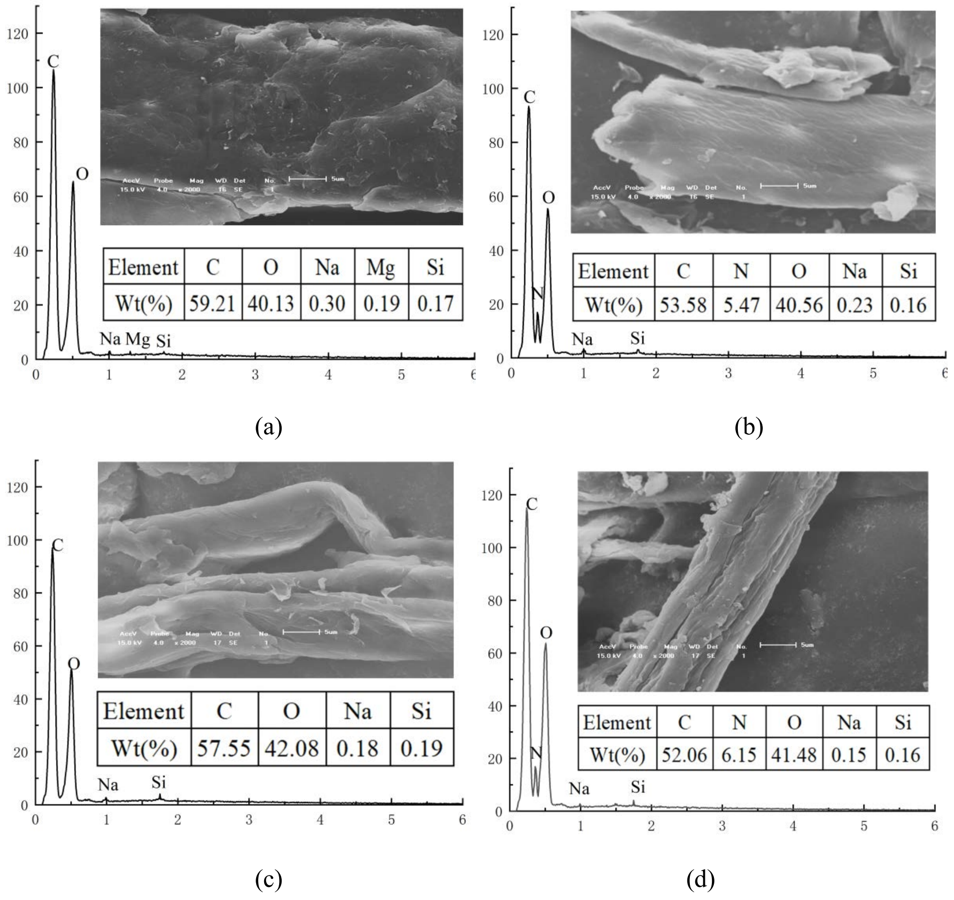


Fig. 2. FTIR spectra of cellulose materials.



Element	C	O	Na	Mg	Si
Wt(%)	59.21	40.13	0.30	0.19	0.17

(a)

Element	C	N	O	Na	Si
Wt(%)	53.58	5.47	40.56	0.23	0.16

(b)

Element	C	O	Na	Si
Wt(%)	57.55	42.08	0.18	0.19

(c)

Element	C	N	O	Na	Si
Wt(%)	52.06	6.15	41.48	0.15	0.16

(d)

Fig. 3. SEM images and EDS elemental analysis of cellulose materials: (a) Cell, (b) Cell-CS, (c) Cell-CA, and (d) Cell -CA-CS.

which may justify improvement the adsorption performance of cellulose. The Cell-CA modified by citric acid caused obviously wrinkled and the broken surface, which may result in the specific surface area increased of Cell-CA (Fig. 3c). The Cell-CA-CS modified by citric acid and chitosan obviously wrinkled and attached some irregular flakes and curled particle (Fig. 3d). The results of energy-dispersive X-ray spectroscopy (EDS) showed that the content of N element in Cell-CS and Cell-CA-CS increased, which further illustrated the inferred that flake and curled particles were chitosan particles.

