#### **RESEARCH ARTICLE**

# Removal of phenol by powdered activated carbon adsorption

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Abstract In this study, the adsorption performance of powdered activated carbon (PAC) on phenol was investigated in aqueous solutions. Batch adsorption studies were performed to evaluate the effects of various experimental parameters like PAC type, PAC dose, initial solution pH, temperature and pre-oxidation on the adsorption of phenol by PAC and establish the adsorption kinetics, thermodynamics and isothermal models. The results indicated that PAC adsorption is an effective method to remove phenol from water, and the effects of all the five factors on adsorption of phenol were significant. The adsorption rate of phenol by PAC was rapid, and more than 80% phenol could be absorbed by PAC within the initial 10 min. The adsorption process can be well described by pseudosecond-order adsorption kinetic model with rate constant amounted to 0.0313, 0.0305 and 0.0241 mg  $\cdot \mu$ g  $^{-1} \cdot min^{-1}$ with coal, coconut shell and bamboo charcoal. The equilibrium data of phenol absorbed onto PAC were analyzed by Langmuir, Freundlich and Tempkin adsorption isotherms and Freundlich adsorption isotherm model gave the best correlation with the experimental data. Thermodynamic parameters such as the standard Gibbs free energy ( $\Delta G^{\circ}$ ), enthalpy ( $\Delta H^{\circ}$ ) and entropy ( $\Delta S^{\circ}$ ) obtained in this study indicated that the adsorption of phenol by PAC is spontaneous, exothermic and entropy decreasing.

**Keywords** phenol, powdered activated carbon, adsorption, kinetics, isotherms

# 1 Introduction

Over the past few decades, there has been a great concern for phenolic compounds in the aquatic environment due to their occurrence in various channels and waterways. Phenols, as naturally occurring compounds and artificial

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chemicals, are detected in a variety of industrial wastewaters, including refineries, coking operations, coal processing, pharmaceuticals, plastics, wood products, as well as pesticide, paint and paper industries[1,2]. Phenol have a high toxic and great risk to human health and the environment, which can cause negative health effects on brain, digestive system, eyes, heart, kidney, liver, lungs, skin as well as causing genetic damage[3–5]. Thus, the removal of phenol from drinking water is of great importance, and has been received particular concerns in the last few decades.

Different approaches including chemical oxidation, catalytic oxidation, biodegradation, membrane separation, adsorption and many other technologies are used to remove phenol from aqueous solutions and they can be divided in three categories: biologic, chemical and physical [6]. Among various technologies, the adsorption technology which is simple and effective has been used extensively for the removal of phenol [7]. There are various adsorbents in use and activated carbons are the most widely used adsorbents due to their excellent adsorption abilities for organic pollutants. Previous work has shown that activated carbon is an effective adsorbent for organic compounds removal, especially for phenolic compounds [8–10]. Powdered activated carbon (PAC), compared to granular activated carbon, has a much faster adsorption rate and a larger adsorption capacity of various organics usually related to their much higher surface area, pore volume, and porosity [9]. Considering its fast adsorption rate and large adsorption capacity, PAC is widely used in drinking water purification, wastewater treatment and especially emergency treatment of sudden pollution.

The origin of phenolic compounds (e.g., phenol) in source water is widespread. For example, phenolic compounds were usually used to industrial production, and were transferred to rivers and lakes. Also, they were produced by the metabolism of microorganism (e.g., algae) and aquatic plant in source water. Therefore, it is essential to remove the phenolic compounds during water treatment. Generally, the conventional water treatment processes (coagulation-sedimentation-filtration) were difficult to remove these phenolic compounds effectively in polluted source water [11]. PAC adsorption pretreatment processes may be employed to increase the conventional treatment performance on removing phenolic compounds, because powdered activated carbon is an inexpensive treatment option (capital cost) that can readily be added to an existing water treatment system. Thus, PAC is an attractive alternative for the enhanced treatment of polluted raw water, especially the removal of odor and color compounds in the algae outbreak [12], but little report were found on the removal of individual representative compound (e.g., phenol) by PAC adsorption.

The objective of this study is to investigate the adsorption performance of phenol on PAC. The effects of PAC type, PAC dose, solution pH, temperature and preoxidation on phenol absorption were studied. Furthermore, the equilibrium and kinetic data of the adsorption studies were analyzed to understand the adsorption kinetics, isotherms, and thermodynamics of phenol adsorption onto PAC.

