

# Study of Cr(VI) adsorption onto nitrogen-containing activated carbon preparation from bamboo processing residues

Tong Xin Shang · Ji Zhang · Xiao Juan Jin · Jian Min Gao

Received: 26 August 2013 / Accepted: 4 December 2013 / Published online: 18 March 2014  
© The Japan Wood Research Society 2014

**Abstract** Nitrogen-containing bamboo charcoals were prepared using bamboo processing residues, and modified by melamine or urea. The iodine value of the products we obtained was analyzed, and two samples were chosen for the Cr(VI) adsorption. The experimental results show that under the KOH and carbon ratio of 3:1 ( $w_1/w_2$ ), activation temperature 800 °C and activation time 1 h, the activated carbons modified by melamine boasted the iodine value of 1144 mg/g and the activated carbons modified by urea boasted the iodine value of 1263 mg/g. In addition, the equilibrium adsorption capacity is 95.3 mg/g for the activated carbons modified by melamine with the adsorbent dosage of 1.0 g/L at an initial pH 2 in the presence of 100 mg/L  $K_2Cr_2O_7$  at 30 °C for 180 min and it is 94.2 mg/g for the activated carbons modified by urea in the same reaction condition. The pseudo-second-order kinetic model can better reflect the two kinds of nitrogen-containing activated carbons adsorption kinetic process of Cr(VI). The adsorption process conforms to the Langmuir model, indicating that the process is single molecular layer adsorption.

**Keywords** Bamboo processing residues · Nitrogen-containing activated carbon · Adsorption · Cr(VI)

## Introduction

Bamboo grows quickly, and it will grow into useful timber in a short time. So it becomes the most important resources

that get a wide range of applications in industry. A large number of residues were produced in the process of bamboo timbers. According to the statistical analysis [1–6], bamboo utilization rate usually <40 % in the process of bamboo floor, bamboo plywood, bamboo mat and so on. Therefore, more than 60 % of the bamboo in processing becomes residues. However, only a subsection of the residues are utilized, and the majority are burnt or discarded. Apart from wasting resource, it seriously pollutes the environment. Consequently, to make full use of resource, it is necessary to find a new method that can utilize the bamboo processing residues efficiently. Preparing activated carbons from bamboo is an excellent way to utilize bamboo timbers efficiently and a direction for the industrial application of bamboo [7]. Also, the activated carbons were provided with the better porosity structure and the higher adsorption capacity for the toxic inorganic ion [8] from water.

Chromium(Cr) compounds are widely used in industry such as electroplating, metal finishing, leather tanning, and pigments. The predominant use of chromium in industry unfortunately introduces an environmental concern. Cr exists almost exclusively in the Cr(III) oxidation state or in the Cr(VI) oxidation state. In the environment Cr(III) is typically not a problem, and its relative toxicity is low. In contrast, Cr(VI) compounds are toxic chemicals and genotoxic carcinogens [9]. Thus, the presence of Cr(VI) ions in the environment is posing serious problems and causing great public concern [10, 11]. Currently, the United States Environmental Protection Agency (USEPA) has set a maximum contaminant level (MCL) for chromium at 0.1 parts per million (ppm) in drinking water [12]. The increasing concern with Cr(VI) pollution significantly motivates the investigation and development of new and improved materials to

T. X. Shang · J. Zhang · X. J. Jin (✉) · J. M. Gao  
School of Material Science and Technology, Beijing Forestry University, 35 Qinghua East Road, Haidian, Beijing 100083, China  
e-mail: jxj0322@163.com

address the problems. A wide range of technologies have been investigated for the removal of Cr(VI) from water [13–19]. Adsorption using activated carbons proved to be the most efficient technique [15–19].

Chemical modifications could improve the adsorption capacity of activated carbons. Also, the nature and concentration of surface functional groups may be modified by various post-activation treatment methods, e.g., for incorporation of nitrogen into the carbon structure, carbons are treated with ammonia, urea, dicyanodiamine, *N,N*-dimethylformamide, melamine at high temperatures. Oxidation pretreatment of the active carbon using nitric acid enhanced the incorporation of nitrogen into the carbon by ammonia treatment. Another way to prepare nitrogen-containing carbons is carbonization of a nitrogen-rich precursor and activation of carbonized polymer by steam. These modified carbons have well-developed micropore and mesopore. The nitrogen chemical functions are transformed during heat treatment. In the char and activated carbons, the nitrogen is present in six-membered rings included in polyaromatic structures [20–27]. The presence of heterocyclic nitrogen compounds incorporated in the carbon matrix and having free pair of electrons increase the electron donor capacity of solids. Therefore, nitrogen-containing activated carbons are effective adsorbents of heavy metal ions through the education of donor–acceptor complexes. Lorenc-Grabowska et al. [28] studied the influence of an enhanced amount of nitrogen functionalities in activated carbon upon the adsorption of phenol from water. They found that the affinity of phenol towards the surface of the nitrogen-containing activated carbon was enhanced with the increase in nitrogen content.

In this paper, two chemically activated carbons modified by melamine and urea were prepared from bamboo processing residues and utilized in Cr(VI) adsorption. The effects of activation temperature and KOH/carbons on the yield and iodine value were investigated. The influence of several parameters, such as pH, temperature, initial concentration of Cr(VI), adsorbent dosage and contact time, on the adsorption process was also investigated. Furthermore, the characterization of Cr(VI) adsorption was described by the kinetics models and adsorption isotherms.

## Materials and methods

### Materials

Bamboo processing residues were collected from bamboo processing factory in Beijing Forestry University.

Other chemicals with analytical grade were purchased from Beijing Lanyi Chemical reagent.

### Adsorbent preparation

Carbonization process was carried out in nitrogen atmosphere (50 mL/min) at the temperature increase rate of 10 °C/min to the final temperature of 500 °C, separately, maintained for 1 h. The carbonized sample was then ground and screened out with sieves. The fraction in the particle diameter ranged from 40 meshes to 60 meshes. The particle samples were dried in a 105 °C oven for 8 h; in activation step, 3 g of the oven-dried samples was mixed with melamine and urea at the ratio of 2:3 ( $w_1/w_2$ ), separately. The N-modified activated carbons with melamine or urea were obtained, they were marked NAC. Then the resulting mixture was soaked in a 50 % KOH solution for 16 h at the mass ratio impregnation 3:1 ( $w_1/w_2$ ). The samples were then activated at 800 °C for 60 min in nitrogen atmosphere. The obtained activated carbons with melamine and urea modified were marked as AC<sub>1</sub> and AC<sub>2</sub>, respectively. These activated carbons were boiled first with 1 M HCl solution and then with distilled water until the pH of solution reach to about 6–7. Finally, these activated carbons were dried at 105 °C in an oven for 8 h.