3.3. Brunauer–Emmett–Teller analysis

The specific surface area and pore volume of Cell, Cell-CS, Cell-CA and Cell-CA-CS were measured by the N_2 adsorption method, result as shown in Table 1. After Cell and Cell-CA are modified with chitosan, the specific surface areas of Cell-CS and Cell-CA-CS were slightly reduced, indicating that the chitosan in Cell-CS and Cell-CA-CS had a larger molecular weight, and it was not inserted into the Cell and Cell-CA, but attached to the surface of the Cell and Cell-CA through the mutual attraction of positive and negative charges, this was consistent with the analysis result of the infrared spectrum in Fig. 2. At the same time, during the modification of Cell and Cell-CA by chitosan, some of the chitosan solution may enter the interior of Cell and Cell-CA and occupy their pores, resulting in the decrease in the specific surface area of Cell and Cell-CA. In addition, the specific surface Cell-CA area increased from 2.027 to 4.601 $m^2 g^{-1}$ after modified with citric acid, indicating that the structure of the cell destroyed by citric acid and resulted in the specific surface area increased, which was consistent with the results in Fig. 3c.

3.4. Adsorption kinetics

Adsorption kinetics were used to describe changes in Cd(II) adsorption rates with time and display the adsorption equilibrium time of the adsorbent. As shown in Fig. 4, Cd(II) in the solution was adsorbed sharply by the cellulose-modified at the first minute, and reached adsorption equilibrium with 20 min for all treatments. The equilibrium adsorption capacity of Cell-CA-CS was 20.08 mg g^{-1}, which was significantly higher than that of Cell, Cell-CS, and Cell-CA (being 7.12, 11.84 and 9.95 mg g^{-1}, respectively). It indicated that the adsorption effect of cellulose for Cd(II) in water was increased significantly through the compound modification by chitosan and citric acid. In the system of Cd(II)-cellulose in water, Cd(II) can reacted rapidly with the binding sites in the cellulose and chitosan at the first minute, mainly non-specific adsorption. With the decease of the binding sites in the cellulose material, specialistic adsorption appeared and the adsorption rate slowed down [26].

The intra-particle diffusion model assumes that the adsorption process was a complex physical and chemical mixed adsorption process. As shown in Fig. 5, the adsorption process divided into three stages: the first stage was the surface diffusion process, Cd(II) diffused to the surface of the cellulose materials; the second and third stages were the intra-particle diffusion process, Cd(II) diffused in the pores of the cellulose materials. In Fig. 5 the curve of equilibrium adsorption capacity of cellulose materials adsorbing Cd(II) vs. $t^{0.5}$ was a straight line that does not pass through the origin, indicated that intra-particle diffusion was not only one step to control the process of cellulose materials adsorption of Cd(II) but also other step concerned with surface diffusion and intra-particle diffusion.

The models of pseudo-first-order kinetic, pseudo-second-order kinetic and intra-particle diffusion were all used to fit the kinetic of cellulose materials adsorption for Cd(II) in water (Table 2). As shown in Table 2, both of the pseudo-first-order model and pseudo-second-order model ($R > 0.95$, $p < 0.01$) were fitted to described the kinetic characteristics of Cd(II) adsorption of cellulose materials in water other than the intra-particle diffusion model. In addition, the values of $Q_{e,2}$ calculated from pseudo-second-order kinetic model were closer to the experimental values of equilibrium adsorption capacity (7.11, 11.81, 9.88

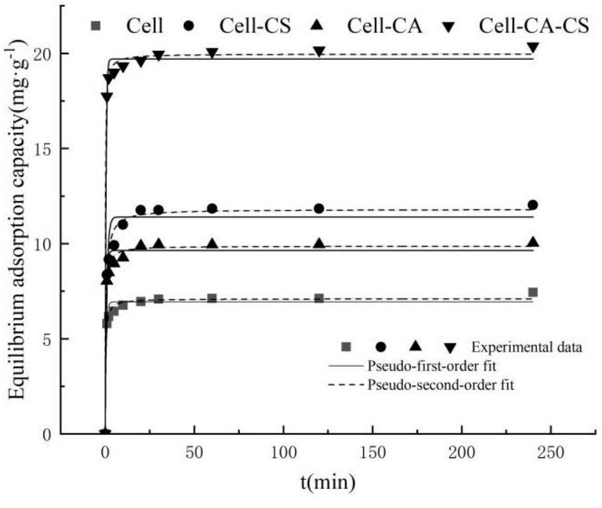


Fig. 4. Adsorption kinetic curve of cellulose materials for Cd(II) at 298 K, pH = 5.0.