# 2 Materials and methods

#### 2.1 Materials

All solutions were prepared with ultrapure water produced by an 18 M $\Omega$  water purification system (Billerica, USA). Standard Phenol (99%) was purchased from Sigma-Aldrich (St Louis, USA). The stock solution was prepared at a concentration of 200 mg·L<sup>-1</sup>. Potassium permanganate, sodium hydroxide and hydrochloride were A.R. grade and supplied from Sinopharm Chemical Reagent Co. (Shanghai, China). The PAC used in this work included coal, coconut shell and bamboo charcoal. The main performance parameters of different PAC were shown in Table 1. Before use, PAC was triturated and heated at 80°C in distilled water for 3 h to remove some ash and impurities, and then oven-dried at 100°C until weight invariableness. The dried PAC was stored in an air-tight container. The pH of the solution was adjusted by using 0.1M NaOH and HCl.

#### 2.2 Analytical methods

The concentration of phenol was determined by using high

performance liquid chromatography (HPLC, Shimadzu LC-2010 AHT), with a shim-pack VP-ODS column (250 mm  $\times$  4.6 mm) and ultraviolet detector setting wavelength of 280 nm at 30°C. The mobile phase is composed of methanol/water (70/30, v/v). The flow rate of mobile phase is 0.8 mL  $\cdot$  min <sup>-1</sup>.

#### 2.3 Adsorption procedure

All the adsorption experiments were run at a batch mode in a 250 mL sealed glass bottle installed in a thermostatic water shaker  $(160 \text{ r} \cdot \text{min}^{-1})$  with a constant reaction temperature of 25°C. An extra bottle with the same initial concentration of phenol and without adding PAC was always added in order to detect any phenol loss during the experiments. The final concentration of phenol in this bottle was almost the same with the initial concentration, verifying that no losses occurred.

The reaction was initiated by adding PAC to 200 mL water solution containing  $1000 \,\mu g \cdot L^{-1}$  phenol in the reactor.  $4 \text{ g} \cdot \text{L}^{-1}$  PAC solution was prepared by mixing 0.4 g PAC in 100 mL water. Different dosages of PAC ranging from 10 to  $50 \text{ mg} \cdot \text{L}^{-1}$  were obtained by adding  $4 \text{ g} \cdot \text{L}^{-1}$  PAC solution with different volumes into reactors. The pH values of phenol solutions were adjusted with 0.1 M HCl and/or 0.1 M NaOH after adding PAC. To clarify the effect of pre-oxidation on adsorption of phenol, KMnO<sub>4</sub> (1 mg $\cdot$ L<sup>-1</sup>) was added to the reaction solutions with the adsorbents. After equilibrium (about 2 h), the mixing was stopped, and the mixed solution was filtered by a 0.22 µm filter (There was little change in the phenol concentrations before and after filtration). The residual phenol was quantified by HPLC. Phenol removal by PAC was calculated as follows (Eq. (1)):

$$q_{\rm e} = (C_0 - C_{\rm e})V/m,\tag{1}$$

where  $q_e$  is the amount of adsorbed phenol at equilibrium  $(\mu g \cdot m g^{-1})$ ;  $C_0$  and  $C_e$  are initial and equilibrium concentrations of phenol  $(\mu g \cdot L^{-1})$ , respectively; V is the solution volume (liter); and m is the mass of the adsorbent (mg).

#### 2.4 Adsorption kinetics

All the kinetics tests were performed in a series of 250 mL sealed glass bottles containing phenol solutions which were placed on the identical reactor motioned in adsorption procedure at 25°C without pH adjustment. 20 mg  $\cdot$  L<sup>-1</sup> PAC

 Table 1
 Main performance parameters of different PAC

carbon type	mesh number	iodine value $/(mg \cdot g^{-1})$	methylene blue value $/(mg \cdot g^{-1})$	specific surface area $/(m^2 \cdot g^{-1})$				
coal charcoal	200	800~1100	130	> 900				
coconut shell charcoal	200	900~1200	130	>1000				
bamboo charcoal	200	900~1200	135	> 1050				

was added to 200 mL 1000  $\mu$ g·L<sup>-1</sup> phenol solution. At different time intervals of 1, 3, 5, 10, 30, 60, 120 min, samples were collected for phenol analysis. Phenol removal by PAC at a specific time was defined as follows (Eq. (2)):

$$q_t = (C_0 - C_t)V/m, \tag{2}$$

where  $q_t$  is the amount of adsorbed phenol at time t ( $\mu$ g·mg<sup>-1</sup>); V is the solution volume (liters);  $C_0$  and  $C_t$  are the initial and remaining phenol concentrations in solution before reaction and at time t ( $\mu$ g·L<sup>-1</sup>), respectively; and m is the mass of the adsorbent (mg).

