



Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers

Qing-Song Liu, Tong Zheng, Peng Wang*, Ji-Ping Jiang, Nan Li

State Key Laboratory of Urban Water Resource and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China

ARTICLE INFO

Article history:

Received 14 July 2009

Received in revised form 3 November 2009

Accepted 10 November 2009

Keywords:

Adsorption

Activated carbon fibers

Substituted phenols

Isotherm

Kinetics

Mechanism

ABSTRACT

Activated carbon fibers (ACFs) were used for the adsorption of phenol, 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (DCP), 2,4,6-trichlorophenol (TCP), 4-nitrophenol (4-NP) and 2,4-dinitrophenol (DNP) from aqueous solutions, and the adsorption capacities followed the order of TCP > DNP \approx DCP > 4-NP > 4-CP > 2-CP > phenol. Adsorption isotherms at different temperatures were determined and modeled with Langmuir, Freundlich and Redlich–Peterson equations. Thermodynamic parameters were calculated and correlated with the adsorption behaviors. The effects of solution pH on the adsorption were also studied. The adsorption mechanism was discussed based on the experimental results, and the π – π interactions, solvent effects, hydrophobic interactions and molecular dimensions were considered to be important in the adsorption. Kinetic studies showed rapid adsorption kinetics of the phenols, due to the open pore structure of the ACFs. The kinetics was fitted with the pseudo-first-order, pseudo-second-order and intraparticle diffusion models. Steric effects on adsorption kinetics were observed for TCP, 4-NP and DNP, but serious impact on the ultimate uptake was only found for DNP. The relationship between the steric effects and the molecular dimension was also proposed.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Phenol and its derivatives are used in a number of applications such as chemical, pharmaceutical, petroleum, paper, wood, rubber, dye and pesticide industries [1]. Phenols are classified as priority pollutants due to their toxicity to organisms even at low concentrations. Their adverse environmental and public health impacts have been proved by increasing evidences, such as death of aquatic life, inhibition of the normal activities of microbial community and carcinogenicity to animals [2]. In view of the high toxicity, wide prevalence and poor biodegradability of phenols, it is necessary to remove them from wastewaters before discharge into water bodies.

Various processes have been employed for the removal of phenols from aqueous media including advanced oxidation [3], membrane filtration [4], biological degradation [5], electrochemical oxidation [6], photocatalytic degradation [7] and adsorption [8,9]. Among these methods, adsorption is still the most versatile and widely used, since it can effectively remove many types of pollutants and the design and operation are convenient. Activated carbon remains extensively used in practice due to their mechanic stability, high adsorption capacity and fast adsorption

rate [10]. In recent years, a new form of carbon adsorbent: activated carbon fibers (ACFs) have been intensively developed and applied [11]. ACFs are commonly microporous with large surface area and narrow pore size distribution. The microporous nature endows ACFs with advantages in adsorption, as the adsorption energy is enhanced within low-size pores [12]. Furthermore, ACFs have large external surface and their micropores are directly exposed on the surface, giving rise to a fast adsorption rate [13].

The adsorption of organics onto activated carbon has been studied in a large number of literatures, and the results demonstrated that the adsorption behaviors depend mainly on the characteristics of the activated carbon, the molecular properties of the organics and the operational conditions. The characteristics of the activated carbon such as surface area, pore size distribution and surface functional groups play an important role in the adsorption, as they determine the interactions between the organics and the activated carbon at the interface [14,15]. The effects of the molecular properties such as molecular size, solubility, pK_a and electron distribution have been revealed, which might influence the affinity between the organics and the carbon surface [16–18]. Furthermore, the operational conditions such as solution pH and temperature are also involved in the adsorption, which might have implications on the adsorbent/adsorbate interactions [19,20].

The adsorption performance of ACFs for some phenols including 2,4-dichlorophenol [21,22], pentachlorophenol [23], 4-nitrophenol [24] and chlorophenols [25] have been reported in previous stud-

* Corresponding author at: P.O.B. 2650, 202 Haihe Road, Nangang District, Harbin 150090, China. Tel.: +86 451 86283801; fax: +86 451 86283801.

E-mail address: pwang73@vip.sina.com (P. Wang).

ies. However, a comparative study is still needed to improve our knowledge about the adsorption properties of ACFs and the impact of the substituent groups. It is generally assumed that the substituent groups are not directly involved in the interactions with the carbon surface [8], but they would change the molecular properties which in turn affect the adsorption process. In this study phenol, 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (DCP), 2,4,6-trichlorophenol (TCP), 4-nitrophenol (4-NP) and 2,4-dinitrophenol (DNP) were adsorbed from aqueous solutions onto ACFs, and the adsorption characteristics including isotherm, kinetics, thermodynamics, mechanism and effects of molecular properties and pH were studied.