Table 1
Specific surface area and pore volume of cellulose materials

Sample	Cell	Cell-CS	Cell-CA	Cell-CA-CS
Brunauer–Emmett–Teller ($m^2 g^{-1}$)	2.027	2.013	4.601	4.587
Pore volume ($cm^3 g^{-1}$)	0.018	0.018	0.032	0.031
Pore diameter (nm)	12.866	13.076	7.891	7.978

Table 2
Fitting results of the kinetic equation model

Model	Parameter	Cell	Cell-CS	Cell-CA	Cell-CA-CS
	$Q_{e,1}$ (mg g^{-1})	6.941	11.402	9.644	19.700
Pseudo-first-order	k_1	1.640	1.103	1.614	2.230
	R	0.976**	0.956**	0.976**	0.983**
	$Q_{e,2}$ (mg g^{-1})	7.105	11.805	9.876	19.965
Pseudo-second-order	k_2	0.532	0.169	0.372	0.371
	R	0.992**	0.989**	0.993**	0.998**
	k_{p1}	0.1446	0.3585	0.2138	0.2636
	S_1	5.7477	8.1908	7.9231	17.7821
	R	0.872	0.911*	0.934*	0.833
	k_{p2}	0.0160	0.0382	0.0340	0.0307
Intra-particle diffusion	S_2	6.6133	10.7471	9.0178	19.0180
	R	0.979**	0.837	0.803	0.998**
	k_{p3}	0.0019	0.0011	0.0005	0.0017
	S_3	6.9610	11.7471	9.9067	19.9730
	R	0.956**	0.966**	0.979**	0.996**

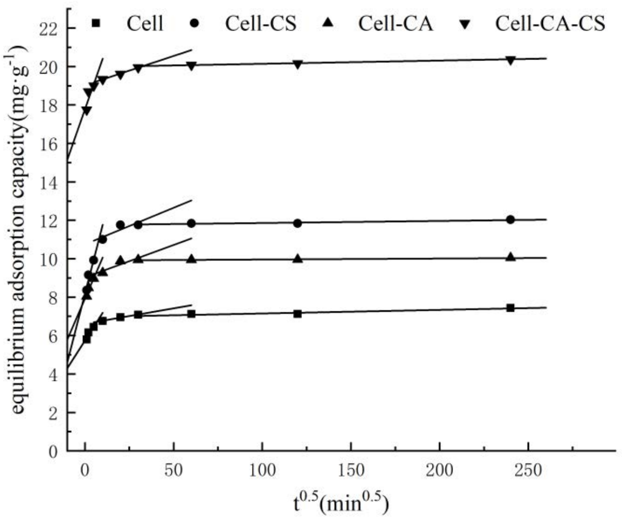


Fig. 5. Intra-particle curve of cellulose materials for Cd(II) at 298 K, pH = 5.0.

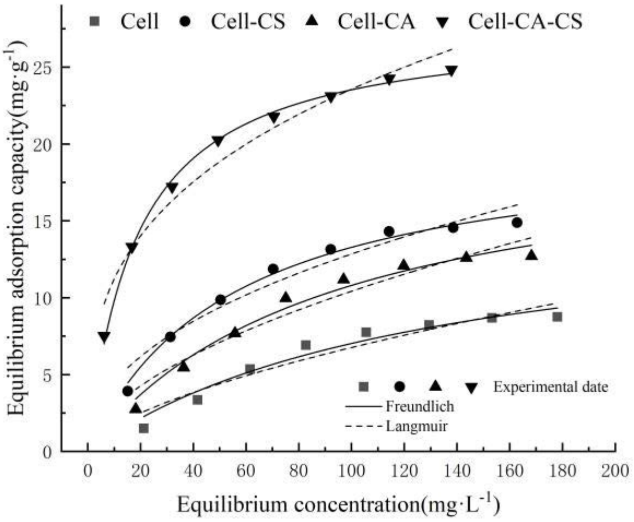


Fig. 6. Adsorption isotherms curves of cellulose materials for Cd(II) at 298 K, pH = 5.0.