### 2.5 Adsorption isotherms

The adsorption isotherm tests were similar with the kinetic tests. However, the samples were taken after equilibrium (about 2 h). Different PAC dosages ranging from 0 to 100 mg  $\cdot$ L<sup>-1</sup> were added into the phenol solutions with the same initial concentration. The adsorbents were separated by filtration before phenol analysis. Experiments were conducted at 15°C, 25°C and 35°C, respectively.

## 3 Results and discussion

## 3.1 Adsorption of phenol by PAC

#### 3.1.1 Effect of carbon type

Different powdered activated carbon shows different adsorption characteristics. In this study, three different PAC including coal, bamboo and coconut shell charcoal were employed as adsorbents to investigate the effect of carbon type on the adsorption of phenol. Removal of phenol by various PAC is shown in Fig. 1. When adding



**Fig. 1** Effect of different carbon types on absorption of phenol (PAC dose =  $20 \text{ mg} \cdot \text{L}^{-1}$ , initial phenol concentration =  $1000 \text{ } \mu\text{g} \cdot \text{L}^{-1}$ , stirring speed =  $160 \text{ r} \cdot \text{min}^{-1}$ , temperature =  $25 \text{ }^{\circ}\text{C}$ )

50 mg·L<sup>-1</sup> PAC to phenol solution with a concentration of 1000  $\mu$ g·L<sup>-1</sup>, the phenol removal by bamboo charcoal, coconut shell charcoal and coal charcoal were 51.44%, 54.32% and 65.82%, respectively. The results indicated that the phenol removal efficiencies of all the three PAC were significant and followed the order of bamboo charcoal > coconut shell charcoal > coal charcoal. This can be explained as bamboo charcoal had maximum specific surface area (Table 1) which exposed most active sites for binding of phenol.

Figure 1 also shows that the adsorption of the phenol significantly increased more than 80% adsorption capacity of PAC within 10 min, and no significant changes were observed over the next 20–120 min. However, the contact time for phenol adsorption was 2 h to make sure that full equilibrium was attained.

#### 3.1.2 Effect of carbon dose

The effect of PAC dose on the adsorption of phenol was investigated by adding different adsorbent doses into 1000  $\mu g \cdot L^{-1}$  phenol solution (Fig. 2). With increasing PAC dosage from 10 to 50 mg  $\cdot L^{-1}$ , the removal of phenol increased with decreasing adsorption capacity of PAC (Table 2). The increasing phenol removal may be due to the increased adsorbent surface area and availability of more vacant surfaced sites [13]. Adsorption capacity decreased because of the decreasing phenol equilibrium concentration in solution with increasing PAC dose, which was compatible with the results of the isotherm study.



Fig. 2 Effect of different carbon doses on absorption of phenol

#### 3.1.3 Effect of initial pH

Previous studies show that initial pH is an important factor affecting the adsorption capacity of adsorbent. This is attributed to the change of the charge of the adsorbent surface with the change in pH value. The experiments were

PAC dose $/(\text{mg} \cdot \text{L}^{-1})$	adsorption capacity $/(\mu g \cdot mg^{-1})$					
	bamboo charcoal	coconut shell charcoal	coal charcoal			
10	24.96	21.22	20.14			
20	19.67	16.58	14.71			
30	15.65	12.49	12.06			
40	14.46	11.82	11.21			
50	13.16	10.86	10.29			