### Cr(VI) adsorption experiments

The stock Cr(VI) solution with a Cr(VI) concentration of 1000 mg/L was prepared using the same method described in a previous work [29]. For the adsorption experiment, the concentration of Cr(VI) was determined using UV–visible spectrophotometer at 540 nm wavelength, using 1,5-diphenyl carbazide. The amount of Cr(VI) adsorbed by the adsorbent  $q_e$  (mg/g) was calculated according to the following equation:

$$q_e = \frac{(c_0 - c_1) \times V}{1000 m} \quad (1)$$

where  $c_0$  (mg/L) and  $c_1$  (mg/L) are the concentrations of Cr(VI) before and after the adsorption, respectively;  $V$  (mL) is the volume of the Cr(VI) solution and  $m$  (g) is the weight of the adsorbent.

The adsorption percentage is calculated according to:

$$\% = \frac{c_0 - c_1}{c_0} \times 100. \quad (2)$$

The kinetics study was performed in a 100 mL 100 mg/L Cr(VI) solution at pH 2. The adsorbent feed was 1.0 g/L. The effect of the adsorbent feed on the Cr(VI) uptake was also studied in a 100 mL 100 mg/L Cr(VI) solution at pH 2, with the adsorbent feed increasing from 0.1 to 2.0 g/L. To study the effect of pH on the adsorption of Cr(VI), a series of 100 mL Cr(VI) solution was adjusted with HCl or NaOH. The adsorbent feed was 1.0 g/L. For the adsorption isotherm study, 100 mL Cr(VI) solutions with the different concentrations ranging from 50 to 280 mg/L was used. The pH was kept at 2 while the adsorbent feed was 1.0 g/L.

Adsorption model

*Kinetic model*

Pseudo-first-order [30], pseudo-second-order [31] and intra-particle diffusion kinetic models [32] were used to fit the adsorption kinetic data.

The pseudo-first-order kinetic equation is

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

which has a linear form of

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

where  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant for the pseudo-first-order kinetic equation and  $q_e$  (mg/g) and  $q_t$  (mg/g) are the amounts of solute adsorbed per unit adsorbent at equilibrium and at time  $t$  (min), respectively.

The pseudo-second-order kinetic equation is

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

which has a linear form of

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the rate constant for the pseudo-second-order kinetic equation.

The intra-particle diffusion model is

$$q_t = k_{\text{dif}} t^{1/2} + C \tag{7}$$

where  $k_{\text{dif}}$  is the intra-particle diffusion rate constant,  $k_{\text{dif}}$  and  $C$  can be obtained from the slope and intercept of the plot  $q_t$  versus  $t^{1/2}$ .

*Isotherm models*

The adsorption equilibrium was evaluated by the models of Langmuir [33] and Freundlich [34]. The parameters of each model were calculated by non-linear fitting using Origin 7.5 software (OriginLab, USA).

The simplest model for adsorption events corresponds to the Langmuir isotherm which is used to describe adsorption by homogenous surface is given by:

$$q_e = q_{\text{max}} \frac{k_L c_e}{1 + k_L c_e} \tag{8}$$

which has a linear form of

$$\frac{c_e}{q_e} = \frac{1}{q_{\text{max}}} c_e + \frac{1}{k_L q_{\text{max}}} \tag{9}$$

where  $q_e$  is the amounts of solute adsorbed per unit adsorbent at equilibrium (mg/g),  $q_{\text{max}}$  is the saturation

capacity (mg/g),  $c_e$  (mg/L) is the equilibrium concentration of the adsorbate and  $k_L$  is the Langmuir constant (L/mg).

Another simple equation for representing adsorption by heterogeneous surface:

$$q_e = k_F c_e^{1/n} \tag{10}$$

which has a linear form of

$$\log q_e = \log k_F + \frac{1}{n} \log c_e \tag{11}$$

where  $k_F$  is a constant indicative of the adsorption capacity of the adsorbent and  $n$  is an empirical constant called the Freundlich coefficient. Values of parameter  $n$  of this model are close to 1 which resulting from linearity of isotherms.

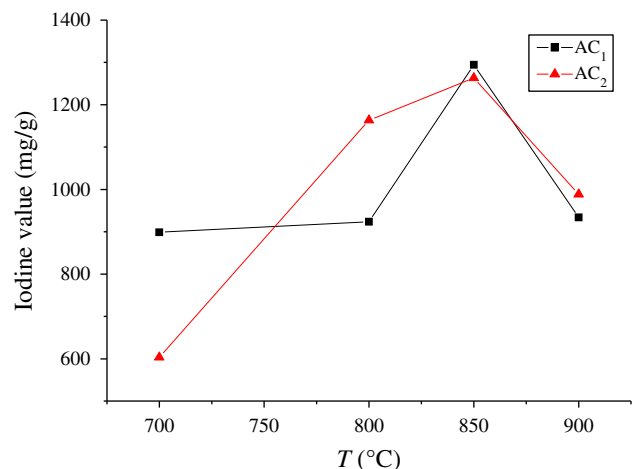
**Results and discussion**

Adsorbent characterization

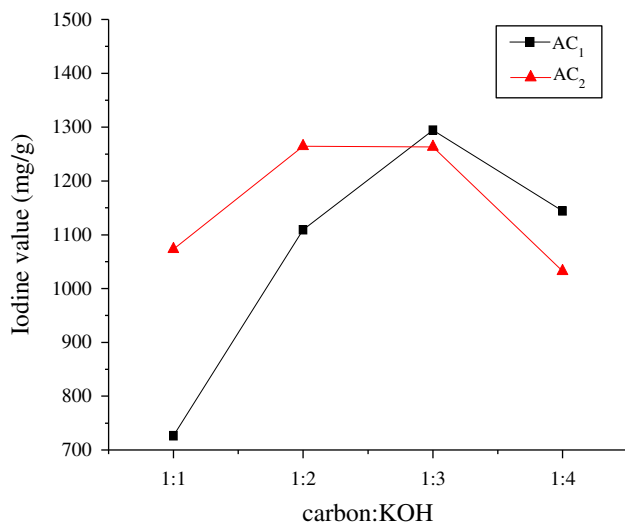
Two batteries of NAC prepared from different activation condition and modified with melamine and urea were studied, respectively. The iodine adsorption capacity of NAC was used as a parameter to choose the better activated carbons. Besides, the elemental analysis of the better activated carbons was carried out.

