Thermodynamics and kinetics of cadmium adsorption onto oxidized granular activated carbon

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Abstract

Cadmium sorption behavior of granular activated carbon oxidized with nitric acid was systematically studied by sets of the equilibrium and time-based experiments under various conditions. The cadmium adsorption capacity of oxidized granular activated carbon enlarged with an increase in pH, and reduced with an increase in ionic strength. Experimental data were evaluated to find out kinetic characteristics. Adsorption processes were found to follow pseudo-second order rate equation. Adsorption isotherms correlate well with the Langmuir isotherm model and the maximum sorption capacity of cadmium evaluated is 51.02 μmol/g. Thermodynamic parameters were calculated based on Van't Hoff equation. Equilibrium constant K_d was evaluated from Freundlich isotherm model constants, Langmuir isotherm model constants, and isotherms, respectively. The average change of standard adsorption heat ΔH^0 was –25.29 kJ/mol. Negative ΔH^0 and ΔG^0 values indicate the adsorption process for cadmium onto the studied activated carbon is exothermic and spontaneous. The standard entropy ΔS^0 was also negative, which suggests a decrease in the freedom of the system.

Key words: cadmium; granular activated carbon; thermodynamics; kinetics; adsorption

Introduction

Heavy cadmium pollution in natural waters caused by industrial accidents have aroused great attention in China recently, as it did in Beijiang River, Guangdong Province and Xiangjiang River, Hunan Province. Cadmium is a typical kind of heavy metals. Its harmful effects include a number of acute and chronic disorders (Rao *et al.*, 2006). Due to its low-concentration-long-term effect in drinking water, cadmium belongs to the chemicals list of endocrine disruptors issued by USEPA, World Wildlife Funds, and some other agencies, as well as the lists of priority control pollutants by USEPA (Waisberg *et al.*, 2003). The discharge of industrial effluent, even in small amounts, may cause damage to aquatic environment and threat the safety of water supply, as the two cases happened in China.

Adsorption is an attractive process, in view of its efficiency and the ease with which it can apply to the treatment of wastewater and water containing heavy metals. The use of some adsorbents for the removal of Cd(II) from aqueous solution has been reported, such as lignocellulosic biosorbent (Shin and Rowell, 2005), bone chare (Choy and Gordon, 2005), Mexican erionite (García-Sosa and Solache, 1997), tree fern (Ho and Wang, 2004), goethite (Collins *et al.*, 1999), sludge-soil mixture (Adriano *et al.*, 2003), Pinus pinaster bark (Vázquez *et al.*, 2002) and cassava waster biomass (Horsfall and Abia, 2003). Some of the adsorbents are not suitable for drinking water treatment processes because of their unstable chemical structures which may result in leaching problems. What's more, processes of water plant are settled and not easy to be changed. So, it is more economical to treat the newly emerged pollutants by promoting conventional processes ability.

Much attention has been paid to research of the metal ion/carbon interaction at the solid-aqueous interface. However, the removal efficiency of pollutants by granular activated carbon (GAC) varies from one to another, partly because the sorption characteristics of activated carbon depend much on their resources, manufacturing processes and chemical or physical pretreatments (Rao *et al.*, 2006; Youssef *et al.*, 2004; Saänchez-Polo and Rivera-Utrilla, 2002). Particularly, several researches were performed under the conditions of pseudo-equilibrium. Despite a lot of studies on this issue, doubts about the influence of the chemical nature on the adsorption of cadmium in aqueous solution still remain. The adsorption mechanism of cadmium and the type of interactions that govern these processes are not fully understood yet. Metal uptake mechanisms of activated carbons were complex and the significance of each interaction may also change with the sorption conditions, such as temperature (Lyubchik *et al.*, 2004).

The study presented herein is aimed at cadmium

removal by oxidized granular activated carbon in drinking water treatment processes. Aiming to understand the mechanisms of cadmium adsorption from aqueous solution, the sorption conditions such as pH, ionic strength and initial metal concentration had been studied. And also the nature of sorption with respect to its thermodynamic and kinetic aspects was evaluated. A particular objective of this study was a comparison of different calculation methods of thermodynamics and the evaluation of thermodynamic parameters (entropy, enthalpy, free energy) of the Cd(II) adsorption on the activated carbon oxidized by nitric acid.