Table 2 Absorption capacity of PAC under different PAC doses



**Fig. 3** Effect of different initial solution pH values on absorption of phenol. (bamboo charcoal, initial phenol concentration = 1000  $\mu g \cdot L^{-1}$ , stirring speed = 160 r·min<sup>-1</sup>, temperature = 25 °C)

performed in the initial pH range of 3.0-11.0. The influence of pH on the adsorption behavior of bamboo charcoal for phenol is presented in Fig. 1. It can be seen that the removal efficiency increased slightly when the pH increased from 3.0 to 9.0, and dropped sharply with the increase of pH higher than 9.0. The pKa value of phenol is 9.9 and the pH of the zero-point charge of the PAC is about 6.2[14]. The surface of PAC show gradually the more negative values as the pH increased. At lower pH (pH < 6.2), phenol is inhibited in the acidic medium and this may be attributed to the positive charged PAC surface and the presence of H<sup>+</sup> ion competing with the phenol for the adsorption sites [15]. At pH > 9, especially when pH is higher than 9.9, phenol as a weak acid is partially ionized and the negatively charged phenol ions are repelled by the negatively charged PAC surface. The low phenol removal at high pH may also be a result of the competition between the  $OH^{-}$  ions and the phenol anions [13].

#### 3.1.4 Effect of temperature

The effect of temperature on phenol adsorption is shown in Fig. 4. The removal of phenol decreased with increasing solution temperature from  $15^{\circ}$ C to  $35^{\circ}$ C, indicating the



**Fig. 4** The effect of temperature on adsorption of phenol (bamboo charcoal, initial phenol concentration =  $1000 \,\mu g \cdot L^{-1}$ , stirring speed =  $160 \, r \cdot min^{-1}$ , temperature =  $25 \, ^{\circ}C$ )

adsorption of phenol on PAC was favored at higher temperatures. This effect suggests that the adsorption mechanism associated with phenol onto PAC involves a temperature dependent process. Previous study [10] observed a similar trend with TCP adsorbed onto activated carbon. In this study, further thermodynamic study was carried out to clarify the effect of temperature on phenol adsorption.

#### 3.1.5 Effect of pre-oxidation

Potassium permanganate was used as a pre-oxidant in this study. The PAC dose was in the range of  $10-40 \text{ mg} \cdot \text{L}^{-1}$ . As shown in Fig. 5, the effect of pre-oxidation on phenol adsorption is significant. The phenol removal increased more than 15% when adding  $1 \text{ mg} \cdot \text{L}^{-1}$  potassium permanganate into the adsorption solutions. This enhancement in removal efficiency may be attributed to the phenol oxidation by potassium permanganate and the increasing sorption capacity of PAC in the presence of potassium permanganate. Previous work demonstrated that oxidizing agents such as oxygen, hydrogen peroxide and potassium permanganate enhanced the sorption capacity due to the formation of dimers and trimers on the carbon surface in

Fig. 5 Removal effect of phenol by PAC associated with potassium permanganate (potassium permanganate dosage =  $1 \text{ mg} \cdot \text{L}^{-1}$ )

oxidizing environment [16].

#### 3.2 Adsorption kinetics

The efficiency and the rate of process and the equilibrium time are described by adsorption kinetics. Three models, the pseudo-first-order kinetic model [17], the pseudo-second-order kinetic model [18,19] and the intra-particle diffusion model [20] were used to investigate the mechanism of adsorption of phenol on PAC.

The first-order mechanism can be expressed by the following equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \tag{3}$$

where  $q_e$  and  $q_t$  are the amounts of phenol adsorbed  $(\mu g \cdot m g^{-1})$  at equilibrium and at time *t* (min), respectively, and  $k_1$  (min<sup>-1</sup>) is the rate constant adsorption. Values of  $k_1$  at 25°C were calculated from the plots of  $\ln(q_e - q_t)$  versus *t*.

The pseudo-second-order model can be expressed by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e},$$
 (4)

where  $k_2 \text{ (mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}\text{)}$  is the rate constant of secondorder adsorption calculated from the linear plot of  $t/q_t$ versus t at 25°C.

Intra-particle diffusion model was also used to analyze and describe the diffusion mechanism using the following equation:

$$q_t = k_{\rm p} t^{1/2} + \mathbf{L},\tag{5}$$

where  $q_t (\mu g \cdot m g^{-1})$  is the amount of phenol adsorbed at equilibrium at time *t*, L is the intercept and  $k_p$  $(\mu g \cdot m g^{-1} \cdot m i n^{-0.5})$  is the intra-particle diffusion rate constant. Values of  $k_p$  and L can be calculated from the plot of  $q_t$  against  $t^{1/2}$ .