*Effect of activation temperature*

The effects of activation temperature were studied when the resulting mixture was soaked in a 50 % KOH solution for 16 h at the mass ratio impregnation 3:1 ( $w_1/w_2$ ), and the experimental results were shown in Fig. 1. The iodine



**Fig. 1** Influence of activation temperature on the iodine value of NAC. KOH:carbon = 3:1 ( $w_1:w_2$ )



**Fig. 2** Influence of KOH/carbon ratio on the iodine value of NAC.  $T = 850\text{ }^{\circ}\text{C}$

value of AC<sub>1</sub> and AC<sub>2</sub> increased from 899 to 1144 mg/g and 603 to 1263 mg/g with an increase on temperature from 700 to 850 °C, respectively. Then, it decreased from 1144 to 934 mg/g and 1263 to 989 mg/g with an increase of temperature from 850 to 900 °C, respectively. The changing trend of iodine value reflects the changing trend of external surface area of activated carbons. That is to say the external surface area gets the highest value at 850 °C. It was probably that when the activation temperature reached a certain value, the pores would be widened and burnt off. A similar conclusion has been observed by Wu et al. [35]. Based on comprehensive consideration, 850 °C was chosen for optimum activation temperature.

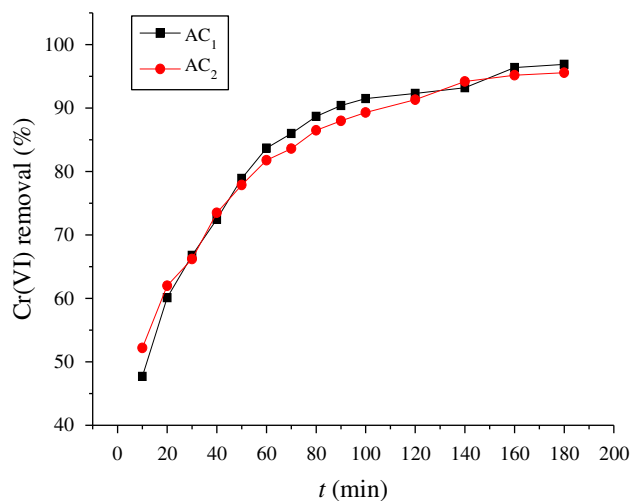
#### Effect of KOH/carbons

The effects of KOH/carbons were studied when the resulting mixture was soaked in a 50 % KOH solution for 16 h and the activation temperature was 850 °C. The experimental results were shown in Fig. 2. As can be seen from Fig. 2, for AC<sub>1</sub>, when the ratio increased from 1 to 3, the iodine value increased from 726 mg/g to 1294 mg/g; and then, with the increasing ratio, the iodine value decreased. The trends of AC<sub>2</sub> could be found as well. It was shown that the external surface area gets the highest value at the ratio of 3:1 ( $w_1/w_2$ ). It was probably that when the KOH/carbons ratio reached a certain value, the pores would be widened and burnt off. A similar conclusion has been observed by Wu et al. [35].

AC<sub>1</sub> took the maximum iodine value at the ratio of 3 and AC<sub>2</sub> took the maximum iodine value at the ratio of 2. However, the iodine value of AC<sub>2</sub> at the ratio of 2 was similar to the value at the ratio of 3. Taking all these factors into consideration, two batteries of NAC activated with the

**Table 1** Elemental analysis of activated carbons

Activated carbons	Elemental analysis		
	C (wt, %)	H (wt, %)	N (wt, %)
Pristine activated carbons	81.77	0.528	1.461
AC <sub>1</sub>	82.03	1.063	6.237
AC <sub>2</sub>	82.61	0.802	4.815



**Fig. 3** Influence of contact time on Cr(VI) ion adsorption. Adsorbent dosage = 1.0 g/L, volume of Cr(VI) solution = 100 mL,  $c_0 = 100\text{ mg/L}$ ,  $T = 30\text{ }^{\circ}\text{C}$ , pH 2

KOH/carbons ratio of 3 at 850 °C were chosen for Cr(VI) adsorption and elemental analysis.

#### Elemental composition

The elemental analysis (contents in carbon, hydrogen and nitrogen) of the activated carbons was carried out using CHNS Analyzer (Thermofinnigan Flash, EA, 1112 series).

C, H, N contents of the activated carbons prepared from bamboo processing residues are shown in Table 1. As can be seen from Table 1, compared with the pristine activated carbons, AC<sub>1</sub> and AC<sub>2</sub> had higher N content, which indicated that modification of the activated carbons makes a great contribution to the N content. Also, it is obviously that N content of AC<sub>1</sub> is higher than AC<sub>2</sub>, which indicated that the N content in the activated carbons has the close relationship with the N content in the modifier.

#### Adsorption behavior

##### Effect of contact time

The adsorption processes as a function of time to determine the point of equilibrium were studied from adsorption

