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Adsorption of heavy metal cadmium(II) ions using chemically modified corncob: mechanism, kinetics, and thermodynamics

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ABSTRACT

As one of the most produced agricultural wastes, corncob is considered for the removal of metal ions from aqueous solution as a low-cost biosorbent. This study reports the preparation of polyacrylamide grafted corncob and its excellent adsorptivity for Cd(II) ions in aqueous solution compared with crude corncobs. The adsorbents were characterized with scanning electron microscopy, BET, Fourier transform infrared, thermo gravimetric analysis, and swelling study. The higher Cd(II) uptake of polyacrylamide grafted corncob than crude corncob was due to increased surface area and number of functional groups (–NH_2) that could complex with metal ions. Higher thermal stability and better swelling property in salt solution were achieved for corncobs after grafting modification. Experimental data greed with the Langmuir isotherm, and maximal adsorption capacities of polyacrylamide grafted and crude corncobs were 18.35 and 4.96 mg g^{-1}, respectively. Kinetics study revealed that adsorption followed pseudo-second-order kinetics, and that chemical sorption was the rate-controlling step. Thermodynamic parameters (free energy ΔG, enthalpy ΔH and entropy ΔS) showed that adsorption was a spontaneous endothermic process.

Keywords: Corncob; Graft copolymerization modification; Heavy metal; Cadmium ions; Adsorption kinetics; Adsorption thermodynamics

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1. Introduction

With rapid industrialization and urbanization in recent decades, China, especially in southwest and coastal areas, are facing serious challenges of heavy metal contamination, which is derived from mining, smelting, the electroplating industry, the petrochemical industry, printing, agriculture, municipal waste, and aquaculture [1]. As one of the major toxic heavy metals, cadmium and its polluted wastewater are causing a serious threat to human health and arousing considerable concern of people and governments [2]. Cadmium in water migrated to the human body through various pathways, such as skin contact, direct ingestion, diet through the water-food chain and water–soil–food chain, inhalation, and oral intake [3]. Cadmium ions in the human body that exceed the

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micronutrient level can cause numerous diseases, such as hypertension, bone lesions, renal dysfunction, lung failure, oesophageal cancer, postmenopausal breast cancer, and liver cancer [2,3]. Therefore, removing cadmium ions from wastewater prior to its emission to the environment is important.

Various conventional treatment technologies, including chemical precipitation, ion exchange, membrane separation, and electrochemical removal, have been used to remove cadmium ions from aqueous solutions [4]. However, these technologies present certain significant disadvantages, such as incomplete removal, production of toxic sludge, high energy requirements, and maintenance cost [4,5]. As one of the most well-known and effective technologies because of its high efficiency and selectable sorbents, adsorption, which removes heavy metals from aqueous solutions by using adsorbents, has been widely studied in past few decades [5]. Activated carbon has been frequently used to remove metal ions from aqueous solutions as an adsorbent, but its high cost restricts its use [6]. Hence, an increasing number of scholars are interested in seeking low-cost alternatives to conventional adsorbents. Recently, agricultural waste or by-products, such as rice husk, sugarcane bagasse, sawdust, orange wastes, and corn stalks, are extensively researched as inexpensive adsorbents [2,6–8]. Corncob is a kind of common agricultural waste that is produced in large quantity and budget, and approximately 18 kg of corncob is achieved with 100 kg of corn grain. Vaughan et al. [9] have studied the chemical composition of corncob and revealed that composition mainly includes cellulose, hemicellulose, and a small quantity of lignin. Cellulose is a straight chain molecule polymer that consists of units of anhydroglucose, as well as several active groups such as hydroxyl, aldehydes, carboxyl and ether groups [10,11]. These functional groups are capable of binding heavy metals by contributing an electron pair to constitute complexes with metal ions in aqueous solutions [10,12]. Therefore, corncobs could be used to remove cadmium ions in solution as low-cost adsorbents. However, raw corncobs present a low adsorption capacity because of intramolecular and intermolecular hydrogen bonds between hydroxyl groups within cellulose chains, which tend to be ranked parallel and constitute a crystalline macromolecular structure that limits the activities of the functional groups [10]. In recent years, numerous scientists have studied the chemical modification of sorbents based on agricultural wastes to improve their adsorption capacities for metal ions in solution [11]. Furthermore, the majority of modifications to agricultural waste adsorbents are achieved by immersion in inorganic and organic chemical solutions, such as hydrochloric acid, sodium hydrate, and citric acid [7,9]. Several experts have recently found that graft copolymerization has become a new effective modification method for adsorbents such as sugarcane bagasse [2], Corn stalk [13], and guar gum [14]. The grafting modification of adsorbents can improve their metal ion uptake by increasing the number of active functional groups from side chains, which were covalently attached to the main chains of polymer backbones [13]. However, studies on graft copolymerization modification of corncobs have rarely been reported.

In this study, crude and chemically modified corncobs were studied as sorbents to remove Cd(II) ions from aqueous solution, and graft copolymerization was used as an efficient method to modify corncobs. O'Connell et al. [5] reported that the chemical initiation of grafted reaction is a good technique that is relatively cheap, easily to apply, and contains a small amount homopolymer. Amide groups (–NH_2) present superior affinity toward metal ions, because their nitrogen atoms are strong Lewis base [15,16]. Hence, this research selected a potassium permanganate ($KMnO_4$)–sulfuric acid (H_2SO_4) redox system as initiator and acrylamide (Am) as monomer in graft copolymerization. Characterizations of adsorbents were obtained by scanning electron microscopy (SEM), Fourier transform infrared (FTIR), surface area and pore size analysis, thermo gravimetric analysis (TGA), differential thermogravimetry (DTG), and swelling study. A series of adsorption experiments on influence factors, adsorption isotherms, kinetics, and thermodynamics was also studied.

2. Materials and methods

2.1. Materials and chemicals

Crude corncobs (CS) was obtained from a farm in Beijing City, China. After washing with fresh water and drying in the sun, the materials were cut into small particles, and 4–6 mm sizes were selected using sieves, and then washed three times with deionized water and dried in an oven at 50℃ until constant weight for further pretreatment.