2. Experimental

2.1. Materials

The ACFs were pitch-based in the form of unwoven fabrics from Sainuoda Co., China, with an average diameter of 4 μm (according to SEM image). They were washed with distilled water and dried at 105 $^{\circ}\text{C}$ for 24 h, stored in a desiccator before use. The phenols were of analytical grade, purchased from Shanghai Chemical Reagent Co., China. Some properties of the phenols are summarized in Table 1.

2.2. ACFs characterizations

The surface physical properties of the ACFs were characterized with a Micromeritics ASAP 2020, using N_2 as the adsorbate at 77 K. The surface area (S) was calculated with the BET equation, the micropore volume (V) was evaluated by converting the adsorption amount at $P/P_0 = 0.99$ to a volume of liquid adsorbate. Based on the assumption of slit-shape pores [27], the average pore size (r) was estimated by the following equation:

$$r = \frac{2V}{S} \quad (1)$$

The Horvath–Kawazoe method was applied to analyze the pore size distribution, which was expected to be suitable for porous carbons with predominant micropores of width below 1 nm [28,29].

The analysis of surface oxygen functional groups was based on the acid–base titration method [30]. For each time 0.5 g ACFs were put in 20 ml 0.01 mol/L NaOH or HCl solution to determine the acidic and basic groups, respectively.

The point of zero charge (pH_{PZC}) was determined by a mass titration method proposed by Noh and Schwarz [31]. Various amounts of ACFs (0.05–0.5 g) were put in 10 ml 0.1 mol/L NaCl solutions (prepared with boiled water). The bottles were sealed and shaken in a thermostat shaker overnight, the equilibrium pH values of the mixtures were measured and the limiting pH was taken as the pH_{PZC} .

Table 1
Some physical properties of the phenols in study.

Phenols	Molecular weight (g/mol)	Molecular size ^a (Å)	Solubility ^b (g/L)	pK_a^b
Phenol	94.1	5.76×4.17	93	9.89
2-CP	128.6	5.76×4.82	28	8.52
4-CP	128.6	6.47×4.17	27	9.37
DCP	163.0	6.47×4.82	15	7.90
TCP	197.4	6.47×5.47	0.9	5.99
4-NP	139.1	6.84×4.17	1.7	7.15
DNP	184.0	6.84×5.76	0.6	4.09

^a Ref. [26].

^b Ref. [8], at 25 $^{\circ}\text{C}$.

2.3. Adsorption procedure

Adsorption experiments were conducted by batch mode in stoppered conical flasks. Stock solutions were prepared by dissolving the phenols in deionized water. For each time 0.100 g ACFs and 100 mL phenol solution were mixed in a flask, which was then shaken in a thermostat shaker at 150 rpm.

In adsorption isotherm studies, solutions with different initial concentrations were added, the pH was not adjusted, and the equilibrium time was set as 24 h, which was enough according to the preliminary experiments. Samples were separated by filtration and the phenol concentrations were analyzed by UV spectroscopy (UV-2550, Shimadzu) at λ_{max} 270, 274, 280, 284, 290, 318 and 353 nm for phenol, 2-CP, 4-CP, DCP, TCP, 4-NP and DNP, respectively [32,33]. Each experiment was duplicated under identical conditions. Blanks containing no ACFs were done and the loss (generally quite low) was considered. The uptake of the adsorbate at equilibrium, q_e (mmol/g), was calculated by the following equation:

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

where C_0 and C_e are the initial and equilibrium concentrations of the phenols (mmol/L) in solution, respectively; V is the volume of the solution (L) and m is the weight of the adsorbent (g).

In pH studies, the solution pH was adjusted by the addition of HCl or NaOH after the mixing of phenols with ACFs, which showed little change during the adsorption process. Experiments were conducted at 25 $^{\circ}\text{C}$, samples were separated after 24 h. The initial concentration for phenol, 2-CP, and 4-CP was 1.5 mmol/L, for DCP was 1.85 mmol/L, for TCP, 4-NP and DNP was 2.0 mmol/L.

The kinetic studies were performed following a similar procedure at 25 $^{\circ}\text{C}$, solution pH was not adjusted, the initial concentration was set as 1.5 mmol/L for each phenol, and the samples were separated at predetermined time intervals. The uptake of the adsorbate at time t , q_t (mmol/g), was calculated by the following equation:

$$q_t = V \cdot \frac{C_0 - C_t}{m} \quad (3)$$

where C_t is the concentration of the adsorbate (mmol/L) in solution at time t .