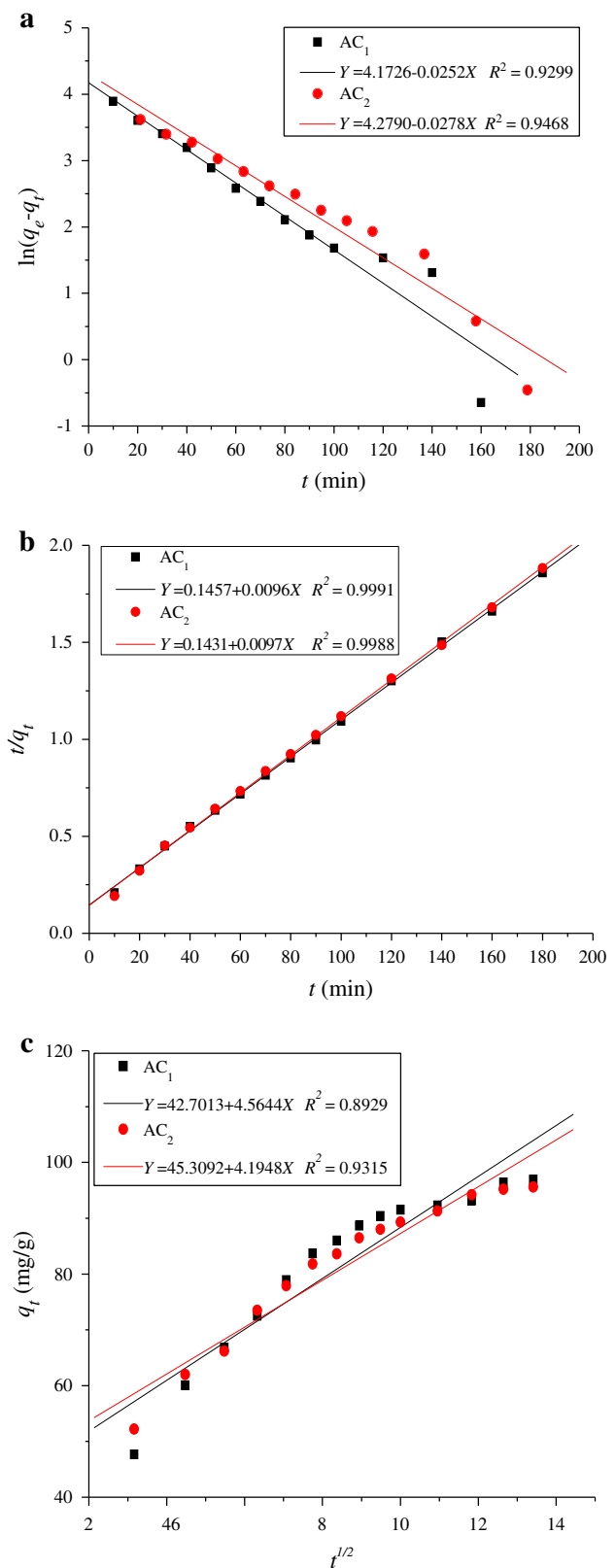
experiments of Cr(VI) ion onto AC<sub>1</sub> and AC<sub>2</sub>, respectively. These experiments were carried out at an initial pH 2 in the presence of 100 mg/L K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> at 30 °C. The results are shown in Fig. 3, where it is clear that adsorption of Cr(VI) ion increases sharply in 80 min and then levels off. The amount of Cr(VI) ion removed reached a maximum after 180 min. The percentage of adsorption of AC<sub>1</sub> and AC<sub>2</sub> is up to 95 %.

In the majority of the studies on kinetic process of metal ion adsorption on various adsorbents, a distinct two-step behavior was reported [36, 37]. Liu and Huang [36] attributed the two-step adsorption characteristic to the heterogeneity of the surface binding sites on sorbents, explaining that different binding sites had different binding affinities to metal ions and resulted in different binding rates. However, Qin et al. [37] asserted that the fast initial sorption owed to the fast transfer of metal ions to the surface of sorbent particles, while the following slow sorption was as a result of the slow diffusion of metal ions into the intra-particle pores of sorbents.

To investigate the mechanism of Cr(VI) adsorption on the two adsorbents and to examine the rate-controlling step of the adsorption process, the pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models (see Fig. 4) were tested to fit the kinetic sorption data. The kinetic parameters acquired from fitting results are summarized in Table 2. For the AC<sub>1</sub>, although the correlation coefficient ( $R^2$ ) of pseudo-first-order equation is nearly 0.95, the equilibrium adsorption capacity,  $q_e$ , derived from the equation is 64.9 mg/g and much lower than the actual amount of equilibrium adsorption (95.3 mg/g). While the same result can be obtained for the AC<sub>2</sub>. Therefore, the pseudo-first-order equation is not a good fit for Cr(VI) adsorption on the two adsorbents. The kinetic adsorption data were further fitted by the pseudo-second-order kinetic model and a better fitting was obtained with a higher correlation coefficient for the two adsorbents. Furthermore, the calculated equilibrium adsorption capacity  $q_e$  of AC<sub>1</sub> and AC<sub>2</sub> is more similar to the actual amount of adsorption equilibrium. The pseudo-second-order model is based on the assumption that the rate-limiting step is a chemical sorption involving balance force through sharing or exchange of electrons between adsorbent and adsorbate [38, 39]. Successful fitting of this model suggests that chemisorption is the rate-controlling step [31]. In addition, from the intra-particle diffusion model,  $C$  value was calculated. The deviation of  $C$  value from zero indicates that intra-particle diffusion is not the sole rate-controlling step and boundary layer diffusion controls the adsorption to some degree [40].

#### Effect of initial Cr(VI) concentration

Assessment of the effect of initial concentration on the adsorption of Cr(VI) on two batteries of NAC was carried out

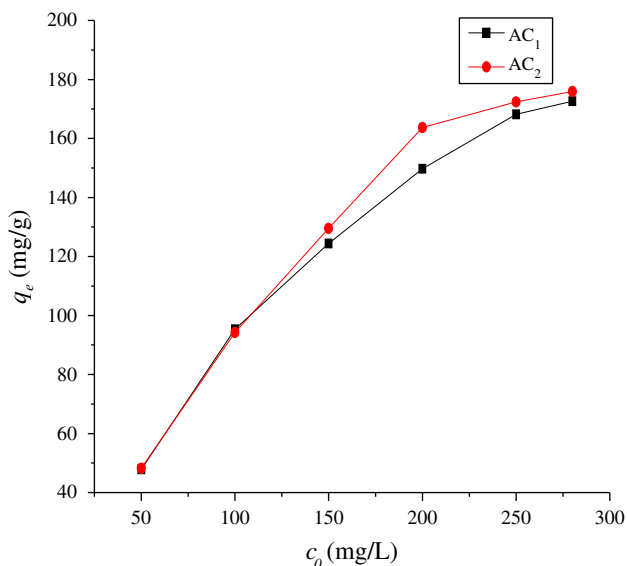


**Fig. 4** Linearized form of pseudo-first-order (a), pseudo-second-order (b) and intra-particle diffusion kinetic plot (c) for Cr(VI) ion adsorption

**Table 2** Kinetics parameters for Cr(VI) adsorption onto AC<sub>1</sub> and AC<sub>2</sub>

Adsorbent	Pseudo-first-order kinetic models $\ln(q_e - q_t) = \ln q_e - k_1 t$			Pseudo-second-order kinetic models $\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$			Intra-particle diffusion kinetic models $q_t = k_{dif} t^{1/2} + C$		
	$q_e$ (mg/g)	$k_1$	$R^2$	$q_e$ (mg/g)	$k_2$	$R^2$	$C$	$k_{dif}$	$R^2$
AC <sub>1</sub>	64.9	0.025	0.9299	104.2	$6.32 \times 10^{-4}$	0.9991	42.7	4.564	0.8929
AC <sub>2</sub>	72.2	0.028	0.9468	103.1	$6.58 \times 10^{-4}$	0.9988	45.3	4.195	0.9315