Comparison of the correlation coefficients  $R^2$  from the three kinetic models(Table 3), the obtained  $R^2$  values for the pseudo-second-order model were greater than 0.999 for all three PAC, suggesting the pseudo-second-order model was fitted best to describe the adsorption behavior of phenol onto PAC. It is concluded that the pseudo-second-order adsorption is predominant and that the chemisorptions mainly controls the rate of the phenol adsorption [7].

Based on the theory proposed by Weber and Morris [20], intra-particle diffusion model is able to identify the diffusion mechanisms and rate controlling steps in the adsorption process. If the adsorption process follows the intra-particle diffusion model, then  $q_t$  versus  $t^{1/2}$  will be linear and if the plot passes through the origin, then intra-particle diffusion is the sole rate limiting step. Otherwise, some other mechanism along with intra-particle diffusion is also involved.

The intra-particle diffusion model (Fig. 6) presents multilinearity and does not pass through the origin, indicating that phenol adsorption may take place in multiple steps and the intra-particle diffusion is not the only rate limiting step.

# 3.3 Adsorption isotherms

In this study, the Langmuir, Freundlich and Tempkin adsorption isotherms [21–23] for phenol absorbed onto PAC were investigated. The Langmuir isotherm equation is expressed as:

$$q_{\rm e} = \frac{K_{\rm L}C_{\rm e}}{1 + a_{\rm L}C_{\rm e}} = q_{\rm m} \frac{a_{\rm L}C_{\rm e}}{1 + a_{\rm L}C_{\rm e}},\tag{6}$$

where  $q_e (\mu g \cdot m g^{-1})$  is the amount of phenol adsorbed per unit mass of adsorbent;  $q_m (\mu g \cdot m g^{-1})$  is the maximum amount of phenol adsorbed;  $C_e(\mu g \cdot L^{-1})$  is the equilibrium

Fig. 6 Intra-particle diffusion model of phenol adsorption by PAC at 25 °C (PAC dose = 20 mg  $\cdot L^{-1}$ )





concentration of phenol; and  $a_{\rm L}$  (L·µg<sup>-1</sup>) is a constant related to the adsorption energy.

The Freundlich isotherm model is an empirical equation and the model is valid for adsorption that occurs on the heterogeneous surfaces [24,25]. The Freundlich isotherm equation is expressed as:

$$q_{\rm e} = \frac{x}{m} = K_{\rm F} C_{\rm e}^{1/n},\tag{7}$$

where  $K_{\rm F}$  (µg <sup>(1-1/n)</sup>·L <sup>1/n</sup>·mg <sup>-1</sup>)and n are the Freundlich constants. K<sub>F</sub> can be defined as the distribution coefficient and indicative of the relative capacity of the adsorbent. The value of n is indicative of adsorption intensity.

The Tempkin isotherm equation can be expressed by:

$$q_{\rm e} = \frac{RT}{z} (\ln A + \ln C_{\rm e}), \tag{8}$$

where RT/z is the Tempkin constant which related to heat of adsorption while *A* is the equilibrium binding constant. *R* is the universal gas constant (8.314 J·mol<sup>-1</sup>·K<sup>-1</sup>) and *T*(K) is the solution temperature.

The constants were obtained from fitting the data to the Langmuir, Freundlich and Tempkin isotherms at different temperatures (Table 4). The most correlation coefficients  $(R^2)$  exceed 0.9 for the three models, suggesting that all models fit the experimental results well, with the Freundlich model fitting the experimental data best. The results were identical with previous work on the adsorption of phenolic compounds [10,13,26]. As shown in Table 4, all the 1/n values (0.7083–0.7456) obtained from the Freundlich model were below one at all solution temperatures, representing that adsorption was favorable. The 1/n values ranging between zero and one is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for 1/n below one indicates a normal Langmuir isotherm while 1/n above one indicates a cooperative adsorption [27]. In this study, all the 1/n values were below one, indicating the adsorption follows a normal Langmuir isotherm. It is the reason that the Langmuir model also gave a good fit. The maximum amounts  $(q_m)$  of the phenol adsorption onto PAC at three temperatures were 59.62, 45.45, 33.67  $\mu$ g·mg<sup>-1</sup> respectively indicating PAC is an effective adsorbent for the removal of phenol in aqueous solution. The  $q_{\rm m}$  values of phenol adsorbed onto PAC decreased as temperature increased, suggesting that the adsorption of phenol may be exothermic. The constant RT/z obtained from Tempkin isotherm decreased with increasing temperature, which also demonstrate the adsorption is an exothermic reaction.