3. Results and discussion

3.1. Surface characteristics of ACFs

The nitrogen adsorption isotherm of the ACFs and the pore size distribution based on the Horvath–Kawazoe method are presented in Fig. 1. The isotherm is H-type characterized of a sharp rise at low-pressure range and a plateau at high pressure range [34], indi-

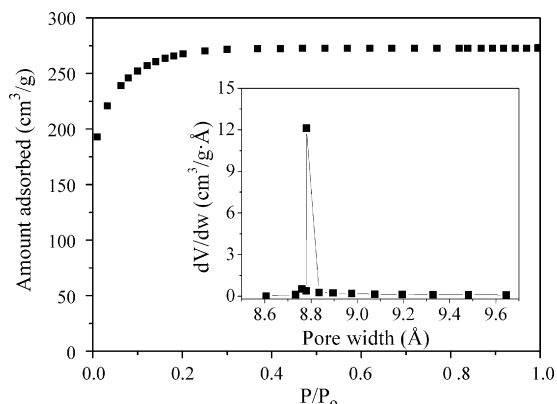


Fig. 1. Nitrogen adsorption isotherm (77 K) and pore size distribution of the ACFs.

cating the microporous nature of the ACFs. The BET surface area and the micropore volume are 920.3 m²/g and 0.422 cm³/g, respectively, which are moderate for ACFs. The pore size distribution curve demonstrates that the distribution is quite narrow and the pore size is centered at about 8.8 Å. The average pore size is calculated as 9.2 Å based on Eq. (1), which is in accordance with the pore size distribution analysis. The amounts of the acidic and basic groups on ACFs surface are measured as 0.12 and 0.15 mmol/g, respectively, which are notably lower than the values reported by other studies [21,23]. The pHPZC value is measured as 6.9, which suggests a neutral surface.

3.2. Equilibrium studies

3.2.1. Adsorption isotherms

The adsorption isotherms of phenols on ACFs were studied at 25, 40 and 55 °C, and the results are presented in Fig. 2 (a)–(h): (a) phenol, (b) 2-CP, (c) 4-CP, (d) DCP, (e) TCP, (f) 4-NP, (g) DNP and (h) phenols at 25 °C. As can be seen, the uptake decreases with the rise of temperature, indicating the exothermic nature of these adsorptions. Compared to phenol, the substituted phenols demonstrate more intense adsorption at low concentration range and higher adsorption capacities, which follow the order of TCP > DNP ≈ DCP > 4-NP > 4-CP > 2-CP > phenol. As phenol has smaller molecular size than the substituted phenols, this result implies that only a small part of the micropores is filled in phenol adsorption, and the micropore filling phenomenon is more evident for the substituted phenols.

Three widely used models: Langmuir, Freundlich and Redlich–Peterson were applied for the fitting of the experimental data. Langmuir model is based on the assumption of a homogeneous adsorbent surface with identical adsorption sites, which can be written as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

where q_m is the maximal adsorption capacity, K_L is a constant related to the free energy of the adsorption. The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called separation factor (or equilibrium parameter), R_L , which is defined by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

The adsorption is considered as irreversible when $R_L = 0$, favorable when $0 < R_L < 1$, linear when $R_L = 1$, and unfavorable when $R_L > 1$.

Freundlich model is an empirical equation assuming heterogeneous adsorptive energies on the adsorbent surface, which can be written as:

$$q_e = K_F C_e^{1/n} \quad (6)$$

where K_F and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively.

Redlich–Peterson model is used as a compromise between Langmuir and Freundlich models, which can be written as:

$$q_e = \frac{K_{RP} C_e}{1 + \alpha C_e^\beta} \quad (7)$$

where K_{RP} are Redlich–Peterson equation constants and β is the exponent which lies between 0 and 1.

The parameters were calculated and summarized in Table 2. Of these models, Redlich–Peterson equation gives the best fitting in most cases, except for several instances in which the β values are beyond 1. Redlich–Peterson equation incorporates the advantages of both Langmuir and Freundlich equations, which can be applied

either in homogeneous or heterogeneous system [35]. In this study, the β values are close to unity, which means that the isotherms conform to Langmuir model better than Freundlich model. Langmuir equation is reasonably applicable in all of the cases with correlation coefficients (R^2) in the range of 0.94–0.99. With the rise of temperature, the q_m value shows some increase for phenol and 2-CP and some decrease for other phenols, possibly resulted from the competitive adsorption of water molecules. The adsorption of water molecules diminishes with the rise of temperature which might be more significant for phenol and 2-CP. The R_L values in this study are in the range of 0.004–0.127, indicating favorable adsorption of these phenols on ACFs. For each phenol, the R_L value increases with the rise of temperature, suggesting reduced affinity between phenol and ACFs. Freundlich equation is usable for some cases but not for others, which is in general not as good as Langmuir or Redlich–Peterson equation. This phenomenon is possibly derived from its assumption of heterogeneous adsorbent surface, whereas the surface of ACFs is relatively uniform. The K_F value shows a decrease tendency with the rise of temperature, and the n values lie mostly in the range of 1–10, indicating favorable adsorption of these phenols.

