Equilibrium and kinetic studies of adsorption of Cd(II) from aqueous solution using modified corn stalk

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ABSTRACT

This paper describes the adsorption of cadmium ions from aqueous solution using acrylonitrile (AN)-modified corn stalk (AMCS). AMCS was characterized by elemental analysis, scanning electron microscopy, surface area and porosity analyzer, Fourier transform infrared and solid-state CP/MAS ^{13}C NMR spectra, and then used to evaluate the adsorption capacity in different pH values, adsorption isotherm, kinetics and thermodynamics in batch experiments. The results showed that AMCS is found to be an effective adsorbent because of its pore size and functional groups (–CN). The pH of 7.0 was an optimal pH for removal of Cd(II) ion and the Langmuir model provides a better fit to the equilibrium data than the Freundlich model, showing a maximum uptake of 12.73 mg g^{-1}, compared to raw corn stalk (RCS) (3.39 mg g^{-1}). Analysis indicated that pseudo-second-order kinetics controlled the adsorption rate. The activation energy (E_a) was 9.43 kJ mol^{-1}. Thermodynamic parameters such as ΔG, ΔH and ΔS were also evaluated to predict the nature of adsorption process.

1. Introduction

Industrial uses of metals and other processes have introduced substantial amounts of potentially toxic heavy metals into the aquatic environment [1]. Cadmium is a major toxic heavy metal, which may cause cancer, lung fibrosis, dyspnea and weight loss to humans [2]. It should therefore be removed before discharge [3]. Various treatment technologies exist for removal of heavy metals from wastewater, including chemical precipitation [4], ion exchange treatment [5], membrane filtration [6,7], electrochemical treatment [8,9]. Application of such technologies mentioned is restricted because of technical or economical constraints. Hence, adsorption as one of the most popular and effective technologies, has been widely studied over recent decades [10], because of its wide range of target pollutants, high adsorption capacity, kinetics and possibly selective adsorbents [11]. Moreover, more and more attention has been directed to low cost adsorbent, which can be defined as abundant in nature, little treatment, or is a by-product of waste material from another industry [3,12,13]. Most of the low-cost adsorbent researches have been focus on agricul-

tural waste, which mainly contains cellulose and shows potential metal adsorption capacity [2]. The basic components of agricultural waste including reactive groups are hydroxyl groups [14]. Other functional groups that facilitate metal complexation can attach to these hydroxyl groups through a variety of chemistries in order to enhance the removal of metal ions of agricultural waste. There have been numerous studies of modification reactions for agricultural waste, such as coconut copra meal [15], waste weed [16], peanut hill [17], sawdust [18], rice husk [19], corncob [20,21], grape bagasse [22], grapefruit peels [23] and so on. The present article reports the feasibility of utilizing corn stalk as a low cost adsorbent material for the removal of cadmium ions from aqueous solution.

Corn is one of the largest production crops in the world, especially in China. Corn cob, corn husk, corn leaf and corn stalk are abundant agriculture residues form corn, but most are burnt without utilization [24]. However, these residues have been studied recently in adsorption [25–27]. As a renewable agriculture waste available abundantly at little cost, corn stalks are mainly composed of cellulose and could achieve increased value when new functionality is added by modification. The cost of chemicals used and the modification methods also have to be taken into consideration in order to produce 'low-cost' adsorbents [3]. Evidently, choosing some chemical agents for modification not only can improve adsorption capacity, but also produce a 'low-cost' adsorbent. Alkaline pretreatment can obtain cellulose which is the main component of agricultural waste, and render it more accessible to further chemical attack [28]. Some treatments of corn stalks

with NaOH are resulted in destroying of ether linkages between lignin and polysaccharides and extracting cellulose of corn [24]. After NaOH treatment, the adsorption capacity of corn stalk is increased [29]. Acrylonitrile (AN) has a high degree of acute toxicity by oral and dermal routes of administration [30] and causes health hazards such as headache, nausea and dizziness, even cancer at relatively different levels [31]. But it can be effectively used to modify other agricultural wastes as a useful and available chemical reagent [32–35]. Hence, acrylonitrile also provides functional groups for corn stalk in further modification.

In this study, we treated corn stalks with NaOH–acrylonitrile–H$_2$SO$_4$ to modify the adsorbents and analyzed their property. The adsorption capacity of the raw and modified adsorbents to remove cadmium (II) from aqueous solution as a function of initial pH was tested, and the adsorption equilibrium was expressed using Langmuir and Freundlich models. Furthermore, two adsorption kinetic models were calculated to analyze the experimental data and lead to characteristization of the reaction mechanisms, which provides information for the design and operation of waste water treatment reactors or equipments [36]. The thermodynamics of these adsorption processes were also investigated.

2. Materials and methods

2.1. Adsorbent preparation

Raw corn stalk (RCS) was obtained from a farm in Guangzhou city, China. After removing the leaves and washing with fresh water, the materials were cut into granules and 2–4 mm size was selected using sieves, then washed three times with deionized water and dried in an oven at 50 °C until constant weight for further pretreatment.

Dried corn stalk (1 g) was then dipped in 50 ml of 1.0 M sodium hydroxide (NaOH), and stirred at 120 r min^{-1} for 18 h at 40 °C. After alkali reaction, the samples were centrifuged to remove superfluous NaOH. Next, the samples were dipped in 10 ml acrylonitrile (AN) solution (98%) for chemical modification, and stirred at 120 r min^{-1}, at 30 °C for 30 min. The modified samples were washed three times with deionized water to remove remaining acrylonitrile, and then washed with 12 g l^{-1} sulfuric acid (H$_2$SO$_4$) to strengthen the modification. Finally, the samples were washed several times with deionized water to pH ≈ 7.0 and dried in an oven at 50 °C until constant weight for further pretreatment. All reagents were of analytical grade and the modified samples were nominated acrylonitrile modified corn stalk (AMCS).

2.2. Adsorbent characterization

Total N of RCS and AMCS were analyzed using an element analyzer (Element vario EL III, Germany). The total exchange capacity (TEC) was based on the nitrogen content incorporated into the final products [37]. TEC is calculated using the following equation [38]

$$TEC = \frac{N\%}{1.4} \tag{1}$$

where TEC is the total exchange capacity (mEq g^{-1}) of RCS and AMCS; N% is the total nitrogen of RCS and AMCS, and 1.4 is a correction coefficient.