Cadmium(II) stock solution was prepared from cadmium nitrate in deionized water. All working solutions were prepared by diluting the stock solutions with deionized water. Diluted hydrochloric acid and sodium hydroxide solution was used for adjusting pH. An orbital shaker was used for adsorption experiments. The concentration of cadmium(II) was determined by an inductively coupled plasma optical emission spectrometer from the Research Center for

Eco-Environmental Sciences, Chinese Academy of Science. High-purity nitrogen (99.999%) was purchased from a Beijing company. Other chemicals and reagents used in this study were of analytical grade and obtained from Sinopharm Chemical Reagent Beijing Co. Ltd.

2.2. Adsorbent preparation

Grafting modification of CS was conducted in a 500 ml four-neck flask according to the following procedures: first, dried corncobs (3.00 g) were immersed in 300 ml of deionized water at 40℃. The liquid was uniformly mixed by electric mixer, and purified N_2 was passed through the vessel for 15 min, then $KMnO_4$ (0.95 g) as initiator was added to the flask, and the flask contents are stirred for 60 min. Secondly, acrylamide (4.26 g) was used as monomer, N,N ′-methylenebisacrylamide (MBA) (0.03 g) and concentrated H_2SO_4 (0.10 ml) were added as cross linker and catalyst, respectively, and the mixture was stirred continuously for 60 min. Finally, after the graft copolymerization, the modified samples (CSGC) were filtrated by suction machine to remove the remaining liquid, and washed thoroughly with ethanol (95%) and copious amounts of deionized water to remove the acrylamide homopolymer. Then, the product was dried to a constant weight at 50℃ in a vacuum oven for further measurements.

2.3. Adsorbent characterization

The superficial morphologies of CS and CSGC were examined by SEM (JSM-6510A). The BET surface area and pore size were measured using a surface area and porosity analyzer (GAPP V-Sorb4800P) with N_2-adsorption techniques. FTIR analysis was conducted on a Nicolet Nexus FTIR spectrometer. The functional groups of CS and CSGC were characterized at a wave number range of 4,000–500 cm^{-1}, the error of wave number is ±5 cm^{-1}. TGA and DTG measurements were carried out under nitrogen flow using a microcomputer differential thermal balance (HCT-3, China). The sample mass was approximately 8 mg, and the scans were run from room temperature to 900℃ at a rate of 10℃ min^{-1}. All these tests were carried out by triplicate and the results are the arithmetic average value.

2.4. Swelling study

Swelling studies were accomplished by immersing CS and CSGC in deionized water and 1% NaCl solution. The samples (0.5 g) of each were immersed in 100 ml swelling solution for 8 h at 303 K until the equilibrium swelling appeared. The swollen samples were removed from the swelling solution, wiped quickly with filter paper to remove droplets on the surface, and then weighed. The calculation formula of percent swelling ratio (P_s) is expressed as follows [17]:

$$p_s = \frac{\text{Weight of the swollen sample} - \text{Weight of dry sample}}{\text{Weight of dry sample}} \times 100 \tag{1}$$

2.5. Adsorption experiments and analysis

A series of sorption experiments was conducted in conical flasks on a shaker at a speed of 130 rpm. The experiment on pH as an influential factor was performed using 50 ml cadmium(II) solution at a concentration is 100 mg l^{-1} and 0.5 g adsorbents was placed at 303 K. That of adsorbent dosages was studied using 50 ml cadmium(II) solution with a pH of 7.0 and concentration of 100 mg l^{-1} at 303 K. The experiment on temperature as an influential factor was operated using 50 ml cadmium(II) solution with a concentration of 100 mg l^{-1} and pH of 7.0, whereas the temperature was maintained at 10, 20, 30, 40, or 50℃. The sorption isotherm experiment was executed using 100 ml cadmium (II) solution containing 0.5 g sorbents. Adsorption kinetics experiment was conducted using 200 ml cadmium(II) solution with a concentration of 50 mg l^{-1}, pH of 7.0, and 0.5 g adsorbents added. The metal adsorption capacity, q_e (mg g^{-1}), and percentage of Cd(II) ion adsorbed for all sorption experiments were calculated using the following mass balance equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

$$\text{Cd(II) adsorbed } \% = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{3}$$

where C_0 and C_e are the initial and equilibrium concentrations (mg l^{-1}), V is the volume of cadmium (II) solution (l), m is the quality of adsorbents (g).

All the determinations were carried out triplicate and the value reported was the arithmetic average. Meanwhile, 0.01 M NaOH or HNO_3 solution was added to the aqueous solution to keep the pH constant throughout the adsorption.

3. Results and discussion

3.1. Modification mechanism

The mechanism of grafting modification for CS is revealed in Fig. 1(a). Cellulose is a large, linear-chain

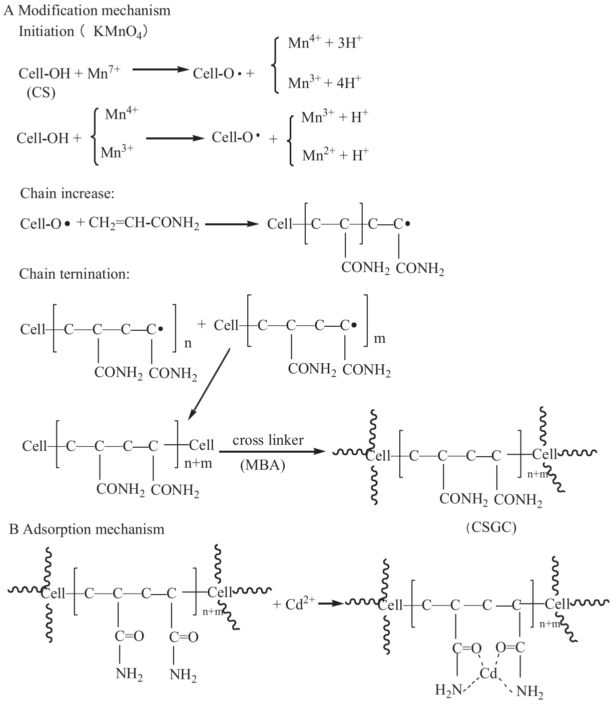

Fig. 1. Modification and adsorption mechanism of cellulose of CS.