3.2.2. Adsorption thermodynamics

The adsorption thermodynamics were studied to gain an insight into the adsorption behaviors. Parameters including Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) are calculated according to the following thermodynamic equations:

$$\Delta G^\circ = -RT \ln K \quad (8)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

where K (L/mol) is from Langmuir equation, R is the gas constant (8.314 J/mol K) and T is the temperature in Kelvin. In the application of Eq. (9), the values of $\ln K$ are plotted against $1/T$, the ΔH° and ΔS° values are calculated from the slope and intercept of the plot.

The thermodynamic parameters are listed in Table 3. Negative ΔG° values are obtained in all cases, revealing the spontaneous nature of these adsorptions. The absolute value of ΔG° rises with the increase in the number of chloro or nitro groups, indicating reinforced adsorption driving force for phenols with higher substitution degree. Generally, the ΔG° value is in the range of 0 to –20 kJ/mol and –80 to –400 kJ/mol for physical and chemical adsorptions, respectively [36]. In this study, the ΔG° values are in the range of –24.1 to –32.9 kJ/mol, indicating that the adsorptions are mainly physical in nature enhanced by chemisorption. The ΔH° values are negative for all phenols, demonstrating the exothermic nature of these adsorptions, which is in agreement with the experimental observations. The magnitude of the ΔH° value lies in the range of 2.1–20.9 and 80–200 kJ/mol for physical and chemical adsorptions, respectively [37]. In this study, the ΔH° values are in the range of –10.3 to –45.3 kJ/mol, whose absolute values decrease with the increase of substitution degree, indicating the reinforcement of physical adsorption. Positive ΔS° value suggests the organization of the adsorbate at the solid/solution interface becomes more random, while negative value suggests the opposite fact. It is also supposed that the change of ΔS° value is related to the displacement of the adsorbed water molecules by the adsorbate [38]. In this study, the ΔS° value rises with the increase in the number of chloro or nitro groups, hence it can be deduced that more adsorbed water molecules are displaced by phenols with higher substitution degrees.

3.2.3. Effects of pH

Solution pH usually influences the adsorption to a large extent, as it affects the properties of both adsorbent and adsorbate. The