Micrographs of RCS and AMCS were examined using a thermal field emission environmental scanning electron microscope (SEM QUANTA 400). The acceleration voltage (Acc. V) was 10.0 kV, and the vacuum-mode was high vacuum. The surface area (BET method) and pore size were determined using surface area and porosity analyzer (ASAP 2020M) with N$_2$-adsorption techniques.

The functional groups of RCS and AMCS were characterized by a fourier transform infrared (FTIR) spectrophotometer, using KBr discs to prepare RCS and AMCS. The chemical structure of RCS and AMCS were analyzed by solid-state CP/MAS ^{13}C NMR spectroscopes. The solid-state CP/MAS ^{13}C NMR spectra were recorded on Bruker AVANCE400 spectrometer at the frequency of 100 MHz with 4 mm MAS BBO prode. Acquisition time was 0.034 s. The delay time was 3 s and the proton 90° pulse time was 6 us. Each spectrum was obtained with an accumulation of 4070 scans.

2.3. Batch experiment and analysis

The aqueous solution of heavy metal was prepared with CdCl$_2$·2.5H$_2$O, which was purchased as reagent grade from Guangzhou Chemical Reagent Co. Ltd. (Guangzhou, China). The adsorption isotherm experiments were performed at 120 rpm on an orbital shaker with 0.5 g of adsorbent in conical flasks containing 50 ml of CdCl$_2$ solution at various concentrations at 293 K. In the adsorption kinetic experiments, at an initial concentration of 100 mg l^{-1} metal solution was used at different temperatures (ranging from 283 to 313 K). The heavy metal concentration was determined by inductively coupled plasma optical emission spectrophotometry (ICP-OPTIMA 5000), and the measured heavy metal concentration was used to calculate the adsorption capacity, q$_e$ (mg g^{-1}) of the adsorbent using the following mass balance equation:

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

where C$_o$ and C$_e$ are the initial and equilibrium concentrations.

3. Results and discussion

3.1. Adsorbent (AMCS) characterization

The nitrogen content (N%) of RCS and AMCS were 1.11% and 3.93%. This indicates that AN introduced the cyano group (–CN) into AMCS in the modification process. According to Eq. (1), the total exchange capacity (TEC) of RCS and AMCS were 0.79 and 2.81 mEq g^{-1}, respectively.

SEM micrographs of RCS and AMCS are shown in Fig. 1. In comparison to the surface of RCS (Fig. 1a and b), AMCS was a homogeneous and highly ordered surface, which indicated that the order of cellulose was improved after removing the lignin, hemicellulose, ash and extractives during modification [39]. AMCS also had many pores, which were more highly bedded (Fig. 1c). The BET surface areas of AMCS and RCS were 6.03 and 2.20 m^2 g^{-1}, respectively. And the pore sizes of AMCS and RCS were 3.55 and 0.95 nm, respectively. These are favorable for adsorption.

The FTIR spectra of AMCS and RCS samples are shown in Fig. 2. As indicated for RCS and AMCS, the strong adsorption peaks at 3430 cm^{-1} confirms the presence of hydroxyl group. The peaks observed at 2920 cm^{-1} are assigned to the C–H group. The peaks at 1645 cm^{-1} are characteristics of the bending mode of the absorbed water [40], and the peaks at 1380 cm^{-1} are characteristics of the bending of the O–H group [41]. In addition, the peaks at 1045 cm^{-1} are attributed to the C–O–C group of primary hydroxyl stretching [42], due to the cellulose structure of the corn stalk, and the peaks at 900 cm^{-1} are the glycosidic C$_1$–H group deforming with ring vibration and OH bending [41]. Compared to RCS, some of the associated functional groups in AMCS had been modified, There was a strong characteristic stretching vibration adsorption band of the cyano group (–CN) at 2252 cm^{-1} in the IR spectrum of AMCS, which can be seen from the nitrogen content (N%) increasing.
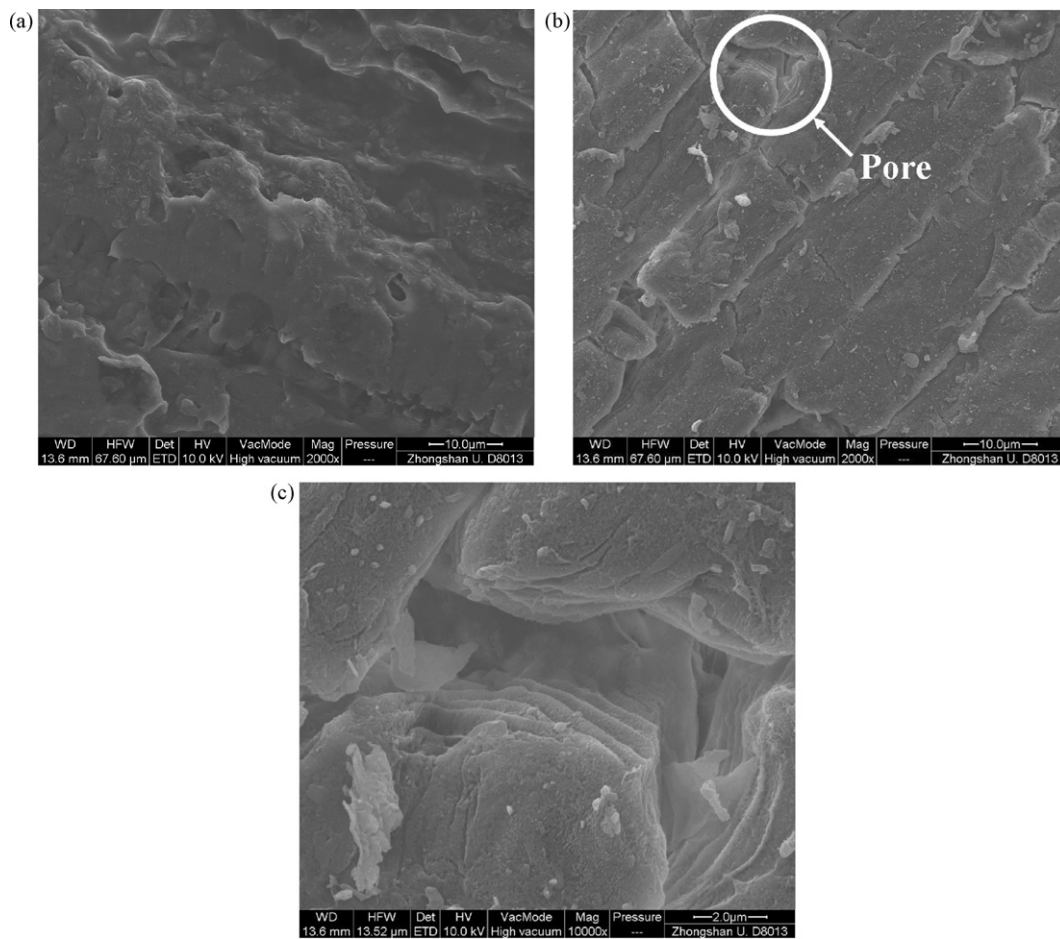
Fig. 1. Scanning electron micrographs of corn stalk: (a) for RCS, (b) for AMCS, and (c) for Pore of AMCS.