1 Materials and methods

1.1 Materials

One commercial JX430 activated carbon (Tangshan Jianxin Co. Ltd., China) was used. Pre-treatment steps were as follows: sieved activated carbon was merged in $CHCl_3$ solution for 4 h, then dried at 393 K in an oven followed by boiling in HNO_3 (1:1) for 1 h. Then the carbon sample was washed with pure water till the effluent pH was near 7, dried at 393 K followed by air oxidation at 573 K for 1 h. Then the carbon, named as GAC-ox, was cooled and stored in an airtight bottle.

1.2 Surface characterization

The texture of the studied carbons was analyzed using nitrogen adsorption measurement with surface area and porosimetry analyzer (Micrometrics Flow Sorb 2300). The apparent surface areas were determined from the adsorption isotherms using the BET equation. The carbon surfaces were characterized by Boehm titration methods and environment scan electronic microscope (XL-30 ES-EM, Philips Co.). The properties (i.e., apparent surface area, surface groups, SEM) of the activated carbon with and without surface modification are given in Table 1 and Fig.1.

1.3 Chemicals and instrumentation

All reagents used were of analytical reagent grade. Stock solution of cadmium was prepared by dissolving appropriate amounts of metal salts in distilled water. The working solutions were prepared by diluting pure water. pH measurements were determined with Orion

Table 1 Surface characteristics and texture parameters of the studied activated carbons

Characteristics	GAC	GAC-ox
S_{BET} (m^2/g)	1050	910
Ash (%)	11	2
Methylene blue	1046	–
Iodine number	198	–
pH$_{zpc}$	6.70	4.30
Acidity (mmol/g)	0.39	1.40
Basicity (mmol/g)	1.23	0.53
Apparent density (kg/m^3)	0.41	–

pH$_{zpc}$: pH zero point of charge.

CHN818. The cadmium concentration was determined by inductively coupled plasma optical emission spectrometry (Optima 2100DV, Perkin Elmer Company). Pure water was obtained by Mill-Q equipment.

1.4 Sorption experiments

1.4.1 Batch experiments

Batch experiments were conducted using a fixed carbon loading of 1.5 g/L to the 250 ml glass bottles containing 100 ml of the cadmium stock solution, which were shaken at 160 r/min in an incubator at controlled temperatures for 3–5 d. The adsorption isotherms were obtained at four different temperatures, i.e. 293, 298, 308, 315 K. All adsorption isotherms were determined at initial pH 6.0 without adding any buffer for the pH control to avoid an additional electrolyte in the system. After the equilibrium time, solution was filtered by membrane filters with a pore size of 0.45 μm and the metal concentrations were measured by inductively coupled plasma optical emission spectrometry. The kinetic adsorption runs were performed at a fixed sorbate concentration (55–60 μmol/L) for a carbon loading of 1.5 g/L and initial pH 6.0 at different temperatures, i.e. 293, 298, 308, 315 K. Blank sample was conducted to assure cadmium loss caused by experiment equipment could be omitted.

1.4.2 Mathematical procedures

The amounts of cadmium uptaken by activated carbon was calculated as:

$$q_t = (c_0 - c_t)V/m$$
$$q_e = (c_0 - c_e)V/m \tag{1}$$
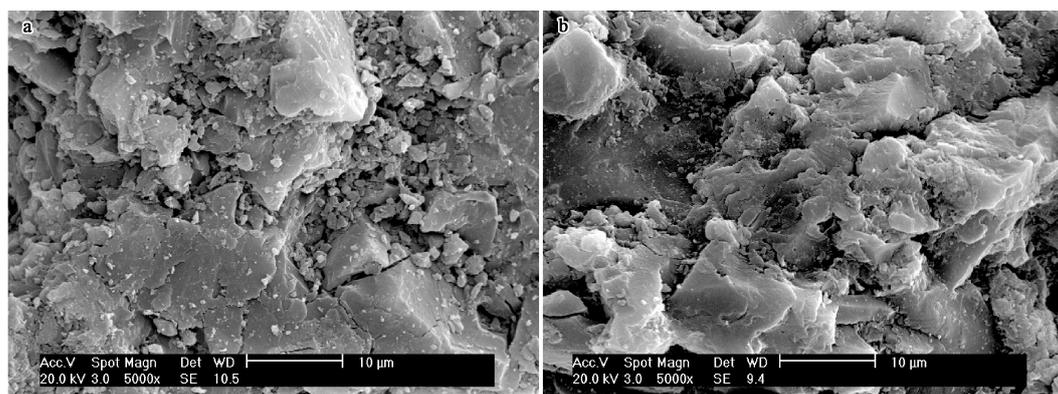
where, q_t and q_e are the amount of metal ions adsorbed

Fig. 1 SEM micrographs of virgin GAC (a) and GAC-ox(b).

onto activated carbon at time t and equilibrium, respectively (μmol/g); c_0, c_t and c_e are the initial, time t and equilibrium concentrations of metal ions in the solution (μmol/L); V is the volume of the aqueous phase (L); m is the dry weight of the carbon (g); t is the adsorption period (min).