#### 3.4 Thermodynamic study

Thermodynamic parameters such as the standard Gibbs free energy ( $\Delta G^{\circ}$ ), enthalpy ( $\Delta H^{\circ}$ ) and entropy ( $\Delta S^{\circ}$ ) associated to the adsorption process and are determined by using following equations[7,23]:

$$\Delta G^o = -RT \ln K, \tag{9}$$

$$\ln K = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R},\tag{10}$$

where *R* is the universal gas constant  $(8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$  and *T* (K) is the solution temperature. *K* is the distribution coefficient which can be calculated as:

$$K = \frac{a_{\rm s}}{a_{\rm e}} = \frac{v_{\rm s}q_{\rm e}}{v_{\rm e}C_{\rm e}},\tag{11}$$

where  $a_s$  is the activity of adsorbed phenol,  $a_e$  is the activity of the phenol in solution at equilibrium,  $v_s$  is the activity coefficient of the adsorbed phenol and  $v_e$  is the activity coefficient of the phenol in solution. *K* can be obtained by plotting  $\ln(q_e/C_e)$  versus  $q_e$  and extrapolating  $q_e$  to zero[28,29]. A straight line can be obtained with the intercept of  $\ln K$ .

The thermodynamic parameters of the phenol adsorption onto PAC are given in Table 5. The  $\Delta G^{\circ}$  for phenol adsorption increased from -9.94 to -9.34 kJ·mol<sup>-1</sup> with temperature increasing from 288 to 308 K, suggesting that adsorption might be more spontaneous at lower temperature. The negative values indicated the adsorption of phenol onto PAC was feasible and spontaneous [19].

The  $\Delta H^{\circ}$  for phenol adsorbed onto PAC was negative  $(-18.59 \text{ kJ} \cdot \text{mol}^{-1})$ , indicating that the adsorption process was exothermic. According to the ranges of energy of adsorption from different forces [30], van der Waals forces

 Table 3 Pseudo-first-order kinetic model, the pseudo-second-order kinetic model and the intra-particle diffusion model kinetic parameters for phenol adsorption by PAC at 25 °C

Adsorbent		first-order kinetic model			pseudo-second-order kinetic model			intra-particle diffusion model	
PAC type	dose /(mg $\cdot$ L <sup>-1</sup> )	$q_{\rm e}$ /(µg·mg <sup>-1</sup> )	$k_1$ /(min <sup>-1</sup> )	$R^2$	$q_{ m e}$ /µg·mg <sup>-1</sup>	$k_2/(\mathrm{mg}\cdot\mu\mathrm{g}^{-1}$ $\cdot\mathrm{min}^{-1})$	$R^2$	$k_{\rm p}/(\mu g \cdot {\rm mg}^{-1}$ $\cdot {\rm min}^{-0.5})$	$R^2$
bamboo charcoal	20	20.0854	0.5795	0.9718	21.7439	0.0313	0.9999	1.4290	0.4603
coconut shell charcoal	20	15.8135	0.3241	0.95976	16.8719	0.0305	0.9999	1.2505	0.5939
coal charcoal	20	13.6833	0.2863	0.9591	14.9812	0.0241	0.9998	1.1350	0.6529

tomanonotiumo	Langmuir			Freundlich			Tempkin		
/K	$q_{ m m}$ /(µg·mg <sup>-1</sup> )	$a_{ m L}$ /(L · mg $^{-1}$ )	$R^2$	$\frac{K_{\rm F}/(\mu g^{(1-1/n)}}{\cdot L^{1/n} \cdot {\rm mg}^{-1}})$	1/ <i>n</i>	$R^2$	$A/(L \cdot mg^{-1})$	RT/z	$R^2$
288	59.5238	1.0650	0.9942	0.2056	0.7456	0.9959	0.0121	12.0404	0.9647
298	45.4545	1.1880	0.9911	0.1962	0.7170	0.9971	0.0111	10.1702	0.9711
308	33.6700	1.2921	0.9570	0.1616	0.7083	0.9740	0.0095	8.8150	0.9203