polymer with large numbers of –OH groups, which provide reaction sites for graft copolymerization [13]. The whole reaction process includes initiation, chain increase, chain termination, and cross linker. In the initiation step, accompanied by the changes in the valences of Mn ions (initiator $KMnO_4$), free radicals were formed at the hydroxyl sites in cellulose structure (CS). Then, the functional groups ($–NH_2$) from the monomer (Am) were introduced into CS, to which the grafting reaction of acrylamide and free radical sites in cellulose are attributed. As a result, the covalent bonds were shaped between monomer and cellulose to produce a chain increase reaction until chain termination occurred and a dimensional cross-linked structure of CSGC is formed after the addition of MBA as cross linker.

3.2. Adsorption mechanism

Metal ions binding in biosorbents may occur by several mechanisms such as adsorption, complexation, chelation, coordination and ion exchange [18,19]. The chemical composition of corncob includes several active groups such as hydroxyl, aldehydes and carboxyl, which are capable of binding heavy metals [11]. Thus, the adsorption mechanism of CS may be the complexation between Cd^{2+} ions and these active groups in corncob and adsorption due to its high surface areas. Whereas the adsorption mechanism of CSGC is mainly interpreted as forming chelates between Cd(II) ions and functional groups ($–NH_2$) in CSGC. This formation is due to the nitrogen atom of $–NH_2$ being a strong Lewis base owing to its vacant double electrons, which could provide a complex for coordination with chemical entities that are low in electrons, such as Cd(II) ions (Fig. 1(b)) [2]. The changes of peaks which represent $–NH_2$ group in FTIR analysis also confirmed this type of mechanism.

3.3. Adsorbent characterization

3.3.1. SEM analysis

The surface morphologies of CS and CSGC before cadmium adsorption were scanned by SEM, which are shown in Fig. 2. Comparison of Fig. 2(a) and (b) shows that CS presents a relatively smooth fiber surface structure, whereas the surface of CSGC has become rough and folded, which was attributed to functional groups ($–NH_2$) grafted on the surfaces of CSGC after graft copolymerization modification, which increased the specific surface area of corncobs [20]. As can also be seen from Fig. 2(c), the appearance of numerous pores on CSGC provided channels and more adsorption sites for Cd(II) from aqueous solution. These sorbent changes are favorable for cadmium adsorption. Meanwhile, the apparent morphology of CSGC after adsorbing Cd(II) are also shown in Fig. 2(d) by SEM analyses. Compared with CSGC before sorption, the surfaces of CSGC after adsorption exhibit some squamae as a result of cadmium ions being adsorbed on the CS of CSGC [21,22].

3.3.2. BET surface area and pore size analysis

As shown in Table 1, the surface area of CS and CSGC were 0.521 and 2.365 $m^2 g^{-1}$, respectively. Therefore, the surface area of sorbent increased by 3.5 times after grafting modification. The total pore volume of CSGC showed no significant change comparison with that of CS, but the percentage of micropore of CS and CSGC were 0.1 and 1.6, respectively. These values are favorable toward adsorption and are consistent with the result of SEM.

3.3.3. FTIR analysis

The FTIR spectra of CS and CSGC are given in Fig. 3(a). From the FTIR spectra of CS, a strong peak that is evident at 3,426 cm^{-1} is attributed to the stretching vibration of hydroxyl group, whereas a

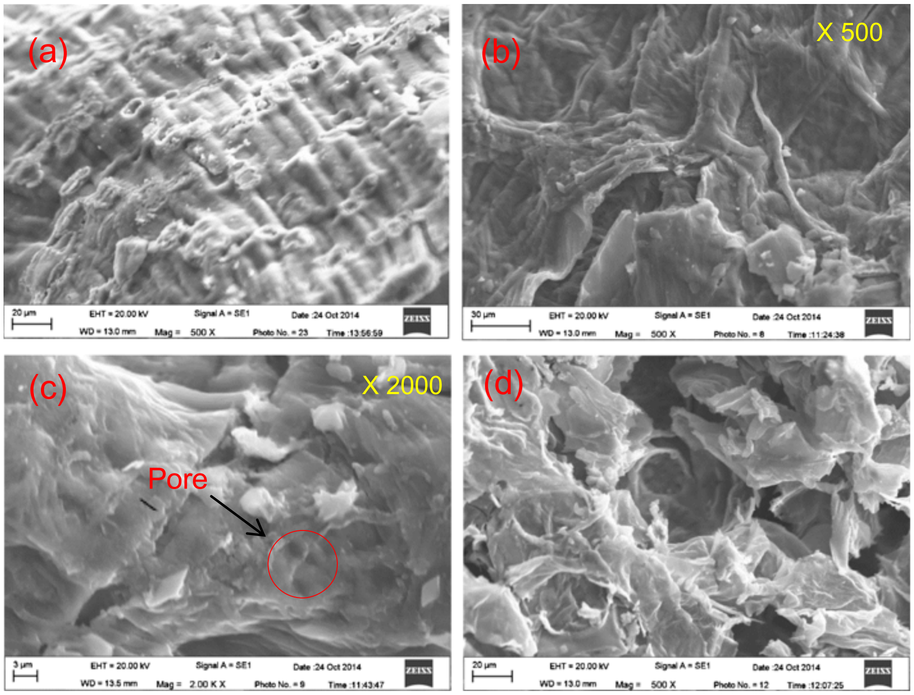

Fig. 2. SEM images of the samples: (a) for CS and (b), (c) for CSGC before adsorption, and (d) for CSGC after adsorption.