and 19.97 mg g^{-1}) than that of the $Q_{e,1}$ from pseudo-first-order model. It was guessed that the adsorption process of cellulose materials for Cd(II) was a multiple adsorption process dominated by chemical adsorption, also including covalent bond force and ion exchange according to the structure characteristics of cellulose, which were consistent with the previous researches of kinetic fitting model of Cd(II) adsorption process in wastewater [27,28].

3.5. Adsorption isotherms

The adsorption isotherms curve of cellulose materials for Cd(II) in water is shown in Fig. 6. The capacity of equilibrium adsorption of cellulose materials for Cd(II) increased with the increase of the initial concentration of Cd(II) in the solution at the temperature 298 K and the cellulose dosage 2.5 g L^{-1}. When the initial concentration of Cd(II) in the solution increased from 25 to 200 mg L^{-1}, the equilibrium adsorption capacity of Cell, Cell-CS, Cell-CA and Cell-CA-CS for Cd(II) increased from 1.49, 3.92, 2.75 and 7.52 mg g^{-1} to 8.75, 14.75, 12.71 and 24.84 mg g^{-1}, respectively.

The models of Langmuir and Freundlich were used to fit the adsorption isotherm of cellulose materials for Cd(II) in water (as shown in Table 3). Both of Langmuir and Freundlich equations could be used to described the adsorption thermodynamic process, and the Langmuir equation had a better fitting result ($R > 0.95$, $p < 0.01$). At the temperature of 298 K, the maximum capacity of

Table 3
Fitting results of Langmuir and Freundlich isotherm models

Sample	T (K)	Langmuir			Freundlich		
		q_m (mg g^{-1})	K_L (L mg^{-1})	R	K_F (L mg^{-1})	n	R
Cell	288	14.982	0.007	0.976**	0.377	1.631	0.950**
	298	16.094	0.008	0.977**	0.393	1.618	0.953**
	308	20.001	0.008	0.982**	0.346	1.501	0.964**
Cell-CS	288	20.461	0.010	0.981**	0.663	1.719	0.956**
	298	20.524	0.018	0.995**	1.578	2.196	0.967**
	308	22.065	0.021	0.996**	1.986	2.307	0.990**
Cell-CA	288	20.686	0.009	0.973**	0.689	1.728	0.944**
	298	20.772	0.010	0.988**	0.809	1.802	0.964**
	308	20.878	0.011	0.995**	0.900	1.803	0.979**
Cell-CA-CS	288	25.641	0.054	0.996**	5.442	3.332	0.944**
	298	27.873	0.057	0.998**	5.334	3.099	0.977**
	308	28.222	0.062	0.995**	5.897	3.234	0.979**

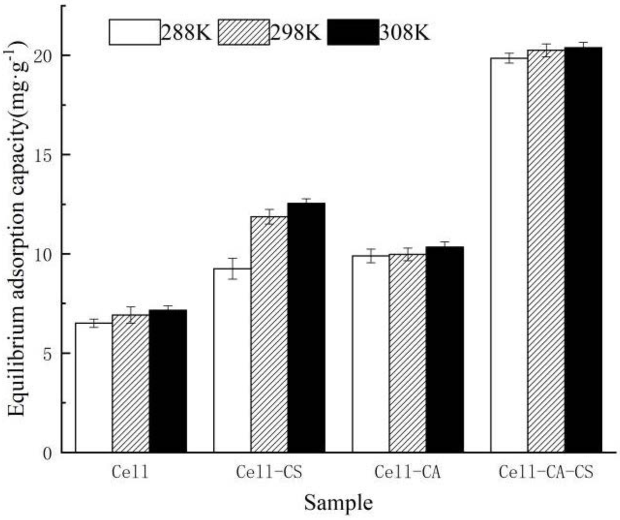


Fig. 7. Adsorption capacity of cellulose materials for Cd(II) at 288 to 308 K, pH = 5.0.