 Table 4
 Langmuir, Freundlich and Tempkin isotherm parameters for phenol adsorption by PAC

Table 5 Thermodynamic parameters for phenol adsorption onto PAC under different temperatures

	$\Delta G/(kJ \cdot mol^{-1})$		$\Delta H/(kJ \cdot mol^{-1})$	$\Delta S/(\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1})$
288 K	298 K	308 K		
-9.94	-9.62	-9.34	-18.59	-30.05

4–10 kJ·mol<sup>-1</sup>, hydrophobic bond forces about 5 kJ·mol<sup>-1</sup>, hydrogen bond forces 2–40 kJ·mol<sup>-1</sup>, coordination exchange about 40 kJ·mol<sup>-1</sup>, dipole bond forces 2–29 kJ·mol<sup>-1</sup>, chemical bond forces > 60 kJ·mol<sup>-1</sup>, it is indicated that in this adsorption reaction system all the mechanisms except chemical bond forces are possible candidates.

The  $\Delta S^{\circ}$  for phenol adsorbed onto PAC was -30.05 J·K<sup>-1</sup>·mol<sup>-1</sup>. The negative value of  $\Delta S^{\circ}$  suggested a decrease in degree of freedom of the adsorbed phenol [24].

# 4 Conclusions

In this study, batch tests were carried out to investigate the adsorption performance of PAC on phenol. The phenol adsorption was significantly influenced by PAC type, PAC dose, initial solution pH, temperature and pre-oxidation. Three adsorption kinetics models (pseudo-first-order kinetic model, the pseudo-second-order kinetic model and the intra-particle diffusion model) and three adsorption isotherms (Langmuir, Freundlich and Tempkin) were used to investigate the mechanism of adsorption of phenol on PAC. The adsorption behaviors can be well described by pseudo second order adsorption kinetic model and Freundlich adsorption isotherm model. Thermodynamic parameters obtained in this study indicated the adsorption of phenol onto PAC is a spontaneous, exothermic and entropy decreasing process.

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# References

1. Damjanović L, Rakić V, Rac V, Stošić D, Auroux A. The

investigation of phenol removal from aqueous solutions by zeolites as solid adsorbents. Journal of Hazardous Materials, 2010, 184(1– 3): 477–484

- Lin S H, Juang R S. Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: a review. Journal of Environmental Management, 2009, 90(3): 1336– 1349
- Megharaj M, Pearson H W, Venkateswarlu K. Toxicity of phenol and three nitrophenols towards growth and metabolic activities of *Nostoc linckia*, isolated from soil. Archives of Environmental Contamination and Toxicology, 1991, 21(4): 578–584
- Nair R J, Sherief P M. Acute toxicity of phenol and long-term effects on food consumption and growth of juvenile rohu *Labeo rohita* (Ham.) under tropical condition. Asian Fisheries Science, 1998, 10 (3): 179–268
- Yang L, Wang Y, Song J, Zhao W, He X, Chen J, Xiao M. Promotion of plant growth and in situ degradation of phenol by an engineered *Pseudomonas fluorescens* strain in different contaminated environments. Soil Biology & Biochemistry, 2011, 43(5): 915–922
- Busca G, Berardinelli S, Resini C, Arrighi L. Technologies for the removal of phenol from fluid streams: a short review of recent developments. Journal of Hazardous Materials, 2008, 160(2–3): 265–288
- Ahmaruzzaman M. Adsorption of phenolic compounds on low-cost adsorbents: a review. Advances in Colloid and Interface Science, 2008, 143(1–2): 48–67
- Kim T Y, Jin H J, Park S S, Kim S J, Cho S Y. Adsorption equilibrium of copper ion and phenol by powdered activated carbon, alginate bead and alginate-activated carbon bead. Journal of Industrial and Engineering Chemistry, 2008, 14(6): 714–719
- Tancredi N, Medero N, Möller F, Píriz J, Plada C, Cordero T. Phenol adsorption onto powdered and granular activated carbon, prepared from *Eucalyptus* wood. Journal of Colloid and Interface Science, 2004, 279(2): 357–363
- Fan J, Zhang J, Zhang C, Ren L, Shi Q. Adsorption of 2,4,6trichlorophenol from aqueous solution onto activated carbon derived from loosestrife. Desalination, 2011, 267(2–3): 139–146
- Bayer C, Follmann M, Melin T, Wintgens T, Laesson K, Almemark M.The ecological impact of membrane-based extraction of phenolic

compounds—a life cycle assessment study. Water Science & Technology—WST, 2010, 62(4): 915–919