Table 1
BET surface area and pore size analysis of CS and CSGC

		Pore volume (100%)			
Adsorbent	BET surface area ($m^2\ g^{-1}$)	Micropore (<2 nm)	Mesopore (2–50 nm)	Macropore (>50 nm)	Total pore volume ($cm^3\ g^{-1}$)
CS	0.521	0.1	8.7	91.2	0.073
CSGC	2.365	1.6	5.6	91.8	0.074

smaller peak at 2,923 cm^{-1} is due to the C–H stretching vibrations of $–CH_2$. The absorption peaks at 1,730 and 563 cm^{-1} in CS, and 1,728 and 530 cm^{-1} in CSGC are assigned to the C=O stretching vibrations of hemicellulose and β-glucoside [23]. The peak of CS at 1,633 cm^{-1} corresponds to O–H scissor vibrations from bonded water molecules, and the peaks at 1,375, 1,253, 1,103, 1,046 and 898 cm^{-1} are attributed to alcohol hydroxyl (–OH) bending vibration and C–O–C bond stretching vibration [24]. The appearance of peaks at 2,360 cm^{-1} both in CS and CSGS may be assigned to the asymmetric stretching vibration of CO_2. In CSGC, the peaks at 2,924 and 2,857 cm^{-1} are due to antisymmetric and symmetric C–H stretching vibration, respectively. Compared with CS, the emergence of new peaks at 1,668 and 1,604 cm^{-1} of CSGS are assigned to C=O stretching vibration and N–H bending vibration from amide [24], and the peaks at 1,441 and 1,112 cm^{-1} are caused by CH_2 vibration and C–O stretching vibration. In addition, the broad peak at 3,413 cm^{-1} is expected to be overlapping peaks caused by O–H stretching band of hydroxyl group and N–H stretching band of amide group [25], significant decrease of peaks at 3,426 and 1,046 cm^{-1} is also expected to be the result of the reaction of hydroxyl and amide. Therefore, the monomer (Am) successfully introduced functional groups ($–NH_2$) into CSGC after graft modification.

Meanwhile, the comparison of infrared spectra of CSGC before and after adsorption is shown in Fig. 3(b) and (c). After the adsorption of cadmium ion, the peak at 3,413 cm^{-1} is shifted to 3,432 cm^{-1}, which may be due to the broad peak at 3,413 cm^{-1} overlapping peaks caused by O–H stretching vibration and

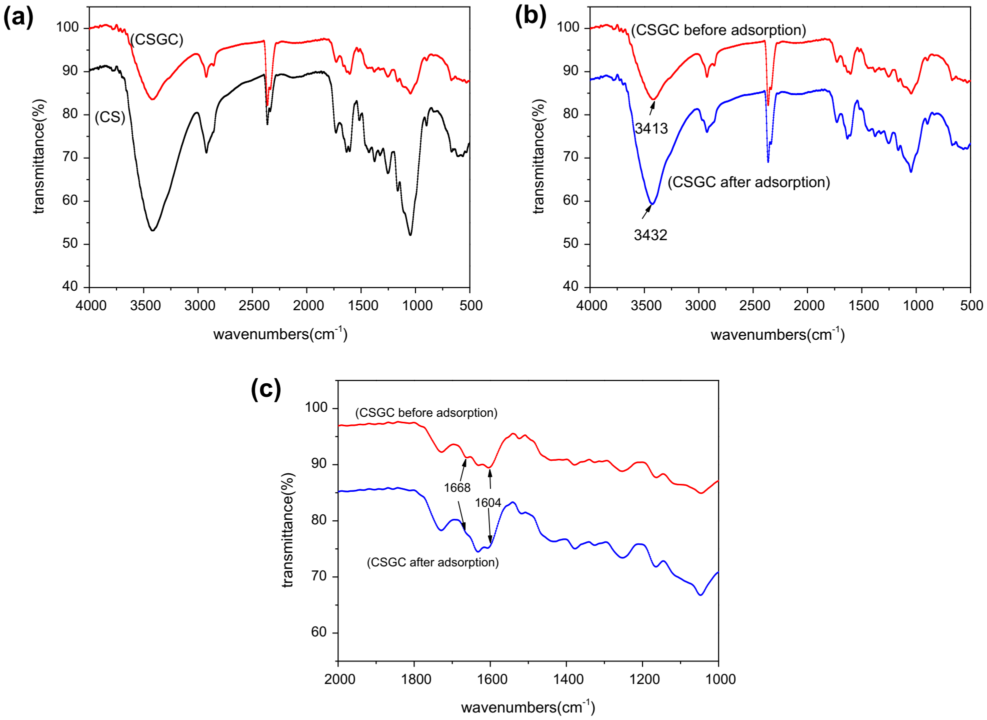

Fig. 3. FTIR spectra of the samples: (a) for CS and CSGC, (b) for CSGC before adsorption and after adsorption, (c) is the partial view of (b) at 2,000–1,000 cm^{-1}.

N–H stretching vibration. Moreover, the peak of N–H stretching vibration weakened or disappeared as a result of the formation of coordination chelates between amide groups in CSGC and cadmium ion in the aqueous solution by adsorption. In addition, we can see from Fig. 3(c) that the peak at 1,668 cm^{-1} induced by C=O stretching vibration of acylamino almost disappeared, and the peak at 1,604 cm^{-1} caused by N–H stretching vibration decreased, which further proved that the adsorption of Cd(II) for CSGC is mainly attributed to the functional groups (–NH_2).

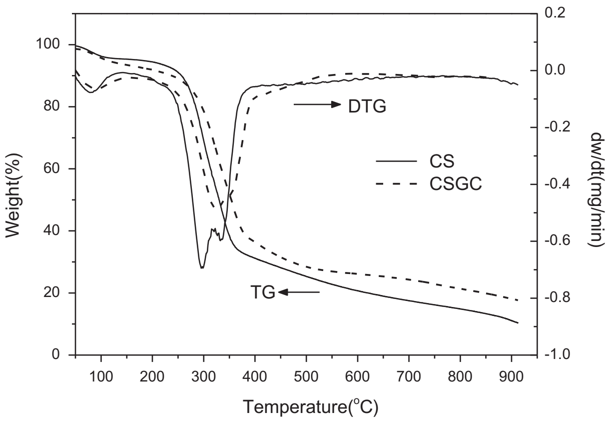

Fig. 4. TG and DTG curves of CS and CSGC.