Fig. 3. shows the CP/MAS ^{13}C NMR spectra of RCS and AMCS. This is the cellulose structure of RCS and AMCS. The signals from 60 to 70 ppm are attributed to C-6, from 70 to 80 ppm to C-2, C-3 and C-5, from 80 to 90 ppm to C-4 and from 98 to 110 ppm to C-1 [39,43]. The signals of RCS are at 105.0 ppm (C-1), 88.7 ppm (C-4 of crystalline cellulose), 83.6 ppm (C-4 of amorphous cellulose), 72.4 ppm (C-2, C-3), 75.0 ppm (C-5) and 64.6 ppm (C-6). For AMCS, the signal at 105.0 ppm (C-1) is still observed; the signal for C-6

disappeared, the intensity of signals for C-4 of crystalline cellulose, C-2 and C-3 decreased and the presence of the signals of the cyano group (–CN) is at 21.59 ppm.

According to Liu et al. [43], The peak between 85 and 90 ppm in ^{13}C NMR spectra is assigned to the crystalline region and the peak between 80 and 85 ppm is for the crystal surface or the disordered component in cellulose, which is may also compose of the two, since native cellulose always include some non-crystalline regions. The decreasing intensity of the signal for C-4 of crystalline cellulose and the disappearance of the signal for C-6 in AMCS is because of the crystalline structure destroying after modification. The decreasing
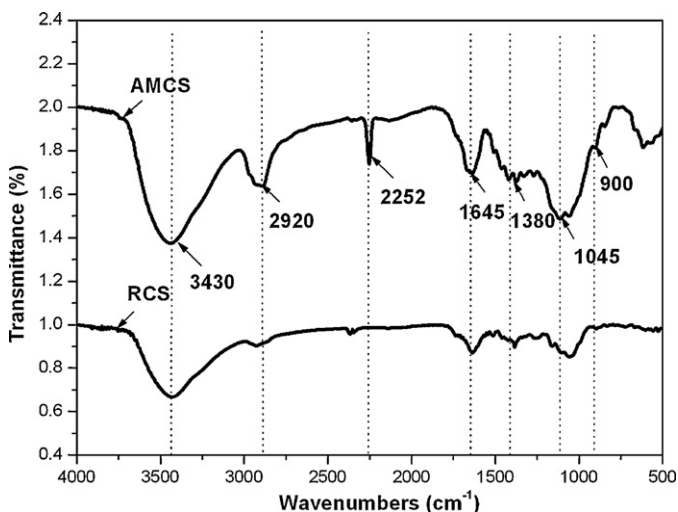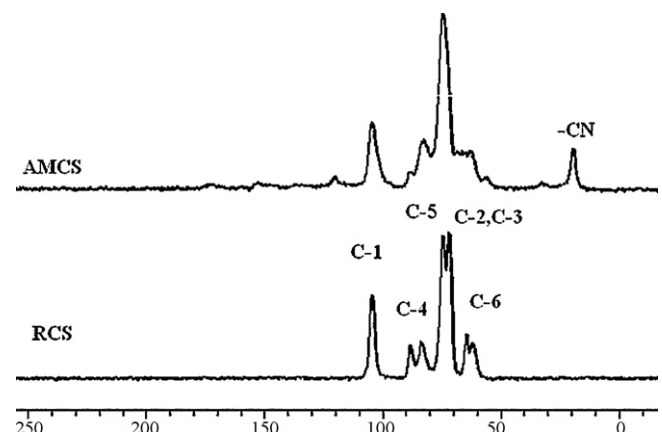

Fig. 2. FTIR Spectra of RCS and AMCS.

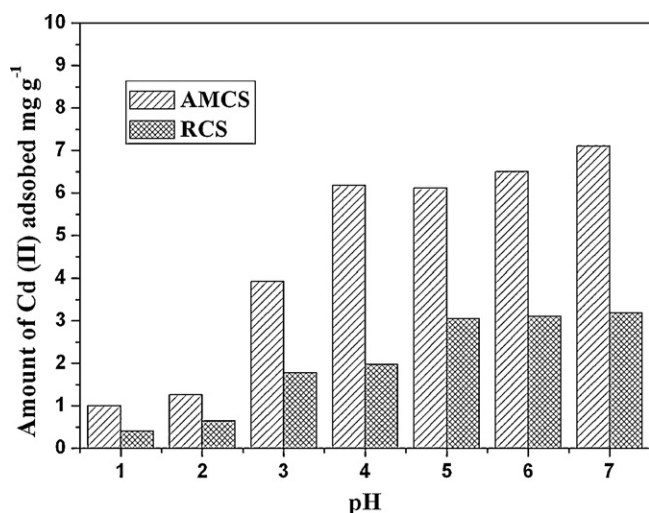**Fig. 3.** Solid-state CP/MAS ^{13}C NMR spectra of RCS and AMCS.