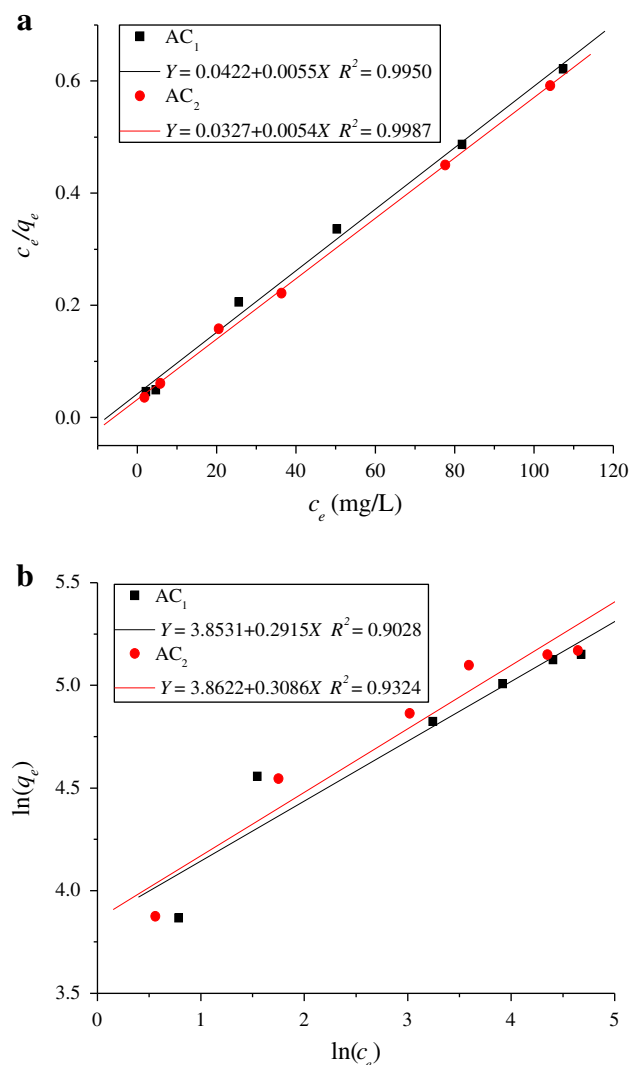
$k_1$  the rate constant for the pseudo-first-order kinetic equation,  $k_2$  the rate constant for the pseudo-second-order kinetic equation,  $k_{dif}$  the intra-particle diffusion rate constant,  $q_e$  the amounts of solute adsorbed per unit adsorbent at equilibrium,  $q_t$  the amounts of solute adsorbed per unit adsorbent at time  $t$  (min)



**Fig. 5** Influence of initial concentration on Cr(VI) ion adsorption. Adsorbent dosage = 1.0 g/L, volume of Cr(VI) solution = 100 mL,  $t = 180$  min,  $T = 30$  °C, pH 2

by varying the adsorptive concentrations from 50 to 280 mg/L at 30 °C for 180 min, and the results are shown in Fig. 5. It was found that the adsorption of Cr(VI) was strongly dependent on initial metal ion concentration. As shown in Fig. 5, the equilibrium adsorption capacities increased when initial concentration of Cr(VI) ions increased.

To describe the Cr(VI) adsorption behavior on two batteries of NAC, isotherm data obtained were fitted to the Langmuir and Freundlich adsorption model. A linear plot was obtained when  $c_e/q_e$  was plotted against  $c_e$  over the entire concentration range evaluated; the straight line indicates that the adsorption complies with the Langmuir model as shown in Fig. 6 and Table 3. Cr(VI) saturation adsorption capacity of AC<sub>1</sub> and AC<sub>2</sub> is 181.8 and 185.2 mg/g, respectively. The equilibrium parameter has  $R_L$  values between 0 and 1 for the two kinds of NAC, indicating favorable adsorption. The Freundlich behavior was also tested in this study. The values of  $1/n$  and  $k_F$  calculated from the intercept and slope of the linear plot are shown in Fig. 6 and Table 3, respectively. McKay et al. [41] reported that an  $n$  value of



**Fig. 6** Linearized Langmuir isotherm plots (a) and Freundlich isotherm plots (b)

2–10 indicates favorable adsorption. The  $n$  values of 3.4 and 3.2 for Cr(VI) suggest that the AC<sub>1</sub> and AC<sub>2</sub> adsorbents are effective for Cr(VI) adsorption.

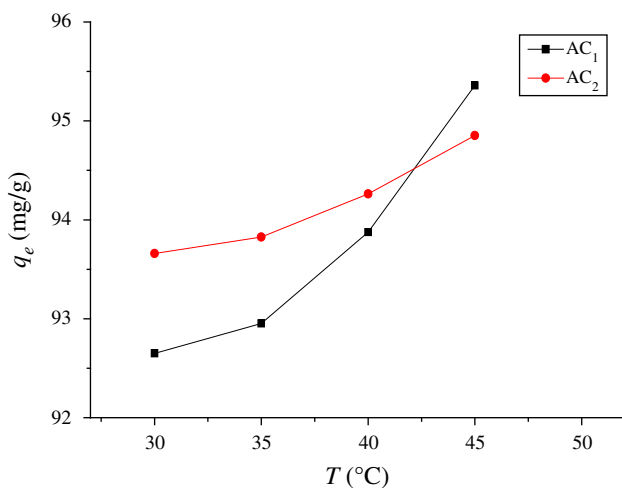
Results described above show that both of the Langmuir and Freundlich equations can describe the experimental data fairly well. However, a comparison of the  $R^2$  values of