theoretical adsorption of Cell, Cell-CS, Cell-CA and Cell-CA-CS for Cd(II) obtained from Langmuir model were 17.45, 23.37, 23.46 and 36.00 mg g^{-1}, respectively, which were closer to that measured in the test. It indicating that the adsorption of Cd(II) in water by cellulose materials may be a process of monolayer adsorption. In addition, the "n" value in Freundlich model for Cell-CA-CS was greater than 1, which indicating that the composite modified cellulose "Cell-CA-CS" had the best adsorption effect for Cd(II) [29].

Temperature has an effect on the adsorption process. The adsorption capacity of cellulose materials for Cd(II) in water at different temperatures of 288, 298 and 308 K is shown in Fig. 7. The equilibrium adsorption capacity of the cellulose material for Cd(II) increased with the temperature when the initial concentration of Cd(II) is 100 mg L^{-1}, the dosage of cellulose is 2.5 g L^{-1} and the temperature is in the range of 288–308 K. Because of the temperature increased may promoted the diffusion rate of molecules in the solution and further stimulate some active sites on the surface of the cellulose, and resulted in the increase of the equilibrium adsorption capacity.

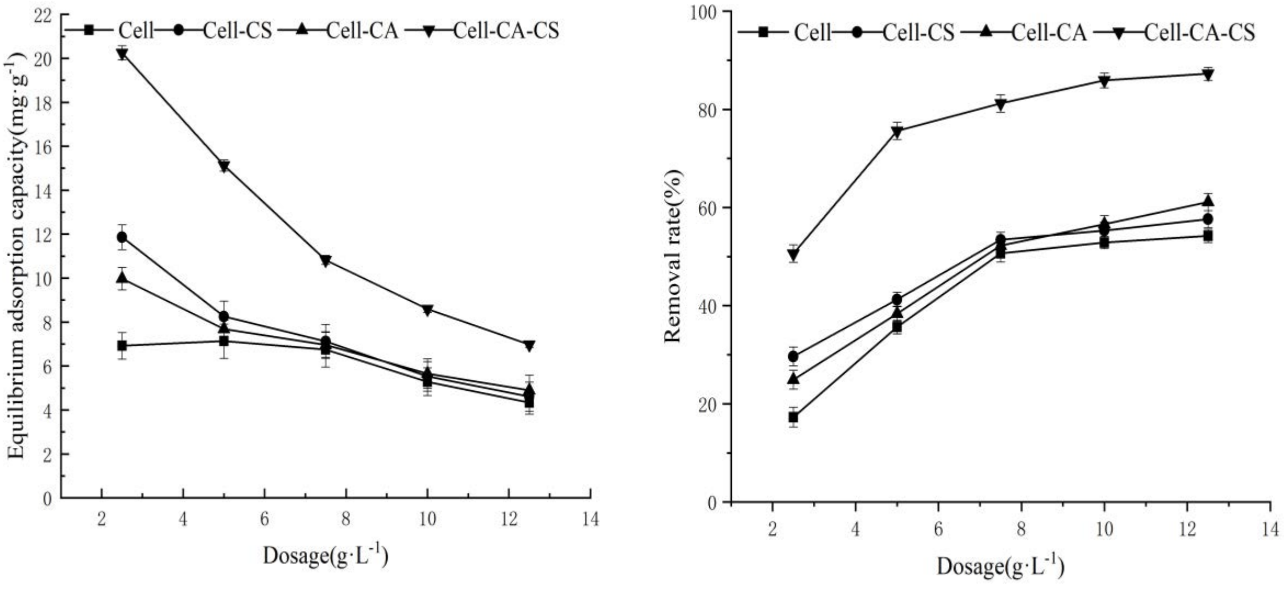
The thermodynamic parameters of adsorption of cellulose materials for Cd(II) is shown in Table 4. The value of ΔG were less than zero and the absolute value of ΔG was in the ranged of 0–20, which indicated that the adsorption process was a spontaneous physical adsorption process. In addition, the values of ΔH and ΔS were all greater than zero, which indicated the adsorption process was an endothermic reaction and the chaos increased. Consequently, it assumed that the adsorption process of Cd(II) in water by Cell, Cell-CS, Cell-CA and Cell-CA-CS were the process of disordered, spontaneous and endothermic reaction.