The sorption kinetic data of cadmium on the adsorbent studied was analyzed in terms of pseudo-first order and pseudo-second order rate equation (Ho and Gordon, 1999).

The linearized form of pseudo-first order rate equation is given as:

$$\lg(q_t - q_e) = \lg q_e - k_1 t / 2.303 \qquad (2)$$

The linearized form of pseudo-second order rate equation is given as:

$$t/q_t = 1/v_0 + t/q_e \qquad v_0 = k_2 q_e^2 \qquad (3)$$

where, k_1 (min^{-1}), k_2 (g/(μmol·min)) are rate constants of pseudo-first order, pseudo-second rate equation, respectively. v_0 is the initial adsorption rate (μmol/(g·min)).

The data for the uptake of cadmium at different temperatures were processed in accordance to the linearized form of the Langmuir and Freundlich isotherm equations:

Langmuir equation: $c_e/q_e = 1/(q_m b) + c_e/q_m$

Freundlich equation: $\lg q_e = 1/n \lg c_e + \lg K_f$

where, q_m (μmol/L) is the maximum sorption capacity, b (L/μmol) is the Langmuir isotherm constant. n, K_f (μmol/g) are Freundlich constants.

The thermodynamic parameters of the adsorption, i.e. the standard Gibbs free energy ΔG^0 (kJ/mol), standard enthalpy ΔH^0 (kJ/mol) and entropy ΔS^0 (J/(mol·K)), were calculated from the Van't Hoff equation.

$$\Delta G^0 = -RT \ln K_d \qquad (4)$$

$$\ln K_d = \Delta H^0 / (-RT) + \Delta S^0 / R \qquad (5)$$

where, the slop and intercept of the plot of $\ln K_d$ versus $1/T$ were used to determine the ΔH^0 and ΔS^0. R is the gas constants (8.314 J/(mol·K)) and T(K) is the absolute temperature.

2 Results and discussion

2.1 Effect of pH

The pH of a solution is an important parameter in adsorption process. Fig.2 shows the variation of cadmium uptake at different pH. The two dash lines in Fig.2 display the theoretical distribution of cadmium species present in aqueous solution at different pH values (Saänchez-Polo and Rivera-Utrilla, 2002). It could also be found that the sorption capacity of GAC-ox was much greater than that of virgin GAC at any pH value. This was mostly ascribed to the fact that the pH$_{pzc}$ of GAC was shifted to a lower pH after modifying with acid, and the total amounts of acidity of GAC-ox increased three times compared to GAC, as shown in Table 1. The removal efficiency was low under acidic conditions and increased with an increase in pH, i.e.
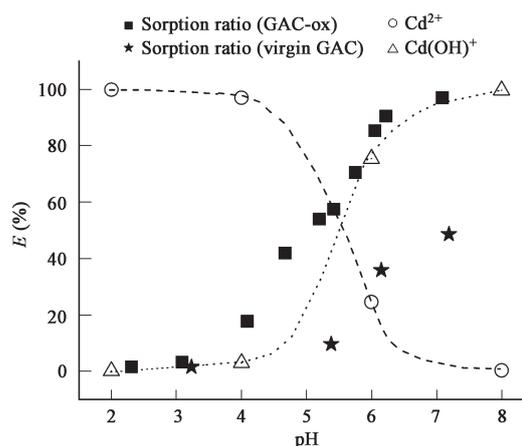
Fig. 2 Removal of cadmium on GAC-ox as a function of pH at 298 K. GAC: 0.4 g/L; I: 0.001 mol/L; Cd^{2+}: 4.5 μmol/L

GAC-ox: from 1.5% at pH 2.31 to 97.0% at pH 7.09; virgin GAC: from 1.6% at pH 3.23 to 48.6% at pH 7.19. This is because higher pH could do benefit to the hydrolization of surface acidic functional groups that took part in the uptake of cadmium such as carboxylic groups (pK$_a$ 3–6). Increasing pH increases the negative charge of carbon surface, which enlarge the cation-exchange capacity of carbon. At the same time, the force of electrostatic attraction were weakened because of the increasing fraction of Cd(OH)$^+$ with the rise in pH. But this effect maybe insignificant compared with those positive effects.