**Table 3** Langmuir and Freundlich isotherm parameters for Cr(VI) adsorption onto AC<sub>1</sub> and AC<sub>2</sub>

Adsorbent	Langmuir adsorption model				Freundlich adsorption model			
	Regression equation	$k_L$	$q_m$	$R_L$	Regression equation	$k_F$	$1/n$	$R_F$
AC <sub>1</sub>	$\frac{c_e}{q_e} = 0.0055c_e + 0.0422$	0.13	181.8	0.9974	$\ln q_e = 0.2915\ln c_e + 3.8531$	47.1	3.4	0.9502
AC <sub>2</sub>	$\frac{c_e}{q_e} = 0.0054c_e + 0.0327$	0.16	185.2	0.9993	$\ln q_e = 0.3086\ln c_e + 3.8622$	47.6	3.2	0.9656

$q_e$  the amounts of solute adsorbed per unit adsorbent at equilibrium,  $q_m$  the saturation capacity,  $c_e$  the equilibrium concentration of the adsorbate,  $k_L$  the Langmuir constant,  $k_F$  a constant indicative of the adsorption capacity of the adsorbent,  $n$  an empirical constant called the Freundlich coefficient



**Fig. 7** Influence of temperature on Cr(VI) ion adsorption. Adsorbent dosage = 1.0 g/L, volume of Cr(VI) solution = 100 mL,  $c_0 = 100$  mg/L,  $t = 180$  min, pH 2

the linearized form of these equations indicates that the Langmuir model yields a better fit than the Freundlich model. Accordingly, the process of Cr(VI) adsorption is single molecular layer adsorption.

*Effect of temperature*

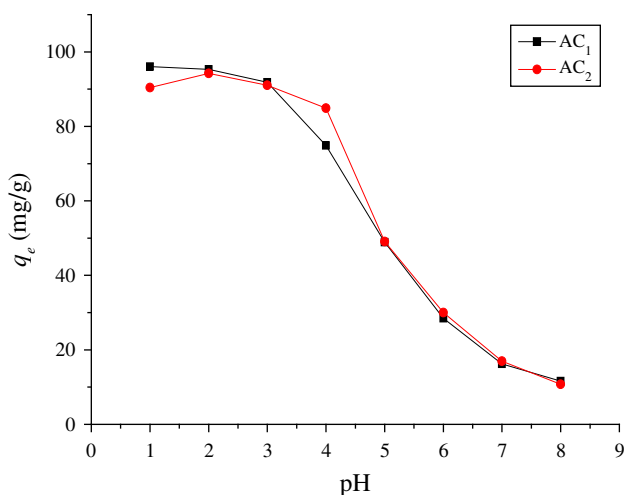
The effect of temperature in the adsorption of Cr(VI) ion on the adsorbents was also investigated. The temperature was varied from 30 to 45 °C at pH of 2, contact time of 180 min and Cr(VI) ion concentration of 100 mg/L. It was observed in Fig. 7 that the adsorption of Cr(VI) ion at various temperature increases with the increase of temperature. This fact indicates that there is a better adsorption at higher temperature, which may be attributed to the formation of much well-structured adsorbed Cr(VI) ions on the two kinds of NAC surface at higher temperature. It is apparent that the adsorption of Cr(VI) ion on AC<sub>1</sub> and AC<sub>2</sub> is an endothermal process. Meanwhile, temperature had little effect on the adsorption capacity and low temperature was more energy efficient. Taking all these factors into consideration, these experiments were carried out at 30 °C.

*Effect of pH*

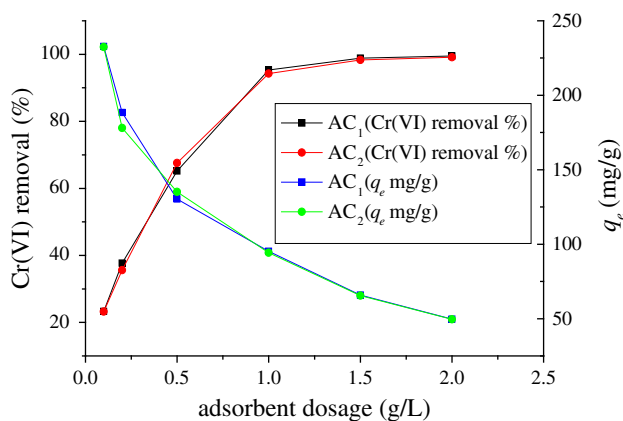
In adsorption processes, the adsorption of heavy metal ions on carbon surfaces can be reduced or increased by the initial pH values of the solutions. In this study, experiments were carried out to examine the influence of initial pH on the adsorption of Cr(VI) with 100 mg/L K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solutions at 30 °C. The adsorption trends of Cr(VI) on AC<sub>1</sub> and AC<sub>2</sub> under different initial pH are shown in Fig. 8. The higher the proton concentration, the higher the efficiency of the Cr (VI) removal. A similar trend has been observed for the removal of Cr(VI) by activated carbon [42], leaf mould [43] and fly ash [44]. It has been explained by a surface-exchange reaction between chromate and hydroxyl ions, which favors chromate adsorption in acidic media [45, 46]. Cr(VI) can exist in the aqueous solution in different ionic forms (HCrO<sub>4</sub><sup>-</sup>, CrO<sub>4</sub><sup>2-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>), which depend on solution pH. The speciation of Cr(VI) influences its charge properties and hence removal by adsorbent [47]. Overall, the dominant form of Cr(VI) at pH 2 is the acid chromate ion species (HCrO<sub>4</sub><sup>-</sup>) and increasing pH shifts the concentration of HCrO<sub>4</sub><sup>-</sup> to other forms (e.g., CrO<sub>4</sub><sup>2-</sup>) [48]. In highly acidic media, the adsorbent surface might be highly protonated and favor the uptake of Cr(VI) in the anionic form, HCrO<sub>4</sub><sup>-</sup> [45]. With increase of pH, from 1 to 8, the degree of protonation of the surface reduced gradually and hence decreased adsorption was noticed. Therefore, the optimum pH of the solution is 2 for Cr(VI) adsorption onto AC<sub>1</sub> and AC<sub>2</sub>.