3.6. Influence of dosage

Exploring the effect of dosage may help improve the utilization rate of cellulose material. The effect of dosage on the adsorption capacities of cellulose materials for Cd(II) in the range of 2.5–12.5 g L^{-1} is shown in Fig. 8. The equilibrium adsorption capacity of Cell for Cd(II) increased firstly and then gradually decreased with the increased of the dosage. When the dosage of Cell was 5.0 g L^{-1}, the maximum adsorption capacity was 7.13 mg g^{-1}. The equilibrium adsorption capacity of Cell-CS, Cell-CA and Cell-CA-CS for Cd(II) decreased with the increase of dosage. The maximum adsorption capacity was 11.87, 9.97 and 20.25 mg g^{-1} for Cell-CS, Cell-CA and Cell-CA-CS at the dosage of 2.5 g L^{-1}, respectively. Furthermore, the adsorption rate of cellulose materials for Cd(II) increased rapidly with the increased of the dosage, however, with the increase of dosage, the degree of increase of adsorption rate slowed down. With the dosage increased from 2.5 to 12.5 g L^{-1}, the adsorption rate of Cell, Cell-CS, Cell-CA and Cell-CA-CS increased from 17.3%, 29.7%, 24.9%

Table 4
Fitting results of thermodynamic

Sample	ΔG (kJ mol^{-1})			ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})
	288 K	298 K	308 K		
Cell	–4.66	–5.15	–5.32	4.87	0.03
Cell-CS	–14.66	–15.80	–16.94	18.2	0.11
Cell-CA	–5.26	–5.70	–6.14	7.40	0.04
Cell-CA-CS	–9.55	–10.02	–10.57	5.11	0.05



(a) (b)

Fig. 8. Absorption capacity of cellulose materials for Cd(II) in different dosage at 298 K.

and 50.6% to 54.2%, 57.6%, 61.1% and 87.3%, respectively. Due to the increasing dosage provided more active site and lead to the adsorption amount of Cd(II) increased [30].

3.7. Influence of pH

The value of pH of the solution may change the surface properties and morphology of the celluloses [31]. As shown in Fig. 9, the adsorption capacity of Cell, Cell-CS, Cell-CA and Cell-CA-CS for Cd(II) increased significantly with the increase of the solution pH, and the most increased capacity occurred at pH value between 3–5. The adsorption capacity increased from 2.67, 5.11, 3.76 and 11.59 mg g^{-1} to 7.12, 11.84, 9.95 and 20.08 mg g^{-1} for Cell, Cell-CS, Cell-CA and Cell-CA-CS, respectively, at the pH value of 3–5. The action of H$^+$ in the solution caused the surface of cellulose protonating at lower pH, forming competitive adsorption with Cd(II) in the solution and inhibiting the adsorption of Cd(II). When the pH value in the solution was greater than 7, the metal ions were easy to precipitate or react with OH$^-$ in the solution, which was not conducive to the adsorption of adsorption materials [32]. Most of the adsorption materials will weaken the adsorption effect of heavy metal ions in the strong acid and alkali environment [32].

3.8. Desorption and regeneration

The desorption and regeneration teat was carried out to evaluate the effectiveness of adsorption, and the regeneration efficiency of different cellulose materials is shown in Table 5. After 5 times of desorption treatments, the removal percentage of Cd(II) in the water for Cell, Cell-CS, Cell-CA and Cell-CA-CS reduced from 53.6%, 57.6%, 61.1%, 87.35% to 38.2%, 42.9%, 30.1%, 56.4%, respectively. This indicated that even though the adsorption performance significantly reduced indeed after desorption, the Cell-modified had a certain regeneration performance after being treated with HNO_3 solution. This may the reason that a part of Cd(II) did not desorbed from cellulose materials due to the formation of stable complexes-Cd(II) through chelation, which difficult to completely desorption the Cd(II) with dilute acid. Although the adsorption capacity of cellulose