- Zhang X J, Chen C, Ding J Q, Hou A X, Li Y, Niu Z B, Su X Y, Xu Y J, Laws E A. The 2007 water crisis in Wuxi, China: analysis of the origin. Journal of Hazardous Materials, 2010, 182(1–3): 130–135
- Tan I A W, Ahmad A L, Hameed B H. Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. Journal of Hazardous Materials, 2009, 164(2–3): 473–482
- Dai M. Mechanism of adsorption for Dyes on activated carbon. Journal of Colloid and Interface Science, 1998, 198(1): 6–10
- Qing C. Study on the adsorption of lanthanum(III) from aqueous solution by bamboo charcoal. Journal of Rare Earths, 2010, 28(1): 125–131
- Zeid N A, Nakhla G, Farooq S, Osei-Twum E. Activated carbon adsorption in oxidizing environments. Water Research, 1995, 29(2): 653–660
- Langergren S, Svenska B K. Zur theorie der sogenannten adsorption geloester stoffe. Kungliga Svenska Vetenskapsa-kademiens, Handlingar, 1898, 24(4): 1–39
- Srihari V, Das A. The kinetic and thermodynamic studies of phenolsorption onto three agro-based carbons. Desalination, 2008, 225(1– 3): 220–234
- Tan I A W, Hameed B H, Ahmad A L. Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon. Chemical Engineering Journal, 2007, 127(1–3): 111–119
- Weber W J, Morris J C. Advances in water pollution research: removal of biologically-resistant polluants from waste waters by adsorption. In: Proceedings of the International Conference on Water Pollution Symposium. Pergamon, Oxford, 1962, 2: 231– 266
- 21. Fernandes A N, Almeida C A P, Debacher N A, Sierra M M D S.

Isotherm and thermodynamic data of adsorption of methylene blue from aqueous solution onto peat. Journal of Molecular Structure, 2010, 982(1–3): 62–65

- Kavitha D, Namasivayam C. Experimental and kinetic studies on methylene blue adsorption by coir pith carbon. Bioresource Technology, 2007, 98(1): 14–21
- Sheha R R, Metwally E. Equilibrium isotherm modeling of cesium adsorption onto magnetic materials. Journal of Hazardous Materials, 2007, 143(1–2): 354–361
- Fu Q, Deng Y, Li H, Liu J, Hu H, Chen S, Sa T. Equilibrium, kinetic and thermodynamic studies on the adsorption of the toxins of *Bacillus thuringiensis* subsp. *kurstaki* by clay minerals. Applied Surface Science, 2009, 255(8): 4551–4557
- Su J, Lin H F, Wang Q P, Xie Z M, Chen Z L. Adsorption of phenol from aqueous solutions by organomontmorillonite. Desalination, 2011, 269(1–3): 163–169
- Fytianos K, Voudrias E, Kokkalis E. Sorption-desorption behaviour of 2,4-dichlorophenol by marine sediments. Chemosphere, 2000, 40 (1): 3–6
- Haghseresht F, Lu G. Q. Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents. Energy & Fuels, 1998, 12(6): 1100–1107
- Li Y H, Di Z, Ding J, Wu D, Luan Z, Zhu Y. Adsorption thermodynamic, kinetic and desorption studies of Pb<sup>2+</sup> on carbon nanotubes. Water Research, 2005, 39(4): 605–609
- Yue Q Y, Li Q, Gao B Y, Yuan A J, Wang Y. Formation and characteristics of cationic-polymer/bentonite complexes as adsorbents for dyes. Applied Clay Science, 2007, 35(3–4): 268–275
- Vonopen B. Kordel W, Klein W. Sorption of nonpolar and polar compounds to soils: processes, measurement and experience with the applicability of the modified OECD-Guideline 106. Chemosphere, 1991, 22(3–4): 285–304