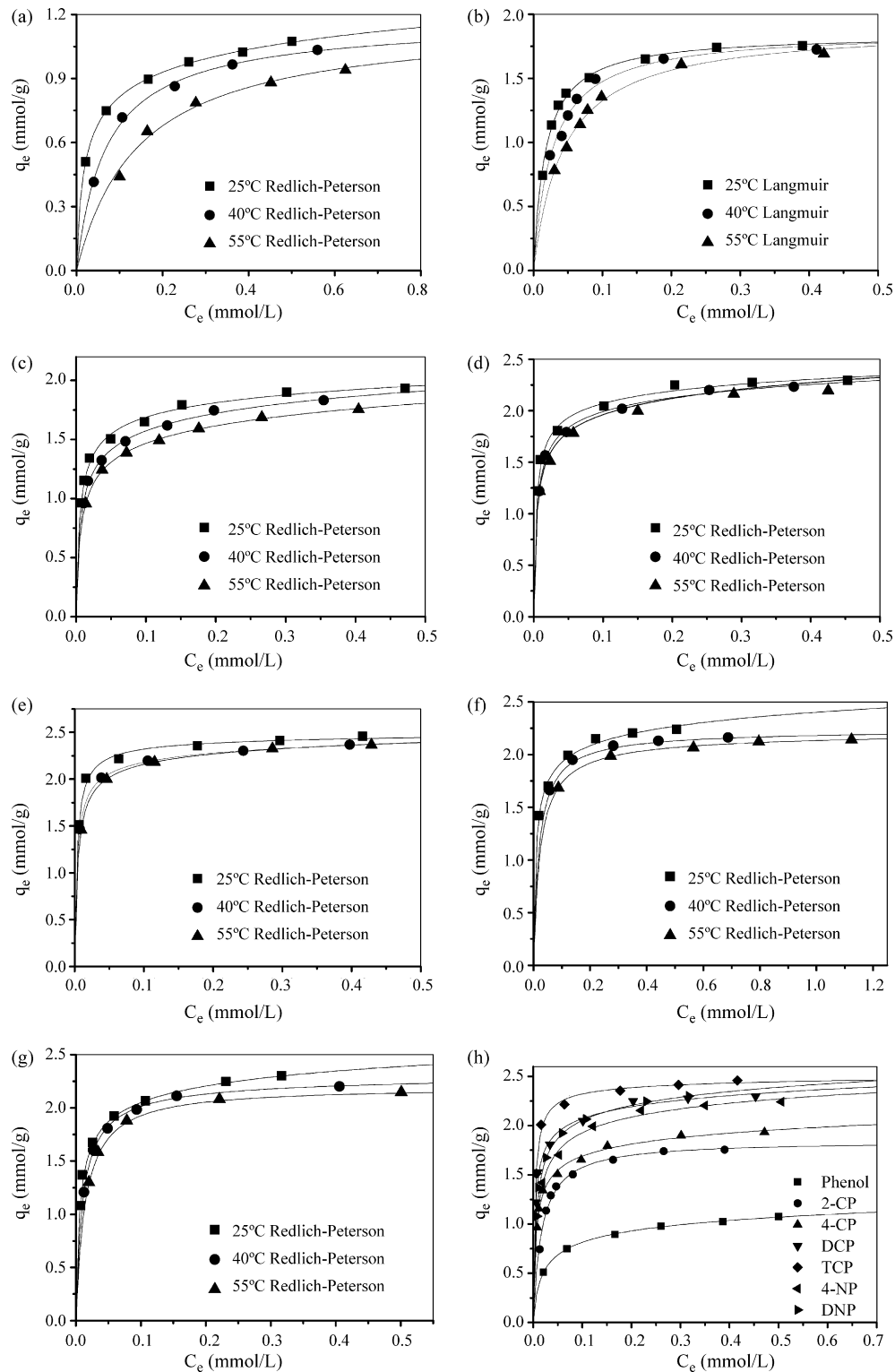


Fig. 2. Adsorption isotherms of various phenols on ACFs.

surface charge of carbon depends on the solution pH and its pH_{PZC} ; the carbon surface is positively charged at $pH < pH_{PZC}$ and negatively charged at $pH > pH_{PZC}$. The adsorbate is mainly in protonated form at $pH < pK_a$ and in deprotonated form at $pH > pK_a$.

The uptakes of the phenols in the pH range of 1–11 were determined and illustrated in Fig. 3. The uptakes are stable at $pH < pK_a$ for each phenol except for a slight decrease at pH 1, due to the

adsorption of protons on the basic sites, which result in decreased interactions between these sites and the phenols. Phenol, 2-CP, 4-CP, DCP and 4-NP have pK_a values higher than the pH_{PZC} of ACFs (6.9), at $pH > pK_a$, the phenols are dissociated and the ACFs surface is negatively charged. Electrostatic repulsion force exists between the phenols and the ACFs surface, whose magnitude depends on the dissociation degree of the phenols and the charge amount of the ACFs surface. With the increase of pH, the phenols are dissociated to

Table 2
Langmuir, Freundlich and Redlich–Peterson parameters for the adsorption of phenols on ACFs at different temperatures.

Phenols, T (°C)	Langmuir				Freundlich			Redlich–Peterson				
	q_m (mmol/g)	K_L (L/mmol)	R_L	R^2	K_F ((mmol/g)(L/mmol) $^{1/n}$)	n	R^2	K_{RP} (L/g)	α (L/mmol) $^\beta$	β	R^2	
Phenol	25	1.089	36.23	0.027	0.975	1.275	4.651	0.976	71.0	59.5	0.887	0.999
	40	1.152	14.47	0.065	0.996	1.283	3.360	0.945	17.3	14.9	0.984	0.998
	55	1.171	6.88	0.127	0.985	1.151	2.784	0.929	6.1	5.5	1.235	0.992
2-CP	25	1.844	58.32	0.017	0.990	2.233	5.383	0.860	96.5	54.3	1.030	0.993
	40	1.871	37.17	0.026	0.977	2.196	4.930	0.861	57.2	35.3	1.064	0.992
	55	1.908	22.72	0.042	0.971	2.250	3.882	0.865	20.3	16.4	1.089	0.993
4-CP	25	1.886	123.78	0.008	0.960	2.267	6.756	0.944	380.5	183.2	0.930	0.989
	40	1.800	94.12	0.011	0.958	2.260	5.885	0.972	339.8	164.0	0.901	0.996
	55	1.730	75.17	0.013	0.949	2.100	5.987	0.976	290.3	147.5	0.895	0.998
DCP	25	2.254	192.82	0.005	0.952	2.654	7.869	0.943	727.9	296.0	0.938	0.984
	40	2.197	144.67	0.007	0.941	2.639	7.199	0.957	620.8	231.0	0.929	0.993
	55	2.155	123.42	0.008	0.941	2.562	7.017	0.973	602.8	249.1	0.910	0.997
TCP	25	2.430	257.63	0.004	0.982	2.741	10.593	0.879	722.8	290.5	0.984	0.986
	40	2.328	209.87	0.005	0.978	2.701	9.051	0.925	690.6	279.1	0.959	0.999
	55	2.344	175.71	0.006	0.977	2.695	8.666	0.931	560.9	225.3	0.955	0.999
4-NP	25	2.257	77.25	0.013	0.956	2.550	7.332	0.946	329.2	131.9	0.928	0.987
	40	2.225	51.92	0.019	0.997	2.305	9.991	0.913	114.3	51.4	0.993	0.999
	55	2.182	38.17	0.026	0.978	2.161	10.99	0.938	96.1	44.1	0.986	0.998
DNP	25	2.272	123.19	0.008	0.973	2.902	5.924	0.943	420.9	165.8	0.929	0.993
	40	2.244	91.87	0.011	0.980	2.663	6.842	0.877	224.8	98.0	0.984	0.998
	55	2.211	72.73	0.014	0.985	2.467	10.986	0.886	155.3	70.6	0.998	0.999