*Effect of adsorbent dosage*

The percentage of Cr(VI) adsorption generally increased with increasing adsorbent dosage up to a certain value and then remained constant. In this study, experiments were carried out to examine the influence of adsorbent dosage on the adsorption of Cr(VI) at an initial pH 2 in the presence of 100 mg/L K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> at 30 °C for 180 min. The adsorption trends of Cr(VI) on AC<sub>1</sub> and AC<sub>2</sub> under different adsorbent dosage are shown in Fig. 9. The result is clear: with increasing adsorbent dosage, more phase contact area, adsorption surface area and adsorption sites were provided. As shown in Fig. 9, when the



**Fig. 8** Influence of initial pH on Cr(VI) ion adsorption. Adsorbent dosage = 1.0 g/L, volume of Cr(VI) solution = 100 mL,  $c_0 = 100$  mg/L,  $T = 30$  °C,  $t = 180$  min



**Fig. 9** Influence of adsorbent dosage on Cr(VI) ion adsorption. Volume of Cr(VI) solution = 100 mL,  $c_0 = 100$  mg/L,  $T = 30$  °C,  $t = 180$  min, pH 2

adsorbent dosage was as high as 2.0 g/L, the removal ratio of Cr(VI) was nearly 100 %. However, the efficiency did not increase linearly with the increase in the adsorbent dosage. When the adsorbent dosage is <1.0 g/L, adsorption rate rose rapidly to 95 %, and the Cr(VI) removal ratio was almost no longer increased at the dosage of 1.0–2.0 g/L. Figure 9 also shows that the adsorption amount of Cr(VI) decreased with increase of adsorbent dosage, which can be attributed to the excessive adsorption sites of adsorbent dosage.

## Conclusions

The work carried out confirmed that NAC can be used as an effective adsorbent for the removal of Cr(VI) from aqueous solutions. According to the experiment, the following

features of AC<sub>1</sub> and AC<sub>2</sub> are summarized as follows:

- (1) AC<sub>1</sub> and AC<sub>2</sub> had good capacity of adsorption on Cr(VI) from aqueous solution. It may be attributed to an increase in the number of basic groups by the N-modified. A similar conclusion has been observed by Budaeva [49]. The amount of solute adsorbed per unit adsorbent at equilibrium is 95.3 mg/g for AC<sub>1</sub> with the adsorbent dosage of 1.0 g/L at an initial pH 2 in the presence of 100 mg/L K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> at 30 °C for 180 min. In the same reaction condition, the amount of solute adsorbed per unit adsorbent at equilibrium is 94.2 mg/g for AC<sub>2</sub>. However, it was shown that the maximum monolayer adsorption of Cr(VI) onto unmodified activated carbon was 8.40 mg/g [50]. Accordingly, the adsorption capacity of nitrogen-containing activated carbons is obviously improved.
- (2) Adsorption of Cr(VI) was found to increase with increase in contact time, Cr(VI) initial concentration and adsorbent dosage. Acidic solution pH was proved to be more favorable for the adsorption of Cr(VI) on the AC<sub>1</sub> and AC<sub>2</sub>.
- (3) The kinetics of the adsorption process was found to follow the pseudo-second-order kinetic model. The equilibrium adsorption capacity obtained from pseudo-second-order kinetic model fitting result was 104.2 and 103.1 mg/g for AC<sub>1</sub> and AC<sub>2</sub>, respectively. In addition, the Langmuir isotherm had a better fitting model than the Freundlich isotherm according to the coefficient correlation ( $R$ ) obtained. The saturation adsorption capacity obtained from Langmuir isotherm fitting result was 181.8 and 185.2 mg/g for AC<sub>1</sub> and AC<sub>2</sub>, respectively.

**Acknowledgments** This study was funded by: (1) State Forestry Administration, project 201204807: the study on the technology and mechanism of the activated carbon electrode from waste hard board. (2) National natural science funding, project: 51172028. Study on the preparation of new chemical warfare materials based stem core of han hamp and self-desorption mechanism to the chemical warfare agent.

## References

1. Yang CF (2000) Study on sustainable developing problems of bamboo industry. *J Bamboo Res* 19(3):71–75
2. Hui CM, Yang YM, Zhou Y, Yang WM, Zhang FQ, Yang ZJ (1999) A probe on the overall plan of bamboo industry development in Yunnan province. *J Bamboo Res* 18(2):42–49
3. Yang H (1999) Current situation of bamboo processing and utilization in Jiangxi province. *J Bamboo Res* 18(4):11–16
4. Nie T (2001) Review and prospect for bamboo building concrete-form industry in Jiangxi province. *J Bamboo Res* 20(1):68–71
5. Zheng RX (1998) Technical analysis of industrial utilization of phyllostachys pubescens. *J Bamboo Res* 17(3):1–10
6. Wang CY, Dai DR, Wang Y, Ye LM, Yang YF, Jiang ZH (1997) Current situation and development countermeasures for processing and utilization of bamboo timber in Zhejiang. *J Bamboo*