Fig. 4. Adsorption capacity of Cd(II) by powder of RCS and AMCS for different of pH.

of the intensity of the signals for C-2 and C-3 indicated that the modification occurred at hydroxyl groups of these positions. The cyano group (–CN) at 21.59 ppm provided evidence of successful modification, which was also determined by the results of FTIR spectra. The nitrogen of the cyano group and the oxygen of the hydroxyl group in cellulose are considered a strong Lewis base because of the presence of vacant double electrons. These doublets can make a complex for coordination with chemical entities low in electrons, such as metal ions [44,45].

3.2. Effect of initial pH

The pH value of the aqueous solution is an important parameter in the adsorption process [45,46]. The experiments were studied over a pH range from 1.0 to 7.0. The effects of initial pH on the adsorption of Cd(II) by RCS and AMCS are presented in Fig. 4. The amount of Cd(II) adsorbed on RCS and AMCS increased repidly as the initial pH was increased in the pH range 1.0–4.0, and increased relatively slowly in the pH range 4.0–7.0, the maximum uptake of Cd(II) occurred at pH 7.0. The adsorption capacities of RCS and AMCS at pH 7.0 were 3.2 and 7.1 mg g^{-1}, respectively.

At lower pH values (pH 1.0), the H_3O^+ ions competed with the Cd(II) for the exchange site in the adsorbent [45], hence H_3O^+ occupied the sites on adsorbents, leaving heavy metal ions in solution. The hydroxyl group also combines easily with H_3O^+ ions to restrict adsorption or the reaction with functional groups. At high pH values (pH 7.0), the concentration of Cd(II) was higher than H_3O^+ ions, so that more exchange sites were provided for heavy metal ions. Ion removal is highly concentration-dependent, the more concen-

Table 1
Parameters for Langmuir and Freundlich equations at 293 K.

Langmuir–Freundlich						
	q_{max} (mg g^{-1})	b (l mg^{-1})	R^2	K_F (mg$^{(1-1/n)}$L$^{1/n}$ g^{-1})	n	R^2
RCS	3.39	0.030	0.945	0.379	2.484	0.837
AMCS	12.73	0.020	0.991	1.251	0.401	0.940

q_{max} is the maximum uptake capacities, b (l mg^{-1}) is the Langmuir constant, K_F and n are the Freundlich constants, R^2 is determination coefficient.
(Experimental conditions: pH 7.0, initial Cd(II) concentration: 100 mg l^{-1})

trated the solution, the better the adsorption [45]. Base on these results, the pH of 7.0 was an optimal pH and selected for the further experiments.

3.3. Adsorption equilibrium

3.3.1. Adsorption isotherm equations

Adsorption isotherms indicate the partition of adsorbate between solution and adsorbent at equilibrium [36]. Langmuir and Freundlich isotherms are the isotherms used most widely [47], and suitable for describing short-term and mono component adsorption of metal ions by different adsorbents [2,48,49]. Wang et al. [39] have noted that modified wheat straw had a homogeneous surface and the adsorption data fit the Freundlich and Langmuir isotherm. In this study, both equations can be used for AMCS, which also had specific homogeneous site. The Langmuir equation is [50]

$$q_{eq} = \frac{q_{max} b c_{eq}}{1 + b c_{eq}} \tag{3}$$

where q_{eq} and q_{max} are the equilibrium and maximum uptake capacities (mg g^{-1}), respectively. c_{eq} is the equilibrium concentration (mg L^{-1}), and b is the equilibrium constant. It can be rearranged to a linear form

$$\frac{c_{eq}}{q_{eq}} = \frac{1}{b q_{max}} + \frac{c_{eq}}{q_{max}} \tag{4}$$

The Freundlich equation is [50]

$$q_{eq} = K_F c_{eq}^{1/n} \tag{5}$$

where K_F and n are the Freundlich constants. A linear form of this equation is

$$\ln q_{eq} = \frac{1}{n} \ln c_{eq} + \ln K_F \tag{6}$$

Langmuir and Freundlich isotherms were applied on the adsorption data. The isotherm parameters and correlation coefficients are tabulated in Table 1. The higher R^2 values showed that the Langmuir isotherm exhibited a better fit to the adsorption data than the Freundlich isotherm. The basic assumption of the Langmuir isotherm

Table 2
Langmuir parameters and conditions for adsorption of Cd(II) by other agricultural wastes.

Agriculture wastes	Langmuir parameters			Reference
	q_{max} (mg g^{-1})	b (l mg^{-1})	R^2	
Coconut copra meal	4.68 (pH 6)	0.141	0.998	[15]
Waste weed (Caulerpa lentillifera)	5.57 (pH 5)	0.742	0.995	[16]
Peanut hulls	5.96	0.717	0.985	[17]
Sawdust	6.72 (pH 7)	0.105	0.990	[18]
Rice husk (Epichlorohydrin)	11.12 (pH 6.6–6.8)	0.378	0.993	[19]
AMCS	12.73 (pH 7)	0.020	0.991	This study
Corncob	7.87(pH 7)	0.140	\	[20]
	19.30 (pH 6)	0.570	\	[21]
	55.20 (pH 6)	0.330	\	
Grape bagasse	53.83 (pH 7)	0.053	0.995	[22]
Grapefruit peels	110.16 (pH 5)	0.005	0.930	[23]

is that there is monolayer coverage of the adsorbate on the surface of adsorbent [51–53] and that adsorption occurs at specific homogeneous sites on the adsorbent [47,54,55]. This indicates that AMCS provided the specific homogeneous sites and adsorption of Cd(II) onto AMCS generated monolayer. The Langmuir isotherm can be used to estimate RCS and AMCS adsorption capacities (q_{max}). It was found that adsorption capacity of corn stalk increased from 3.39 to 12.73 $mg\,g^{-1}$ after modification. These adsorption capacities were compared with some agriculture wastes. It was evident from Table 2 that AMCS, in this study, had a higher uptake capacity for Cd(II) than some materials, but lower than some others.