a higher degree and the ACFs surface is charged more negatively, leading to increased electrostatic repulsion force between them. Electrostatic repulsion force also appears between the adsorbed phenolic anions, as a consequence these anions repel each other in the pores. This effect would be more significant in low-size pores, where the anions are close to each other. Moreover, the dissociation of phenols leads to a decrease in the hydrophobicity, resulting in reduced affinity between phenols and the ACFs surface.

The pK_a values of TCP and DNP are lower than the pH_{PZC} of ACFs, and decreased uptakes at $pH > pH_{PZC}$ are observed for them. At $pK_a < pH < pH_{PZC}$, the uptakes of the two phenols also decrease with the rise of pH. In this pH range, TCP and DNP are partially dissociated and the ACFs surface is positively charged, there exists electrostatic attraction force between them and the ACFs; however, the appearance of repulsion force between the adsorbed phenol anions and the decrease in the hydrophobicity affect the adsorption more heavily. It can also be found that at high pH the uptake of TCP is remarkably lower than other chlorophenols, which probably resulted from the strong electrostatic repulsion force between it and the ACFs surface, as TCP has larger molecular dimension and contacts more tightly with the ACFs. However, the rise in pH affects DNP less seriously; in contrast to TCP, its uptake is higher than 4-NP at high pH range. A possible reason is that the nitro group added on the ortho position withdraws the electron charged by the DNP anion, thus the electron density is dispersed and the electrostatic repulsion force between DNP and the ACFs surface is reduced. Vasiljevic et al. [19] found that the uptake of DNP did not decrease heavily at high pH, in contrast to an obvious drop for that of phenol.

3.2.4. Adsorption mechanism

Three important mechanisms have been proposed to interpret the adsorption behaviors of phenols on activated carbon in previous studies, namely: the electron donor–acceptor complex, the π – π dispersion interactions and the solvent effects [39].

The electron donor–acceptor complex mechanism assumes that the aromatic rings of the adsorbate act as the electron acceptors and the basic sites on the carbon surface serve as the donors [40]. Recently, some studies presented contradictory results to this mechanism [41,42], in which the adsorption capacities of phenols could not be explained by the amounts of the basic sites. In this study, according to the thermodynamic analysis, the adsorption nature is primarily physical which enhances with the increase of substitution degree, indicating that the more favorable adsorption of the substituted phenols could not be attributed to this mechanism.

The π – π interactions derive from the interactions between the π electrons in the aromatic rings of the phenols and those in the graphene layers, which might comprise charge-transfer, dispersive force and polar electrostatic components [43]. The introduction of substituent groups would alter the π – π interactions between phenols and activated carbon. It is proposed that electron-withdrawing groups enhance the π – π interactions by reducing the electron density of π electrons, diminishing the repulsive electrostatic interactions between the aromatic rings [44]. As both nitro and chloro are electron-withdrawing groups, the π – π interactions are enhanced with the increase in the number of these groups. The nitro group has stronger electron-withdrawing ability than the chloro group, hence the π – π interactions are stronger for nitrophenols than for chlorophenols. It is considered that this mechanism

Table 3
Thermodynamic parameters for the adsorption of phenols on ACFs.

Parameters	Phenol	2-CP	4-CP	DCP	TCP	4-NP	DNP
ΔG° (kJ/mol)	25 °C	–26.01	–27.19	–29.05	–30.15	–30.87	–27.88
	40 °C	–24.93	–27.38	–29.80	–30.92	–31.89	–28.25
	55 °C	–24.09	–27.35	–30.62	–31.97	–32.93	–28.77
ΔS° (J/molK)	–64.70	–18.27	52.53	60.59	69.16	29.34	49.02
ΔH° (kJ/mol)	–45.27	–32.76	–13.38	–12.04	–10.25	–19.12	–14.42