2.2 Effect of ionic strength

Adsorption behaviour at different ionic strengths (0.001, 0.01 and 0.1 mol/L KNO$_3$) was investigated. As shown in Fig.3, adsorption capacity decreases gradually with the increase of KNO$_3$ concentration. There is no substantial distinction between 0.001 mol/L isotherm and 0.01 mol/L isotherm. The two curves follows Freundlich isotherm equation ($r^2 > 0.99$), whereas the isotherm of 0.1 mol/L dose not fit Freundlich equation quite well. The equations are:

with 0.001 mol/L KNO$_3$:

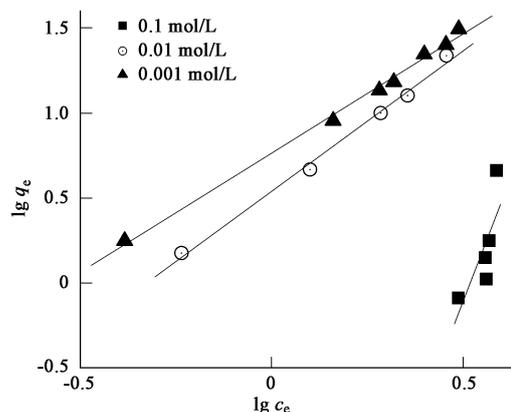$$\lg q_e = 0.7646 + 1.405 \lg c_e \qquad r^2 = 0.997 \qquad (6)$$

Fig. 3 Effect of ionic strength on cadmium adsorption at 298 K. GAC: 0.4 g/L; pH 6.0.

with 0.01 mol/L KNO₃:

$$\lg q_e = 0.5398 + 1.652 \lg c_e \qquad r^2 = 0.997 \tag{7}$$

with 0.1 mol/L KNO₃:

$$\lg q_e = -3.035 + 5.857 \lg c_e \qquad r^2 = 0.772 \tag{8}$$

Adsorption capacity at equilibrium of 0.1 mol/L was about one fourth that of 0.001 mol/L. It seems the sorption processes were hindered partly by K^+ in the solution. Analogical results were also given in some works (Youssef *et al.*, 2004). Dastgheib and Rockstraw (2002) reported the presence of Na^+ decreased heavy metal ion interaction constants and they explained it due to the accumulation of charge in the vicinity of the surface, which created a localized potential that repelled other cations, thus reduced their adsorption potential.

2.3 Effect of contact time and adsorption kinetics

Cadmium uptakes at different temperatures were evaluated as a function of time to determine an optimal contact time. Fig.4 shows the time course of adsorption equilibrium of cadmium onto activated carbon. Sorption equilibrium at each temperature attained within 24–30 h. The kinetic data were analyzed in terms of pseudo-first order and pseudo-second order rate equation and the results are given in Table 2. Actually, pseudo-first order rate equation can only provide good fitness of the original sorption stages in stead of the whole processes. Judging from the regression coefficients, it seems the kinetic behaviour could be satisfactorily explained by pseudo-second order rate equation, of which the regression coefficients are higher than 0.97 and the q_e values calculated are in good agreement with the results of experiments.

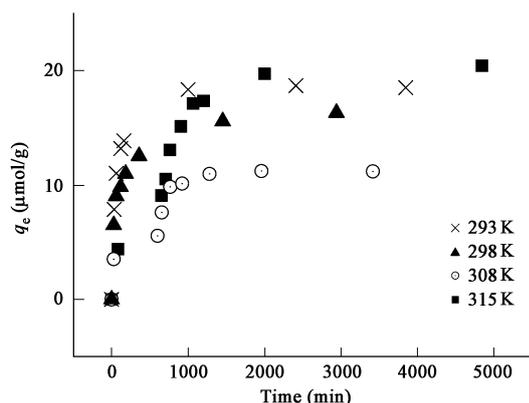The sorption capacity decreased with the increase in temperature and reached minimum at 308 K. Then a further increase in temperature resulted in a drastic rise in the metal uptake. The maximum q_e calculated from pseudo-second order rate equation is 22.68 μmol/g at 315 K. The initial adsorption rate also shows a similar trend. These phenomena suggest a complex sorption mechanism: the co-existence of physisorption, i.e. ion exchange, electrostatic attraction and chemisorption, i.e. surface complexation. With the rise in temperature, the effect on the sorption affinity include a weakening of sorptive forces in the case of the exothermic process and an increasing interaction at high temperature for those endothermic reactions (Lyubchik *et al.*, 2004).