3.3.2. Adsorption kinetics

Kinetic models were used to examine the rate of the adsorption process and to propose potential rate-controlling step [56]. In practice, kinetic studies are carried out in batch experiments using variable initial sorbate concentration, sorbent dose, particle size, agitation speed, pH values and temperatures along with different sorbent and sorbate types [47]. The pseudo-first-order and pseudo-second-order models were examined using different temperatures in this paper.

The pseudo-first-order rate equation is [36,57]

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (7)$$

where q_e and q_t ($mg\,g^{-1}$) refer to the amount of AMCS at equilibrium and time t respectively, and k_1 is the rate constant. The k_1 value can be calculated from the slopes of the linear plot of $\ln(q_e - q_t)$ versus t.

The pseudo-second-order rate equation is [36,57]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (8)$$

where q_e and q_t ($mg\,g^{-1}$) refer to the amount of AMCS at equilibrium and time t respectively, and k_2 is rate constant. The k_2 value can be calculated from the slopes of the linear plots of $\frac{t}{q_t}$ versus t. This model is in agreement with chemical sorption being the rate-controlling step [58].

The plots of the pseudo-first-order equation are shown in Fig. 5. q_{eq}, k_1 and the correlation coefficients at different temperatures are shown in Table 3. The results show that the correlation coefficients for the first-order kinetic model obtained at 283, 293, 303 and 313 K are very low, and the theoretical q_{eq} values are not in agreement with the experimental values, so the pseudo-first-order model does not support the adsorption kinetics of Cd(II) onto AMCS.

The plots of the pseudo-second-order equation are shown in Fig. 6, which shows a good fit with high values of the correlation coefficient and the theoretical q_{eq} values are close to the experimental values (Table 3). This indicates that the adsorption processes best followed the pseudo-second-order model, *i.e.* chemical sorption being the rate-controlling step, in contrast to the pseudo-first-order model.
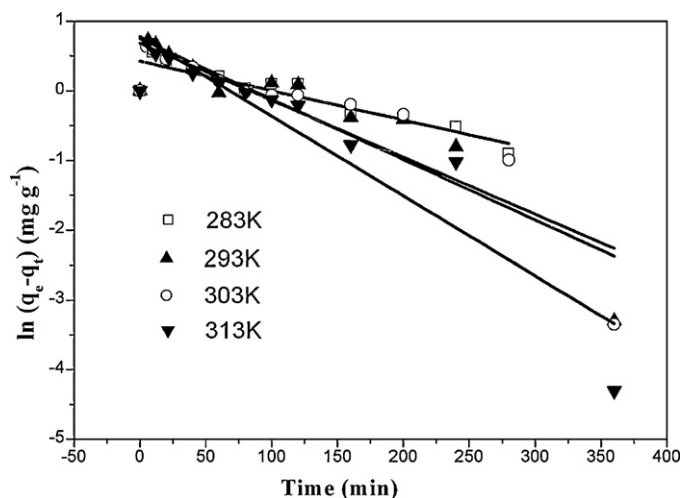

Fig. 5. Pseudo-first-order adsorption kinetic of Cd(II) at different temperatures.
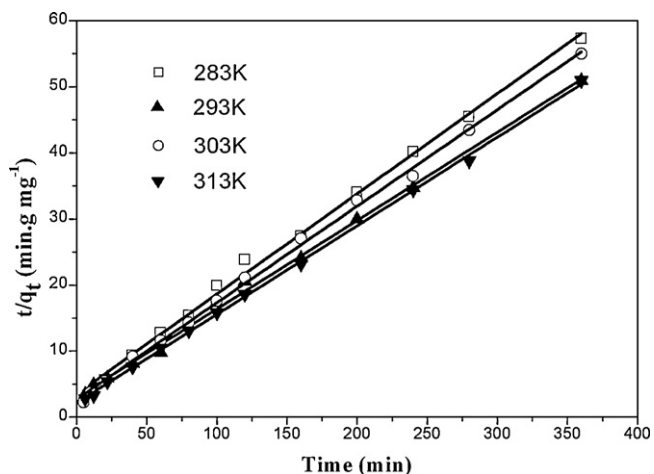
Fig. 6. Pseudo-second-order adsorption kinetic of Cd(II) at different temperatures.

3.3.3. Activation energy

The activation energy E_a was calculated by the linearized Arrhenius equation [59]

$$\ln(k) = \ln(A) - (E_a/RT) \qquad (9)$$

where E_a is the activation energy of adsorption ($kJ\,mol^{-1}$), k is the rate constant which control the process, A is the Arrhenius constant, R is the ideal gas constant (8.314 $J\,mol^{-1}\,K^{-1}$), and T is the solution temperature (K).

From the pseudo-second-order kinetic studies, k_2 is the rate constant which controls the process, *i.e.* k. In this study, activation energy value of 9.43 $kJ\,mol^{-1}$ was obtained from the plot of $\ln k_2$ versus $1/T$ (Fig. 7). In physical adsorption, the activation energy

Table 3
Change of the pseudo-first- and second-order models constants with temperature.