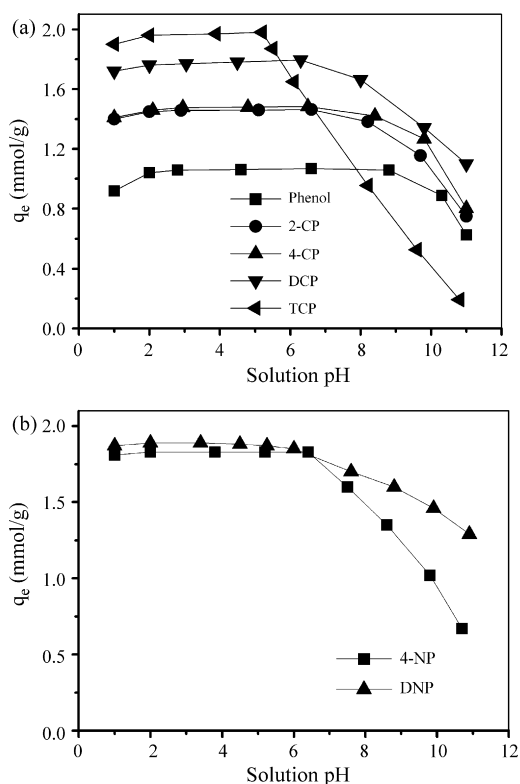


Fig. 3. Effects of solution pH on the adsorption of phenols: 25 °C, initial concentrations: 1.5 mmol/L for phenol, 2-CP and 4-CP, 1.85 mmol/L for DCP, 2 mmol/L for TCP, 4-NP and DNP.

plays an important role in this study, as suggested by other studies dealing with adsorption of phenols on ACFs [21,23].

The solvent effects should be taken into consideration in adsorption studies. Water molecules can be adsorbed on the surface oxygen groups by hydrogen bonding [45], which is unfavorable for the adsorption of phenols as some activate sites are occupied. The solvent effects are closely related to temperature, since temperature influences not only the adsorption of water but also the hydration degree of the phenolic molecules [8]. This factor might explain for the increased adsorption capacities (q_m value in Langmuir equation) and negative entropy changes observed for phenol and 2-CP with the rise of temperature, as the solvent effects are significant for them that diminishes with the rise of temperature.

The hydrophobic interactions are believed to make contributions to the adsorption of phenols [39]. In aqueous solution, the adsorbate with higher hydrophobicity has stronger tendency to be adsorbed and retain on the carbon surface or in the pores. As suggested by the solubilities (Table 1), the hydrophobicities of these phenols in study reinforce with the increase of the substitution degree, which is another reason for the enhanced adsorption of the substituted phenols.

The molecular size also has some implications on the adsorption. The molecules with a suitable size would be adsorbed more favorably since they have more contact sites with the carbon surface. However, if the molecular size is relatively large it might cause the steric effects. This point could explain the seemingly abnormal adsorption behaviors of DNP. Although the π - π interactions between it and the ACFs are stronger and it is more hydrophobic, the adsorption capacity of DNP is only slightly higher than that of 4-NP and similar to that of DCP; decreased DNP adsorption has also been reported by Daifullah and Girgis [46]. The steric effects are possibly caused by the following reasons: some extremely low-size pores might be inaccessible for DNP molecules (molecular sieve

effects); the interior part of the pores might not be reached due to the blockage of the adsorbed molecules; the molecules could not be so compact in pores due to the introduction of the nitro groups.

The influence of electrostatic interactions, which strongly depend on the solution pH, has been discussed in the pH study. The aforementioned factors are considered to be important in the adsorption of phenols on activated carbon. In general, the adsorption mechanism is complex which might also involve other factors such as dispersive force, induction force and ion-exchange interactions.

3.3. Kinetic studies

3.3.1. Kinetic fitting

The adsorption kinetic curves of the phenols are shown in Fig. 4 (adsorption equilibrium has not been reached for 4-NP and DNP at this time range). As can be seen, a large amount of phenols could be adsorbed within a short time, which is an advantage of ACFs over granular activated carbon (GAC). Due to the open pore structure of ACFs, the diffusion resistance is reduced to a large extent, which is usually the rate-controlling step in the case of GAC [39]. In this study, the unwoven form of the ACFs also contributes to the fast adsorption kinetics, which helps to reduce the external mass transfer resistance [47].

The kinetics is fitted with the pseudo-first-order and pseudo-second-order models, which are extensively used in kinetic studies. The pseudo-first-order model can be expressed as [48,49]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (10)$$

where k_1 is the first-order rate constant. The values of $\ln(q_e - q_t)$ are calculated from the experimental data and plotted against t , k_1 is calculated from the slope of the plot.

The pseudo-second-order model can be expressed as [50,51]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (11)$$

where k_2 is the second-order rate constant. The values of t/q_t are plotted against t , q_e and k_2 are calculated from the slope and intercept of the plot.