3.3.4. Thermo gravimetric analysis

The thermal stabilities of CS and CSGC were estimated by TG and DTG curves in Fig. 4. It could be indicated that the thermal stability of CSGC was better compared with that of CS. The decomposition temperatures, that is, the initial decomposition temperature (T_{Di}) and the temperature at the maximum rate of weight loss (T_{max}), were determined from TG curves. The T_{Di} value of CS was approximately 248 ℃, whereas, in the case of CSGC, T_{Di} value was 275 ℃. In the TG curve, an initial slight weight loss of 5.5% was observed in CS between 50 and 180 ℃, and a weight loss of 8.0% was seen in CSGC between 50 and 200 ℃, which may be caused by the volatilization of physically adsorbed water in samples. The thermal stability of the polymer usually was indicated by using the values of T_{max} [26]. The values of T_{max} were found to be 295 and 330 ℃ for CS and CSGC, with the higher value of T_{max} of CSGC indicated its better thermal stability. In addition, the samples were not completely degraded in this temperature range. For CSGC, a weight percent of about 18.6 was retained at 900 ℃, whereas for CS, a weight percent of about 10.5 at 900℃ was maintained. The DTG curves also showed that small peaks occurred in the range of 50 and 150℃ for both CS and CSGC were attributed to the loss of physically adsorbed water. The absolute value of maximum rate of degradation for CSGC was lower and occurred at 330℃, compared with that for CS, which occurred at 295℃. This phenomenon further confirmed that a higher thermal stability was achieved for CSGC after graft modification.

3.4. Adsorbent swelling studies

The swelling results of CS and CSGC were showed in Fig. 5. The higher hydrophilicity of the hydroxy group than acylamino could be attributed to higher stability degree of the hydrogen bond formed by the oxygen atom and hydrogen atom of water molecule than that formed by nitrogen atom [17]. The percent swelling ratio of CSGC was slightly lower than CS in deionized water as a result of the amount of acylaminos increased and hydroxy groups decreased after graft modification. However, in 1% NaCl solution, the percent swelling ratio of CSGC was greater than CS, indicating that the salt resistance of CSGC was increased and favorable for the removal of metal ions in practical salt wastewater. In addition, this find indicates a greater capacity of water absorbent can increase the opportunities of contact between metal ions and adsorption sites. In addition, the percent swelling ratios of both CS and CSGC were shown to decrease in sodium chloride solution compared with that in deionized water in Fig. 5(c) and (d). The percent swelling ratios of CS decreased by 37%, whereas that of CSGC decreased by only 12%, which further confirmed that graft copolymerization strengthened the salt resistance of CSGC in solution.

3.5. Influential factors of adsorption

3.5.1. Effect of initial pH

To study the effects of initial pH values on the adsorption process, the experiments were performed over a pH value range from 2.0 to 7.0. The results are presented in Fig. 6(a). The adsorption capacities of Cd(II) of CS and CSGC rapidly increased as the initial pH value increased from 2.0 to 3.0. This change could be attributed to the competitive adsorption behavior between the H_3O^+ ions and Cd(II). In addition, more H_3O^+ ions occupied the adsorption sites on sorbents at a lower pH value, which lead to

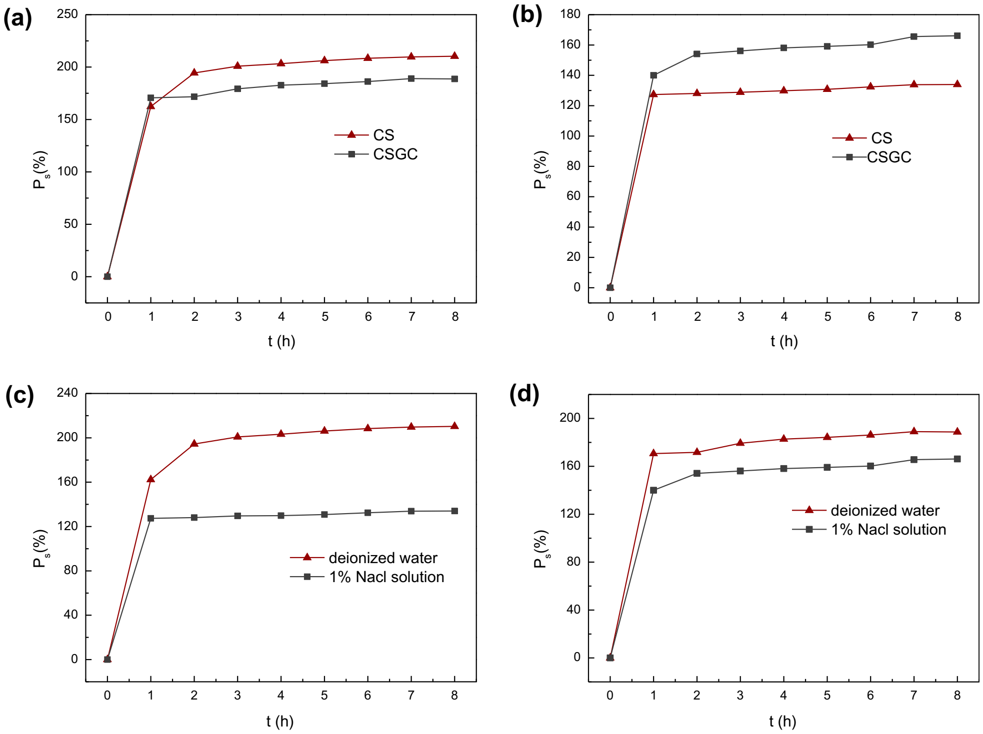

Fig. 5. Swelling capacity of adsorbents: (a) is in deionized water, (b) is in 1% NaCl solution, (c) is for CS, and (d) is for CSGC.