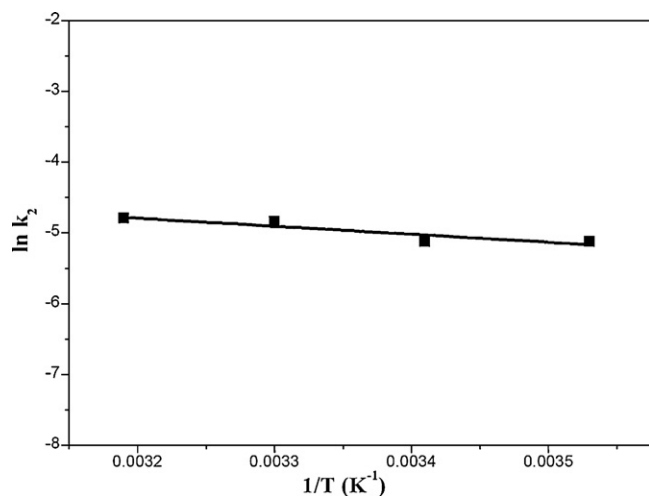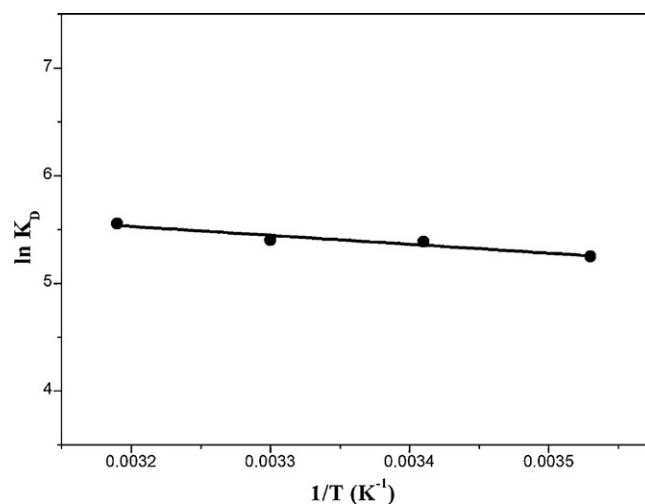| T (K)	Experimental ($mg\,g^{-1}$)	Pseudo-first-order constants			Pseudo-second-order constants		
		q_{eq} ($mg\,g^{-1}$)	k_1 (min^{-1})	R^2	q_{eq} ($mg\,g^{-1}$)	k_2 ($g\,mg^{-1}\,min^{-1}$)	R^2
283	6.28	2.31	0.0029	0.5570	6.60	0.0060	0.9969
293	7.07	7.93	0.0094	0.8663	7.48	0.0059	0.9977
303	6.55	6.13	0.0078	0.7265	6.84	0.0079	0.9980
313	7.07	6.37	0.0095	0.6647	7.46	0.0083	0.9993

q_{eq} ($mg\,g^{-1}$) is the calculated value of equilibrium adsorption capacity, k_1 (min^{-1}) and k_2 ($g\,mg^{-1}\,min^{-1}$) are the rate constants of pseudo-first and second-order kinetic equation. R^2 is the coefficient of determination.
(Experimental conditions: pH 7.0, initial Cd(II) concentration: 100 $mg\,l^{-1}$)

Fig. 7. Plot of $\ln k_2$ versus $1/T$.

Fig. 8. Plot of $\ln K_D$ versus $1/T$.

is small and usually not more than $4.2\,kJ\,mol^{-1}$, since the forces involved in physical adsorption are weak. Chemical adsorption involves forces much stronger than in physical adsorption and the activation energy is between 8.4 and $83.7\,kJ\,mol^{-1}$ [60]. Li et al. [54] noted that chemical adsorption includes activated and nonactivated forms. Activated chemical adsorption means that the rate varies with temperature according to a finite activation energy (between 8.4 and $83.7\,kJ\,mol^{-1}$) in the Arrhenius equation, but the activation energy for nonactivation chemical adsorption is near zero. The results show that the process is one of activated chemical adsorption and the positive value of the activation energy suggested that the rise in solution temperature favors Cd(II) adsorption onto AMCS.

3.4. Thermodynamic equations

The Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) for the adsorption process were obtained using the following formulas [54,61,62]

$$K_D = q_e/C_e \qquad (10)$$

$$\Delta G = -RT \ln K_D \qquad (11)$$

$$\Delta G = \Delta H - T\Delta S \qquad (12)$$

$$\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (13)$$

where T is temperature in (K). and K_D is the distribution coefficient (ml g^{-1}). The enthalpy change (ΔH) and the entropy (ΔS) can be calculated from a plot of $\ln K_D$ versus $1/T$ (Fig. 8). The Gibbs free energy was determined at 283, 293, 303 and 313 K. ΔG, ΔH and ΔS were obtained from Eqs. (10)–(13) and given in Table 4. Negative values of ΔG indicate the adsorption process is spontaneous, and the degree of spontaneity of the reaction increases with increasing temperature. Positive value of ΔH indicates the endothermic

nature of the process. Positive value of ΔS shows that the affinity of AMCS for the Cd(II) ions.

4. Conclusions

The adsorption of Cd(II) ions was investigated using AMCS prepared from corn stalk. It was clear that the adsorption capacity of raw corn stalk increased from 3.39 to $12.73\,mg\,g^{-1}$ after modification. AMCS was an effective adsorbent for Cd(II) removal from aqueous solution. The experimental data obtained at 293 K were fitted with the Langmuir isotherm and the adsorption process best followed the pseudo-second-order model, which is in agreement with chemical sorption being the rate-controlling step. The activation energy (E_a) was $9.43\,kJ\,mol^{-1}$. This indicates that the process is an activated chemical sorption. The negative values of ΔG indicate that the adsorption process is spontaneous. The positive value of ΔH also confirmed it.

References

[1] D.W. O'Connell, C. Birkinshaw, T.F. O'Dwyer, Heavy metal adsorbents prepared from the modification of cellulose: a review, Bioresour. Technol. 99 (2008) 6709–6724.
[2] D. Sud, G. Mahajan, M.P. Kaur, Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solution: a review, Bioresour. Technol. 99 (2008) 6017–6027.
[3] W.S. Wan Ngah, M.A.K.M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review, Bioresour. Technol. 99 (2008) 3935–3948.
[4] C.L. Lai, S.H. Lin, Electrocoagulation of chemical mechanical polishing (CMP) wastewater from semiconductor fabrication, Chem. Eng. J. 95 (2003) 205–211.
[5] V.A. Cardoso, A.G. de Souza, P.P.C. Sartoratto, L.M. Nunes, The ionic exchange process of cobalt, nickel and copper (II) in alkaline and acid-layered titanates, Colloid Surf. A: Physicochem. Eng. Aspects 248 (2004) 145–149.
[6] S.S. Madaeni, Y. Mansourpanah, COD removal from concentrated wastewater using membranes, Filtr. Separat. 40 (6) (2003) 40–46.
[7] J.J. Qin, M.N. Wai, M.H. Oo, F.S. Wong, A feasibility study on the treatment and recycling of a wastewater from metal plating, J. Membr. Sci. 208 (1–2) (2002) 213–221.

Table 4
Value of thermodynamic parameters for the adsorption of Cd(II) on AMCS.