2.4 Adsorption isotherms

Figure 5 shows the isotherms at temperature 293–315 K. Based on the results of kinetics, the sorption duration was set to 72 h to guarantee a real equilibrium. The uptake of cadmium increased with increasing the initial concentrations and reached a plateau, which suggested the equilibrium adsorption capacity of carbon. Although not in the same extent, the change of isotherm along with the variation of temperature is just like that of kinetics. This could be attributed again to the complex sorption mechanisms of cadmium onto studied activated carbon.

We applied two typical adsorption isotherm equations of Langmuir equation and Freundlich equation to fit the experimental data. The constants and correlation coefficients are summarized in Table 3. As can be seen from Table 3, the fit is a little better with Langmuir model than with Freundlich model. The regression coefficients of Langmuir model at all temperatures are greater than 0.96. The Langmuir constants q_e are 51.02, 42.92, 24.51 and 31.06 μmol/g at 293, 298, 308 and 315 K, respectively, which are

Fig. 4 Kinetics of cadmium sorption on the studied activated carbon at different temperatures. GAC-ox: 1.5 g/L; *I*: 0.01 mol/L; c_0: 55–60 μmol/L; pH 6.0.
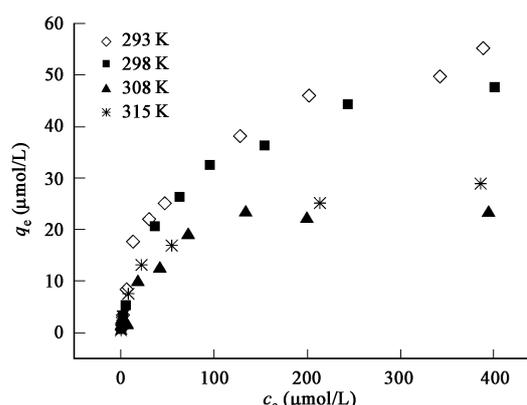

Fig. 5 Cadmium adsorption isotherms of GAC-ox. GAC-ox: 1.5 g/L; *I*: 0.01 mol/L; pH 6.0.

Table 2 Kinetic parameters of cadmium adsorption on the studied activated carbon at different temperatures

Temperature (K)	Pseudo-first order rate equation		Pseudo-second order rate equation		
	k_1 (× 10^{-3} min^{-1})	r^2	q_e (μmol/g)	v_0 (μmol/(g·min))	r^2
293	2.46	0.906	18.83	0.0440	0.999
298	1.53	0.985	16.67	0.0289	0.999
308	1.16	0.915	12.79	0.0212	0.974
315	1.46	0.984	22.68	0.0479	0.994

Table 3 Freundlich equation and Langmuir equation constants

Temperature (K)	Freundlich			Langmuir		
	$1/n$	K_f (µmol/g)	r^2	q_m (µmol/g)	b (L/µmol)	r^2
293	0.568	2.396	0.938	51.02	0.03186	0.967
298	0.622	1.647	0.975	42.92	0.03553	0.962
308	0.506	1.689	0.947	24.51	0.05415	0.998
315	0.604	1.432	0.949	31.06	0.05546	0.996

in accordance with the experimental data. The cadmium isotherms showed Freundlich characteristics with 1/n of 0.50–0.62.

2.5 Adsorption thermodynamics

According to Van't Hoff equation, thermodynamic parameters i.e. the standard adsorption Gibbs free energy ΔG^0, enthalpy ΔH^0 and entropy ΔR^0 can be calculated from the variations of the thermodynamic equilibrium constant K_d, which was determined using the method from literature (Zhang and Zhang, 1998). K_d of the first two methods was derived from the constants of Freundlich and Langmuir model, respectively. K_d of the third method was derived from the adsorption isotherm directly. Both the isotherms (Fig.5) and kinetics (Fig.4) show a turning point with the increase of temperature, while the thermodynamic calculation was based on the linear plot of $\ln K_d$ versus $1/T$ (Fig.6). Thus the application of Van't Hoff equation would not fully coincide with actual sorption processes. Nevertheless it gives some information on the sorption mechanism for studied carbon.