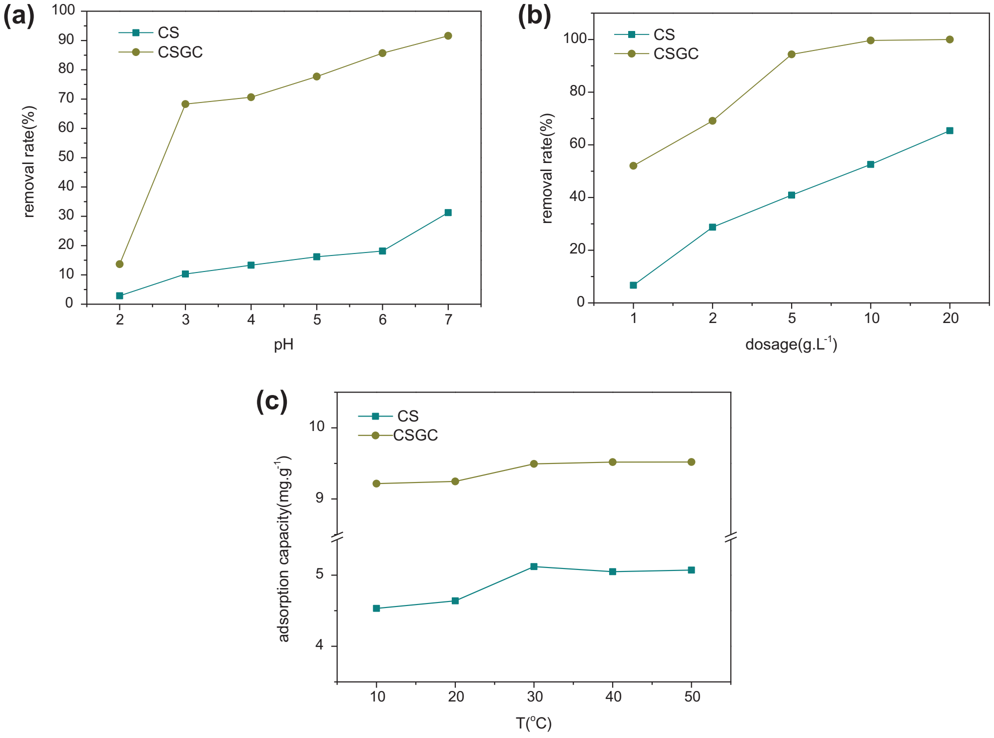

Fig. 6. Effect of initial pH (a), adsorbent dosage (b), and temperature (c) for the adsorption of Cd(II) ions onto CS and CSGC.

more cadmium ions detained in the solution [8]. However, the uptake of Cd(II) rose relatively slowly as initial pH increased in the range of 3.0–7.0, and the maximum adsorption capacity occurred at pH 7.0. The maximum uptake of Cd(II) on CS and CSGC were 3.1 and 9.2 mg l^{-1}, respectively. With the gradual increase in pH, the competitive adsorption between the H_3O^+ ions and Cd(II) was weakened as a result of the decreased concentration of H_3O^+ ions in solution. In other words, the concentration of H_3O^+ ions was considerably lower than Cd(II), so that sorbents provided more adsorption sites for metal ions rather than H_3O^+ ions [2,8]. Basing on these analyses, the pH of 7.0 was revealed to be the best choice of initial pH value for further adsorption experiments.

3.5.2. *Effect of initial adsorbent dosage*

The effect of initial adsorbent amount is shown in Fig. 6(b). From the figure, we can see that the removal rate of cadmium ions in solution increased with increased adsorbent dosage, which was attributed to increased amount of available adsorption sites and specific surface area of sorbents as a result of the increased dose of CS and CSGC [27,28]. The removal rate of metal ions on CSGC has reached 95%, whereas that on CS only reached 41% at the adsorbent dosage of 5 g l^{-1}. These results can be attributed to the functional groups (–NH_2) on CSGC enhancing the uptake of metal ions to a large degree after graft modification, wheras the adsorption capacity of cadmium ions on CS was limited without acylamino.

3.5.3. *Effect of temperature*

Fig. 6(c) shows the effect of temperature on adsorption capacities of cadmium ions on CS and CSGC. The uptake of Cd(II) ions increased gently with raising adsorption temperature from 10 to 30°C, which due to higher temperature accelerated the pervasion of Cd(II) ions in sorbents and formed more free volume inside the adsorbent particles. Meanwhile, the values of the heat of adsorption are $\Delta H = 2.382$ and 0.719 kJ mol^{-1} (Table 2), for the CS and CSGC, respectively. Thus, the adsorption procedures of metal ions on CS and CSGC were endothermic in nature [18,29]. However, the adsorption capacity of Cd(II) ions on CSGC had a slight increase, and that on CS presented no significant changes as adsorption temperature increased from 30 to 50°C, which due to the heat of adsorption is very low, and adsorption on CSGC was

Table 2
Thermodynamic parameters for the adsorption Cd(II) on CS and CSGC

Adsorbent	T (K)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} k^{-1})
CS	283	−8.973	2.382	0.042
	293	−9.934		
	303	−9.914		
	313	−10.205		
	323	−10.573		
CSGC	283	−10.643	0.719	0.040
	293	−11.028		
	303	−11.470		
	313	−11.855		
	323	−12.235		

mainly chemical rather than physical [14]. Apparently, 30℃ was the optimal choice of adsorption temperature value for further adsorption experiments.

3.6. Adsorption isotherms

The adsorption isotherms can reveal the effect of different initial cadmium ion concentrations on the adsorption capacity at adsorption equilibrium position [30]. Among all adsorption isotherm equations, Langmuir and Freundlich are the most commonly applied [13,39]. The theoretical Langmuir isotherm assumes that a monolayer adsorption is present on a homogenous surface, that each adsorbate molecule has a unique adsorption site to be bound without migration, and that the adsorption energy of all adsorption sites is constant [31].

The Langmuir equation can be showed below:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \tag{4}$$

where C_e (mg l^{-1}) and Q_e (mg g^{-1}) are the equilibrium concentration and uptake capacity of adsorbate, respectively, Q_m (mg g^{-1}) is the maximum uptake capacity of cadmium ion, K_L is the Langmuir adsorption constant related to the energy of adsorption.