T (K)	E_a (kJ mol^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})
283	9.43	−12.35	6.85	0.068
293		−13.12		
303		−13.61		
313		−14.46		

ΔG (kJ mol^{-1}) is the Gibbs free energy, ΔH (kJ mol^{-1}) is the enthalpy change and ΔS (kJ mol^{-1} K^{-1}) is the entropy change.

[8] N. Kongsricharoern, C. Polprasert, Electrochemical precipitation of chromium Cr(VI) from an electroplating wastewater, Water Sci. Technol. 31 (9) (1995) 109–117.

[9] N. Kongsricharoern, C. Polprasert, Chromium removal by a bipolar electrochemical precipitation process, Water Sci. Technol. 34 (9) (1996) 109–116.

[10] J.P. Chen, S. Wu, Study on EDTA-chelated copper adsorption by granular activated carbon, Technol. Biotechnol. 75 (2000) 791–797.

[11] G. Crini, Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, Prog. Polym. Sci. 30 (1) (2005) 38–70.

[12] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (1999) 2469–2479.

[13] W.S. Wan Ngah, M.A.K.M. Hanafiah, Biosorption of copper ions from dilute aqueous solutions on base treated rubber (*Hevea brasiliensis*) leaves powder: kinetics, isotherm, and biosorption mechanisms, J. Environ. Sci. 20 (2008) 1168–1176.

[14] C.F. Liu, R.C. Sun, J. Ye, Structural and thermal characterization of sugarcane bagasse phthalates prepared with ultrasound irradiation, Polym. Degrad. Stab. 91 (2006) 280–288.

[15] Y. Ho, A.E. Ofomaja, Biosorption thermodynamics of cadmium on coconut copra meal as biosorbent, Biochem. Eng. J. 30 (2006) 117–123.

[16] P. Pasavant, R. Apiratikul, V. Sungkhum, P. Suthiparinyanont, S. Wattanachira, T.F. Marhaba, Biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} using dried marine green macroalga Caulerpa lentillifera, Bioresour. Technol. 97 (2006) 2321–2329.

[17] P. Brown, I.A. Jefcoat, D. Parrish, S. Gill, E. Graham, Evaluation of the adsorptive capacity of peanut hull pellets for heavy metals in solution, Adv. Environ. Res. 4 (2000) 19–29.

[18] V.C. Taty-Costodes, H. Fauduet, C. Porte, A. Delacroix, Removal of Cd(II) and Pb(II) ions from aqueous solutions by adsorption onto sawdust of Pinus sylvestris, J. Hazard. Mater. B 105 (2003) 121–142.

[19] U. Kumar, M. Bandyopadhyay, Sorption of cadmium from aqueous solution using pretreated rice husk, Bioresour. Technol. 97 (2006) 104–109.

[20] J. Shen, Z. Duvnjak, Adsorption kinetics of cupric and cadmium ions on corncob particles, Process. Biochem. 40 (2005) 3446–3454.

[21] R. Leyva-Ramos, L.A. Bernal-Jacome, I. Acosta-Rodriguez, Adsorption of cadmium (II) from aqueous solution on natural and oxidized corncob, Sep. Purif. Technol. 45 (2005) 41–49.

[22] N.V. Farinella, G.D. Matos, M.A.Z. Arruda, Grape bagasse as a potential biosorbent of metals in effluent treatments, Bioresour. Technol. 98 (2007) 1940–1946.

[23] S. Schiewer, S.B. Patil, Pectin-rich fruit wastes as biosorbents for heavy metal removal: equilibrium and kinetics, Bioresour. Technol. 99 (2008) 1896–1903.

[24] B. Xiao, X.F. Sun, R.C. Sun, Chemical, structural, and thermal characterizations of alkali-soluble lignins and hemicelluloses, and cellulose from maize stems, rye straw, and rice straw, Polym. Degrad. Stab. 74 (2001) 307–319.

[25] J.C. Igwe, A.A. Abia, Equilibrium sorption isotherm studies of Cd(II), Pb(II) and Zn(II) ions detoxification from waste water using unmodified and EDTA-modified maize husk, Electron. J. Biotechnol. 10 (2007) 536–548.

[26] A.A. Abia, O.C. Okpareke, J.C. Igwe, Sorption kinetics and intraparticulate diffusivities of Co, Fe and Cu ions on EDTA-modified maize cob, Int. J. Chem. 15 (3) (2005) 187–191.

[27] N.A.A. Babarinde, J.O. Babalola, R.A. Sanni, Biosorption of lead ions from aqueous solution by maize leaf, Int. J. Phys. Sci. 1 (2006) 23–26.

[28] N. Curreli, M.B. Fadda, A. Rescigno, A.C. Rinaldi, G. Soddu, F. Sollai, S. Vaccargiu, E. Sanjust, A. Rinaldi, Mild alkaline/oxidative pretreatment of wheat straw, Process Biochem. 32 (8) (1997) 665–670.

[29] M. Ščiban, M. Klašnja, B. Škrbić, Adsorption of copper ions from water by modified agricultural by-products, Desalination 229 (2008) 170–180.

[30] M.A. Friedman, R.P. Beliles, Three-generation reproduction study of rats receiving acrylonitrile in drinking water, Toxicol. Lett. 132 (2002) 249–261.

[31] Philip Cole, Jack S. Mandel, James J. Collins, Acrylonitrile and cancer: a review of the epidemiology, Regul. Toxicol. Pharm. 52 (2008) 342–351.

[32] R. Saliba, H. Gauthier, R. Gauthier, Adsorption of heavy metal ions on virgin and chemically modified lignocellulosic materials, Adsorpt. Sci. Technol. 23 (4) (2005) 313–322.

[33] I.G. Shibi, T.S. Anirudhan, Synthesis, characterization, and application as a mercury (II) sorbent of banana stalk-polyacrylamide grafted copolymer bearing carboxyl groups, Ind. Eng. Chem. Res. 41 (2002) 5341–5352.

[34] A. Hashem, Amidoximated sunflower stalks (ASFS) as a new adsorbent for removal of Cu(II) from aqueous solution, Polym. – Plast. Technol. Eng. 45 (2006) 35–42.