The results of standard sorption enthalpy ΔH^0 from three methods are near to each other. The average value is $-(25.29\pm3.34)$ kJ/mol. Negative ΔH^0 value indicates the whole process is exothermic. The standard sorption entropy ΔS^0 is negative too. The fixation of cadmium resulted in the decrease in the freedom of the whole system. However, some process like ion-exchange will release water molecule from solid surface into bulk solution which increase the entropy. Therefore the entropy alteration is the sum of these two processes. In these experiments ion-exchange might not be the main mechanism, for the enthalpy changes for ion-exchange reactions are usually smaller than 8.4 kJ/mol (Lyubchik *et al.*, 2004), while the calculated enthalpy (Table 4) is about three

times of that (–25.29 kJ/mol). Of the first two methods, standard free energy ΔG^0 at all temperatures is negative and changed with the rise in temperature. This suggests the adsorption process is spontaneous in nature and the spontaneity decrease with the increase in temperature. There is a big difference between the ΔG^0 values of the third method and that of the first two methods, which could not be explained sensibly. Hence the third method may not suitable to be used in this experiment. von Oepen *et al.* (1991) have detected the sorption free energy of several kinds of interactions (Van der Waals force is 4–10 kJ/mol, hydrophobic force is about 5 kJ/mol, hydrogen bond is 2–40 kJ/mol, coordination exchange is 40 kJ/mol, dipole force is 2–29 kJ/mol, chemical bond is above 60 kJ/mol). According to our calculations (Table 4), the main interaction between oxidized activated carbon and cadmium are probably hydrogen bond and/or dipole force.

Table 4 Thermodynamic parameters of the cadmium adsorption on the studied activated carbon at different temperatures

Calculation methods of K_d	T (K)	K_d	ΔG (kJ/mol)	ΔS (J/(mol·K))	ΔH (kJ/mol)
$K_d = K_f^n$	293	4.66	–3.54	–80.71	–27.19
	298	3.01	–3.14		
	308	2.82	–2.33		
	315	1.81	–1.77		
$K_d = 1/b$	293	31.39	–8.39	–44.52	–21.44
	298	28.15	–8.17		
	308	18.47	–7.73		
	315	18.03	–7.41		
$K_d = q_e/c_e$	293	0.142	4.86	–109.6	–27.25
	298	0.119	5.41		
	308	0.059	6.51		
	315	0.075	7.21		

3 Conclusions

The sorption capacity of studied carbon could be enhanced with the increase in pH. In this experiment, the removal efficiency is higher than 95% at pH 7. The adsorption process of cadmium is hindered to some extent by ionic strength.

Sorption kinetics follows pseudo-second order rate equation. The regression coefficients are higher than 0.97 and the q_e values calculated are in good agreement with the observation of experiments.

The sorption isotherms follow both Langmuir model and Freundlich model. The maximum sorption capacity under the conditions of this experiment is 51.02 µmol/g.

The change of sorption kinetics and isotherms with the increase in temperature have similar trend. The initial sorption rate and sorption equilibrium capacity decrease with
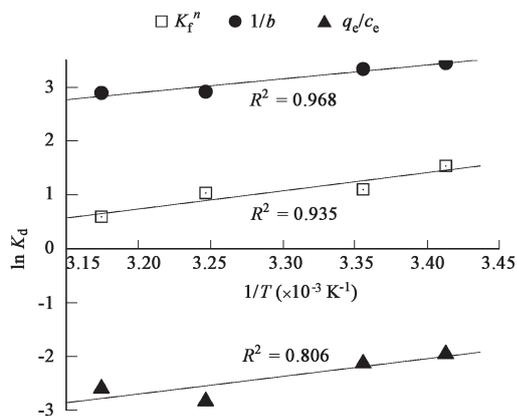

Fig. 6 Van't Hoff plot for the cadmium adsorption on GAC-ox.

the rise in temperature from 293 to 308 K, then increase with the further rise in temperature. The adsorption of cadmium onto studied activated carbon is rather a complex process, the mechanism of which may include both physic-sorption and chemi-sorption. Thermodynamic parameters calculated based on different methods show the average change of standard adsorption heat ΔH^0 is –25.29 kJ/mol and the adsorption process is exothermic and spontaneous.

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