The Freundlich isotherm model assumes that the adsorption appears on a reversible heterogeneous surface and the adsorption energy of a metal ion binding to a site of adsorbents related to whether or not the adjacent sites are already occupied [13,32]. The equation of the isotherm model is presented as follows:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{5}$$

where Q_e and C_e have the same meanings as mentioned earlier, K_f is the constant which related to the adsorption capacity of adsorbents and $1/n$ is the Freundlich adsorption constant which related to the intensity of adsorption.

The values of Langmuir and Freundlich adsorption isotherm constants and linear regression correlations for Cd(II) adsorption of CS and CSGC are presented in Fig. 7 and Table 3. A better line-fitting effect (R^2) was observes in Langmuir adsorption isotherms for the Cd(II) adsorption rates of CS and CSGC than Freundlich isotherms model, which shows that the adsorption process mainly involves monolayer adsorption. The maximum adsorption capacities (Q_m) for Cd(II) on CS and CSGC are 5.85 and 18.47 mg g^{-1}, respectively. The adsorption effect for Cd(II) from aqueous solutions on CSGC is better than that on CS, which is attributes to the larger specific surface area and functional groups of acylamino on CSGC. Meanwhile, the adsorption parameter, K_L, can measure the stability of the complex formed between metal ions and adsorbents, and the higher the value of K_L indicates the higher stability of the formed complex [33]. The K_L values of Cd(II) adsorption from aqueous solution by CS and CSGC are 0.0195 and 0.0266. Therefore, the complex formed between Cd(II) and CSGC is more stable than that between Cd(II) and CS. Adsorption capacities of CS and CSGC are compared with some absorbents prepared from agricultural wastes in Table 4. CSGC has a higher sorption capacity for Cd(II) than some adsorption materials, including the corncob material which have studied, but lower than some others.

3.7. Adsorption kinetics

To research the diffusion rate and determine the rate-determining step during the adsorption process, three well-known kinetic models (the pseudo-first-order, second-order kinetic, and Elovich equation) are used for fitting kinetic rates of adsorption of Cd(II)

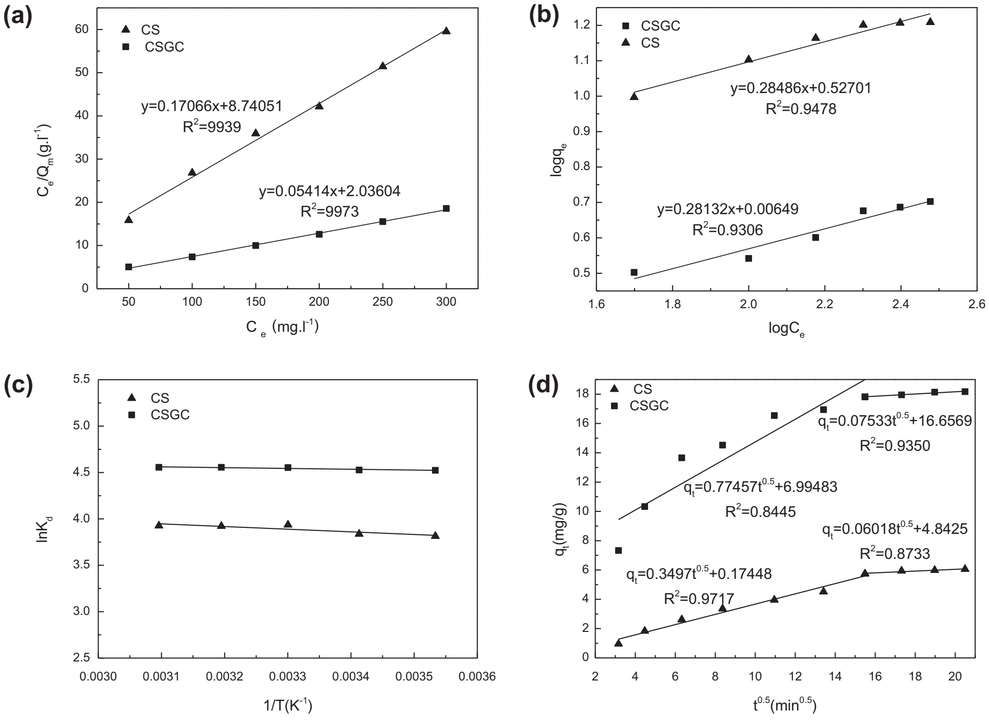

Fig. 7. Langmuir adsorption isotherm (a), Freundlich adsorption isotherm (b), Plot of ln K_d vs. $1/T$ (c) and Intra-particle diffusion model (d) for the adsorption of Cd(II) ions.

Table 3

Langmuir and Freundlich isotherm model constants and linear regression correlations for Cd(II) adsorption of CS and CSGC

	Langmuir			Freundlich		
Adsorbents	Q_m (mg g^{-1})	K_L (l mg^{-1})	R^2	K_f	n	R^2
CS	5.85	0.0195	0.9939	3.3652	3.5105	0.9478
CSGC	18.47	0.0266	0.9973	1.0151	3.5547	0.9306

from aqueous solutions by CS and CSGC. The fitting parameters of all kinetic models are presented in Table 5. The pseudo-first-order model assumes that the changes of adsorption rate depended on the number of sorption sites that are unoccupied by adsorbate numerators [30]. Its equation is given as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (6)$$

where q_t and q_e (mg g^{-1}) are adsorption amount of cadmium ions at time t (min) and equilibrium, respectively, and k_1 (min^{-1}) is the rate constant of pseudo-first-order model which is obtained from the slope of the linear plot of $\log(q_e - q_t)$ vs. t.

The pseudo-second-order kinetic model suggests that the probable rate-determining step is chemical surface reaction rather than Physical reaction, and the equation is expressed as [31]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

where q_t and q_e (mg g^{-1}) are adsorption amount of cadmium ions at time t (min) and equilibrium, respectively, and k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order model which is calculated form the slope of the linear plot of t/q_t vs. t.