[35] S. Kamel, E.M. Hassan, M. El-Sakhawy, Preparation and application of acrylonitrile-grafted cyanoethyl cellulose for the removal of copper (II) ions, J. Appl. Polym. Sci. 100 (2006) 329–334.

[36] Y. Wang, B.Y. Gao, W.W. Yue, Q.Y. Yue, Adsorption kinetics of nitrate from aqueous solution onto modified wheat residue, Colloids Surf. A: Physicochem. Eng. Aspects 308 (2007) 1–5.

[37] U.S. Orlando, A.U. Baes, W. Nishijima, M. Okada, A New procedure to produce lignocellulose anion exchangers from agricultureal waste materials, Bioresour. Technol. 83 (2002) 195–198.

[38] J.A. Laszlo, Preparing an ion exchange resin from sugarcane bagasse to remove reactive dye from wastewater, Textile Chem. Color 28 (5) (1996) 13–17.

[39] Y. Wang, B. Gao, Y. Wen, Q. Yu, Preparation and utilization of wheat straw anionic sorbent for the removal of nitrate in aqueous solution, J. Environ. Sci. 19 (2007) 1305–1310.

[40] R.C. Sun, X.F. Sun, J. Tomkinson, Hemicellulose and their characterization, ACS Symposium Ser. 864 (2004) 2–22.

[41] C.F. Liu, R.C. Sun, A.P. Zhang, J.L. Ren, Z.C. Geng, Structural and thermal characterization of sugarcane bagasse cellulose succinates prepared in ionic liquid, Polym. Degrad. Stab. 91 (2006) 3040–3047.

[42] J.X. Sun, X.F. Sun, H. Zhao, R.C. Sun, Isolation and characterization of cellulose from sugarcane bagasse, Polym. Degrad. Stab. 84 (2004) 331–339.

[43] C.F. Liu, F. Xu, J.X. Sun, J.L. Ren, S. Curling, R.C. Sun, P. Fowler, M.S. Baird, Physicochemical characterization of cellulose from perennial ryegrass leaves (*Lolium perenne*), Carbohydr. Res. 341 (2006) 2677–2687.

[44] M.N.V. Prasad, H. Freitas, Removal of toxic metals from solution by leaf, stem and root phytomass of *Quercus ilex* L. (holly oak), Environ. Pollut. 110 (2000) 277–283.

[45] H. Aydın, Y. Bulut, Ć. Yerlikaya, Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents, J. Environ. Manage. 87 (2008) 37–45.

[46] V.C. Taty-Costodes, H. Fauduet, C. Prote, A. Delacroixs, Removal of Cd(II) and Pb(II) ions from aqueous solutions by adsorption onto sawdust of Pinus Sylvestris, J. Hazard. Mater. 105 (1–3) (2003) 121–142.

[47] J. Febrianto, et al., Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies, J. Hazard. Mater. (2008), doi:10.1016/j.jhazmat.200806.042.

[48] Z. Aksu, U. Acikel, T. Kutsal, Investigation of simultaneous biosorption of copper (II) and chromium (VI) on dried chlorella vulgaris from binary metal mixtures: application of multicomponent adsorption isotherms, Sep. Sci. Technol. 34 (1999) 501–524.

[49] Y. Ho, C.T. Huang, H.W. Haung, Equilibrium sorption isotherm for metal ions on tree fern, Process Biochem. 37 (2002) 1421–1430.

[50] M.R. Sangi, A. Shahmoradi, J. Zolgharnein, G.H. Azimi, M. Ghorbandoost, Removal and recovery of heavy metal from aqueous solution using Ulmus carpinifolia and Fraxinus excelsior tree leaves, J. Hazard. Mater. 155 (2008) 513–522.

[51] K.K. Singh, A.K. Singh, S.H. Hasan, Low cost biosorbent 'wheat bran' for the removal of cadmium from wastewater: kinetic and equilibrium studies, Bioresour. Technol. 97 (2006) 994–1001.

[52] M. Nadeem, A. Mahmood, S.A. Shahid, S.S. Shah, A.M. Khalid, G. McKay, Sorption of lead from aqueous solution by chemically modified carbon adsorbents, J. Hazard. Mater. B 138 (2006) 604–613.

[53] E.I. El-Shafey, Sorption of Cd(II) and Se(II) from aqueous solution using modified rice husk, J. Hazard. Mater. 147 (2007) 546–555.

[54] Q. Li, L. Chai, Z. Yang, Q. Wang, Kinetic, thermodynamics of Pb(II) adsorption onto modified spent grain from aqueous solution, Appl. Surf. Sci. (2008), doi:10.1016/j.apsusc.2008.11.024.

[55] E. Pehlivan, B.H. Yanik, G. Ahmetli, M. Pehlivan, Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp, Bioresour. Technol. 99 (2008) 3520–3527.

[56] A.Y. Dursun, Ç.S. Kalayci, Equilibrium, kinetic and thermodynamic studies on the adsorption of phenol onto chitin, J. Hazard. Mater. B 23 (2005) 151–157.

[57] X.Y. Yang, A.D. Bushra, Kinetic modeling of liquid-phase adsorption of reactive dyes on activated carbon, J. Colloid Interface Sci. 287 (2005) 25–34.

[58] Y.S. Ho, G. McKay, A kinetic study of dye sorption by biosorbent waste product pith, Conserv. Recy. 25 (1999) 171–193.

[59] Y.S. Ho, J.C.Y. Ng, G. McKay, Kinetics of pollutant sorption by biosorbents: review, Sep. Purif. Method 29 (2000) 189–232.

[60] Z. Aksu, G. Karabbayır, Comparison of biosorption properties of different kinds of fungi for the removal of Gryfalan Black RL metal- complex dye, Bioresour. Technol. 99 (2008) 7730–7741.

[61] R.J. Willson, A.E. Beezer, The determination of equilibrium constants, ΔG, ΔH and ΔS for vapour interaction with a pharmaceutical drug, using gravimetric vapour sorption, Int. J. Pharm. 258 (2003) 77–83.

[62] C. Namasivayam, R.T. Yamuna, Adsorption of chromium (VI) by a low cost adsorbent: Biogas residual slurry, Chemosphere 30 (1995) 561–578.