Table 5
Regeneration efficiency of Cd(II) from cellulose materials

Usage count	Cell	Cell-CS	Cell-CA	Cell-CA-CS
1	53.2%	57.6%	61.1%	87.3%
2	49.8%	52.6%	55.8%	81.8%
3	44.3%	47.7%	48.2%	77.6%
4	41.7%	45.5%	39.6%	68.9%
5	38.2%	42.9%	30.1%	56.4%

has decreased after recycling, it was feasible to use its adsorption capacity in actual wastewater treatment, as well as find a suitable analytical solution for desorption.

3.9. Probable mechanism analysis

This study demonstrated that the adsorption capacity of cellulose was increased to varying degrees after single and composite modification by chitosan and citric acid. Cell-CS was observed that chitosan was attached to the surface of Cell, and chitosan itself had good adsorption performance for Cd(II); Cell-CA was observed that the surface of Cell modified with citric acid increased C=O, C=O interacts with Cd(II) to achieve adsorption; Cell-CA-CS has both the characteristics of Cell-CS and Cell-CA, so it was possible to improve the adsorption capacity of Cell to Cd(II) in water of. At the same time, the physical adsorption capacity of chitosan to Cd(II) was greater than the interaction force between C=O and Cd(II), and the adsorption capacity of Cell-CS was greater than that of Cell-CA. In addition, the adsorption performance of cellulosic materials is affected by many factors. With the increase of temperature, dosage and pH, the active sites and electrostatic force on the surface of cellulose materials increase, which was conducive to the effect of cellulose materials on Cd(II) of adsorption.

4. Conclusions

In this paper, cellulose was extracted using corn straw as the raw material. Then the cellulose used to prepare three cellulose materials (Cell-CS, Cell-CA and Cell-CA-CS) by citric acid, chitosan single and compound modification. The modification of citric acid and chitosan introduced C=O groups and N–H characteristic peaks on the surface of cellulose, respectively. The adsorption kinetics of Cd(II) in water by the cellulose materials could be described by pseudo-second-order kinetic model, and the adsorption isotherms can be described by Langmuir model. The adsorption process was spontaneous, endothermic and disordered. Furthermore, composite modified cellulose had higher adsorption capacities and performance for Cd(II) than single modified cellulose. With the increase of temperature, adsorption solution pH (in the range of 2–7) and dosage, the adsorption capacity of Cd(II) in water by cellulose materials increased gradually. The results of desorption and regeneration demonstrated that cellulose materials still had adsorption capacity for Cd(II) after repeated 5 times. In general, it was feasible and had great potential to extract cellulose from corn straw for wastewater treatment. In the future, the adsorption capacity of cellulose materials for the treatment of various types of wastewater will be further improved.

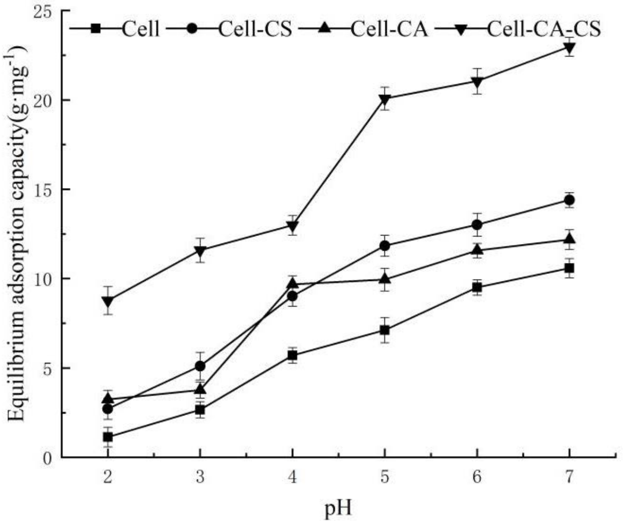


Fig. 9. Absorption capacity of cellulose materials for Cd(II) under different pH at 298 K.

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