The Elovich kinetic model can also be used to explain the adsorption process. The equation is expressed as:

Table 4
Comparison of the maximum adsorption capacity ($Q_{\max}$) values of Cd(II) ion by agricultural wastes as adsorbents

Adsorbent	Modification method	$Q_{\max}$ (mg g^{-1})	Refs.
Lignin from beech and poplar woods	Alkali glycerol delignification	6.7–7.5	[35]
Orange wastes	Water washed and crushed	48.3	[36]
Juniper wood	Water washed	2.8–3.2	[37]
Juniper bark	Water washed	8.6–10.3	
Areca waste	Crushed and water washed	1.12	[39]
Ground wheat stems	Water washed and crushed	11.6	[11]
Apple pomace	Succinic anhydride	91.74	[38]
Rice husk	Water washed	8.58	[7]
	Sodium bicarbonate	16.18	
	Epichlorohydrin	11.12	
Corn stalk	Acrylonitrile	12.73	[8]
Corn stalk	Grafted acrylonitrile	22.17	[13]
Sugarcane bagasse	Water washed	3.53	[2]
	Grafted acrylonitrile	14.28	
Corncob	Citric acid	8.89	[9]
Corncob	Water washed	4.96	This study
	Grafted acrylamide	18.35	This study

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln t \tag{8}$$

where a (mg g^{-1} min^{-1}) and b (mg g^{-1}) are the Elovich coefficients which relate to the initial adsorption rate and activation energy, respectively, and they could be obtained from the liner plot of q_t vs. ln t.

As shown in Table 5, the fitting results of three kinetic models indicate that the best conformity of the experimental data to pseudo-second-order kinetics, which presents the highest values of R^2. In addition, the values of theoretical absorption capacity (q_{eq}), which are calculated from pseudo-second-order kinetic equation, closely approximates the experimental absorption capacity. Hence, we can infer that chemical sorption is the rate-controlling step during the adsorption process as a result of the pseudo-second-order model, which best interpreted the adsorption mechanism for CS and CSGC.

Meanwhile, the intra-particle diffusion model was inspected to examine the effect of diffusion on adsorption rate [31]:

$$q_t = k_p t^{0.5} + C \tag{9}$$

where k_p (mg g^{-1} min$^{-0.5}$) and C are the rate constant and the intercept which relates to the thickness of the boundary layer of intra-particle diffusion at different stage, respectively.

The adsorption of Cd(II) on CS and CSGC occurred via two steps before reaching the equilibrium adsorption state in Fig. 7(d). The fast adsorption and slow adsorption phases were attributed to external surface film diffusion and pore diffusion, respectively [34]. In addition, we can infer that external surface adsorption could be the rate-controlling step of Cd(II) adsorption from aqueous solutions by CS and CSGC according to the K_{p1} values, which were considerably higher than K_{p2} values as shown in Table 6 [31].

3.8. Thermodynamic equations

The values of thermodynamic parameters (Gibbs free energy change ΔG, enthalpy change ΔH and entropy change ΔS) are related to the practical application of the adsorption process. These parameter values of Cd(II) ion adsorption with CS and CSGC were calculated using the following equations [8]:

$$k_d = q_e/C_e \tag{10}$$

$$\Delta G = -RT\ln k_d \tag{11}$$

$$\ln k_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{12}$$

where k_d is the distribution coefficient (mg g^{-1}), T is the adsorption temperature (k), R is universal gas constant (8.314 J k^{-1} mol^{-1}), ΔG is Gibbs free energy

Table 5
Fitting parameter values of pseudo-first-order, pseudo-second-order and Elovich kinetic models

		Pseudo-first-order			Pseudo-second-order			Elovich		
Adsorbent	Experimental (mg g^{-1})	q_{eq} (mg g^{-1})	k_1 (min^{-1})	R^2	q_{eq} (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2	a	b	R^2
CS	4.96	4.6739	0.0069	0.9403	5.6022	0.0035	0.9967	1.6110	0.7427	0.8748
CSGC	18.35	9.5089	0.0118	0.9072	18.4298	0.0033	0.9990	0.5661	3.2169	0.8950

Table 6
The fitting parameter values of intra-particle diffusion model

	Fast phase		Slow phase	
Adsorbents	K_{p1}	R^2	K_{p2}	R^2
CS	0.3497	0.9717	0.06018	0.8733
CSGC	0.77457	0.8445	0.07533	0.9350

change (J mol^{-1}), ΔH is enthalpy change (J mol^{-1}) and ΔS is entropy change (J mol^{-1} k^{-1}).

The values of ΔG at different temperature were calculated using Eqs. (10)–(12), whereas the values of ΔH and ΔS were obtained from the slope and intercept of the plot between $\ln k_d$ vs. $1/T$ (Fig. 7(c)) and given in Table 2. The negative values of ΔG suggested that the adsorption processes of Cd(II) ions on CS and CSGC were spontaneous. In addition, the absolute value of ΔG increased with ascending temperature, which indicated that high temperature was beneficial to the adsorption of Cd(II) ions. The positive value of ΔH further proved that the adsorption was an endothermic progress in nature. In addition, positive value of ΔS indicated the good affinity of sorbents for Cd(II) ions, as well as increasing randomness in the adsorption system [14].

4. Conclusions

The adsorption capacity of Cd(II) of CSGC (Q_{max} = 18.35 mg g^{-1}) was considerably higher than that of CS (Q_{max} = 4.96 mg g^{-1}), which was due to the increase in the amount of functional groups (acylamino) and adsorption sites on the surface after grafting modified adsorbent. Meanwhile, higher thermal stability and better swelling property in salt solution were achieved for CSGC. Adsorption equilibrium experiments indicated that Langmuir isotherm and second-order kinetics are the models that best fit the experimental data of removing Cd(II) ions from aqueous solutions using CS and CSGC. The thermodynamic parameters showed that adsorption is a spontaneous endothermic process. Hence, CSGC could be a promising candidate for the removal of Cd(II) ions from wastewater.

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