- Res 16(1):55–60
7. Jiang SH, Zhang QS, Jiang SX (2002) Research progress of the theory and application for effective utilization of bamboo charcoal. *J Northeast Forestry Univ* 30(4):53–56
  8. Mu GN, Yang ZM, Yang CF (1994) Adsorption of lanthanum(III) ion in aqueous solution by activated carbon made from bamboo. *Chem Indus For Prod* 14(1):61–65
  9. Blowes D (2002) Tracking hexavalent Cr in groundwater. *Science* 295(5562):2024–2025
  10. Leonard A, Lauwerys RR (1980) Carcinogenicity and mutagenicity of chromium. *Mutat Res* 76(3):227–239
  11. De Flora S, Bagnasco M, Serra D, Zanacchi P (1990) Genotoxicity of chromium compounds: a review. *Mutat res* 238(2):99–172
  12. U.S. Environmental Protection Agency (2003) National primary drinking water standards. <http://www.epa.gov/safewater/consumer/pdf/mcl.pdf>. Accessed 25 Jan 2014
  13. Brooks CS (1991) Metal recovery from industrial waste. Lewis Publishers, Michigan, pp 32–73
  14. Deng B, Lan L, Houston K, Brady PV (2003) Effects of clay minerals on Cr(VI) reduction by organic compounds. *Environ Monit Assess* 84(1–2):5–18
  15. Park SJ, Jang YS (2002) Pore structure and surface properties of chemically modified activated carbons for adsorption mechanism and rate of Cr(VI). *J Colloid Interf Sci* 249(2):458–463
  16. Zhao NQ, Wei N, Li JJ, Qiao ZJ, Cui J, He F (2005) Surface properties of chemically modified activated carbons for adsorption rate of Cr(VI). *Chem Eng* 115(1–2):133–138
  17. Das DD, Mahapatra R, Pradhan J, Das SN, Thakur RS (2000) Removal of Cr(VI) from aqueous solution using activated cow dung carbon. *J Colloid Interf Sci* 232:235–240
  18. Manuel PC, Jose MM, Rosa TM (1995) Chromium(VI) removal with activated carbons. *Water Res* 29(9):2174–2180
  19. Aggarwal D, Goyal M, Bansal RC (1999) Adsorption of chromium by activated carbon from aqueous solution. *Carbon* 37(12):1989–1997
  20. Xiao B, Boudou JP, Thomas KM (2005) Reactions of nitrogen and oxygen surface groups in nanoporous carbons under inert and reducing atmospheres. *Langmuir* 21:3400–3409
  21. Biniak S, Pakula M, Szymanski GS, Swiatkowski A (1999) Effect of activated carbon surface oxygen- and/or nitrogen-containing groups on adsorption of copper (II) ions from aqueous solution. *Langmuir* 15:6117–6122
  22. Pietrzak R, Jurewicz K, Nowicki P, Babel K, Wachowska H (2007) Microporous activated carbons from ammoxidised anthracite and their capacitance behaviours. *Fuel* 86(7–8):1086–1092
  23. Bagreev A, Bashkova S, Bandosz TJ (2002) Adsorption of SO<sub>2</sub> on activated carbons: the effect of nitrogen functionality and pore sizes. *Langmuir* 18:1257–1264
  24. Raymundo-Piñero E, Cazorla-Amorós D, Linares-Solano A (2003) The role of different nitrogen functional groups on the removal of SO<sub>2</sub> from flue gases by N-doped activated carbon powders and fibres. *Carbon* 41:1925–1932
  25. Biniak S, Szymanski G, Siedlewski J, Światkowski A (1997) The characterization of activated carbons with oxygen and nitrogen surface groups. *Carbon* 35(12):1799–1810
  26. Figueiredo JL, Pereira MFR, Freitas MMA, Órfão JJM (1999) Modification of the surface chemistry of activated carbons. *Carbon* 37:1379–1389
  27. Stavropoulos GG, Samaras P, Sakellaropoulos GP (2008) Effect of activated carbons modification on porosity, surface structure and phenol adsorption. *J Hazard Mater* 151:414–421
  28. Lorenc-Grabowska E, Gryglewicz G, Diez MA (2013) Kinetics and equilibrium study of phenol adsorption on nitrogen-enriched activated carbons. *Fuel* 114:235–243
  29. Qiu JY, Wang ZY, Li HB, Xu L, Peng J, Zhai ML, Yang C, Li JQ, Wei GS (2009) Adsorption of Cr(VI) using silica-based adsorbent prepared by radiation-induced grafting. *J Hazard Mater* 166(1):270–276
  30. Hameed BH, Ahmad AA, Aziz N (2007) Isotherms, kinetics and thermodynamics of acid dye adsorption on activated palm ash. *Chem Eng J* 133:195–203
  31. Ho YS, McKay G (2000) The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Res* 34(3):735–742
  32. Weber WJ, Morriss JC (1963) Kinetics of adsorption on carbon from solution. *J Saint Eng Div Am Soc Civ Eng* 89(17):31–60
  33. Limousin G, Gaudet JP, Charlet L, Szenknect S, Barthès V, Krimissa M (2007) Sorption isotherms: a review on physical bases, modeling and measurement. *Appl Geochem* 22(2):249–275
  34. Do DD (1998) Adsorption analysis: equilibria and kinetics. Imperial College Press, London, pp 1–57
  35. Wu Y, Jin XJ, Zhang J (2013) Characteristics of nitrogen-enriched activated carbon prepared from waste medium density fiberboard by potassium hydroxide. *J Wood Sci* 59:133–140
  36. Liu C, Huang PM (2000) Kinetics of phosphate adsorption on iron oxides formed under the influence of citrate. *Can J Soil Sci* 80:445–454
  37. Qin F, Wen B, Shan XQ, Xie YN, Liu T, Zhang SZ, Khan SU (2006) Mechanisms of competitive adsorption of Pb, Cu, and Cd on peat. *Environ Pollut* 144:669–680
  38. Mohan D, Singh KP, Singh VK (2006) Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth. *J Hazard Mater* 135:280–295
  39. Kula I, Uğurlu M, Karaoğlu H, Çelik A (2008) Adsorption of Cd (II) ions from aqueous solutions using activated carbon prepared from olive stone by ZnCl<sub>2</sub> activation. *Bioresour Technol* 99:492–501
  40. Li Q, Zhai JP, Zhang WY, Wan MM, Zhou J (2007) Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by sawdust and modified peanut husk. *J Hazard Mater* 141:163–167
  41. McKay G, Otterburn MS, Sweeney AG (1980) The removal of colour from effluent using various adsorbents—III. Silica: rate processes. *Water Res* 14(1):15–20
  42. Selvi K, Pattabhi S, Kadirvelu K (2001) Removal of Cr(VI) from aqueous solution by adsorption onto activated carbon. *Bioresour Technol* 80(1):87–89
  43. Sharma DC, Forster CF (1994) The treatment of chromium wastewaters using the sorptive potential of leaf mould. *Bioresour Technol* 49(1):31–40
  44. Xue HQ, Jing ZQ, Wang Z (2011) Adsorption analysis of Cr(VI) by fly ash composite material in aqueous medium. *Adv Mater Res* 142:143–147
  45. Li CC, Zhang YW, Peng J, Wu H, Li JQ, Zhai ML (2012) Adsorption of Cr(VI) using cellulose microsphere-based adsorbent prepared by radiation-induced grafting. *Radia Phys Chem* 81(8):967–970
  46. Dupont L, Guillon E (2003) Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran. *Environ Sci Technol* 37(18):4235–4241
  47. Qiu YP, Cheng HY, Xu C, Sheng GD (2008) Surface characteristics of crop-residue-derived black carbon and lead(II) adsorption. *Water Res* 42(3):567–574
  48. Wang XS, Chen LF, Li FY, Chen KL, Wan WY, Tang YJ (2010) Removal of Cr(VI) with wheat-residue derived black carbon: reaction mechanism and adsorption performance. *J Hazard Mater* 175(1–3):816–822

49. Budaeva AD, Zoltoev EV (2010) Porous structure and sorption properties of nitrogen-containing activated carbon. *Fuel* 89 (9):2623–2627
50. Wang XJ, Wang Y, Wang X, Liu M, Xia SQ, Yin DQ, Zhang YL, Zhao JF (2011) Microwave-assisted preparation of bamboo charcoal-based iron-containing adsorbents for Cr(VI) removal. *Chem Eng J* 174:326–332