The constants of the two models are listed in Table 4. The pseudo-first-order model gives poor fitting with low R^2 values and notable variances between the experimental and theoretical uptakes. The pseudo-second-order model fits the experimental data quite well for all phenols, the R^2 values are close to unity and the experimental and theoretical uptakes are in good agreement. Recently, Wu et al. [52] pointed out that the pseudo-second-order model was suitable for the adsorption of lower molecular weight

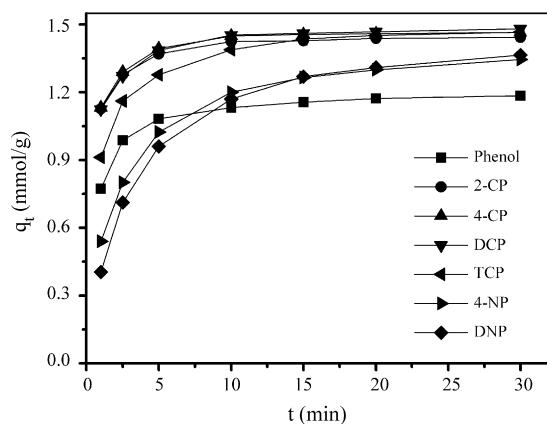


Fig. 4. Adsorption kinetics of phenols on ACFs: 25 °C, initial concentration 1.5 mmol/L.

Table 4

Pseudo-first-order and pseudo-second-order constants for the adsorption of phenols on ACFs at 25 °C.

Phenols	q_{exp}^a	Pseudo-first-order			Pseudo-second-order			
		q_e	k_1	R^2	q_e	k_2	k_2q_e	R^2
Phenol	1.182	1.140	1.031	0.910	1.202	1.502	1.805	0.999
2-CP	1.475	1.430	1.451	0.795	1.487	1.981	2.946	0.983
4-CP	1.478	1.436	1.456	0.819	1.492	2.014	3.005	0.988
DCP	1.487	1.428	1.441	0.797	1.486	1.970	2.927	0.981
TCP	1.492	1.407	0.987	0.653	1.498	1.037	1.553	0.901
4-NP	1.490	1.274	0.414	0.952	1.415	0.400	0.566	0.997
DNP	1.489	1.301	0.298	0.978	1.491	0.247	0.368	0.998

^a Experimental uptakes, obtained after 24 h.

adsorbates on smaller adsorbent particles, which could explain for its applicability in this study. Moreover, they defined the second-order rate index, k_2q_e , and proposed that this index was suitable to describe the adsorption kinetics. In this study, the k_2q_e values follow the order of DNP < 4-NP < TCP < phenol < DCP \approx 2-CP \approx 4-CP (Table 4). As the k_2q_e value is the inverse of the half-life of adsorption process, the adsorption kinetics gets faster in this order, which is consistent with the experimental observations.

The adsorption process of the adsorbate molecules from the bulk liquid phase onto the adsorbent surface is presumed to involve three stages: (1) mass transfer of the adsorbate molecules across the external boundary layer; (2) intraparticle diffusion within the pores of the adsorbent; (3) adsorption at a site on the surface. The intraparticle diffusion model proposed by Weber and Morris [53] is applied to study the adsorption process, which is written as:

$$q_t = k_{\text{id}} t^{1/2} \quad (12)$$

where k_{id} is the intraparticle diffusion rate constant.

The curve-fitting plots of the intraparticle diffusion model are demonstrated in Fig. 5, since 2-CP, 4-CP and DCP show similar adsorption kinetics, only the fitting curve of 4-CP is presented for simplicity. It can be seen that for phenol and 4-CP, the plot can be divided into two portions: a sharp rise portion and a plateau portion. The initial sharp rise portion represents the intraparticle diffusion process, and the plateau portion corresponds to the final equilibrium process [54,55]. The existence of an external layer diffusion process could be deduced by the fact that these plots do not pass through the origin [56]. However, a less-sharp rise portion between the sharp rise and the plateau portions is observed for TCP, 4-NP and DNP. An external layer diffusion process still exists for TCP, but its impact on 4-NP and DNP is less notable. During the initial sharp rise stage, the diffusion of the phenols is restricted mainly by the pore structure of the ACFs; during the following less-sharp rise stage, the diffusion is retarded mainly by

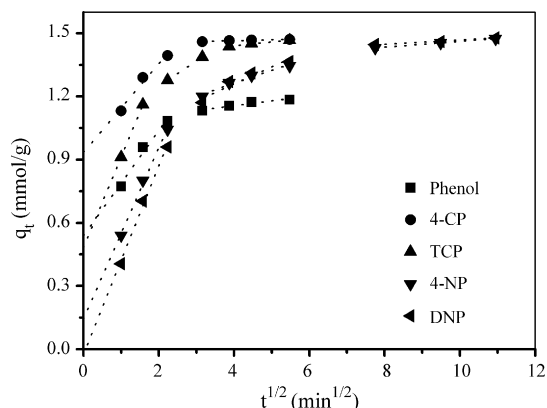


Fig. 5. Intraparticle diffusion model fitting of the adsorption kinetics.

the formerly adsorbed molecules, which will be discussed in detail below.

3.3.2. Steric effects

As shown in Fig. 4, 2-CP, 4-CP and DCP demonstrate similar adsorption kinetics, while other phenols exhibit slower initial adsorption rates. For phenol, it should be noted that its adsorption driving force is weaker due to a relatively lower ultimate uptake; in fact, its adsorption kinetics is remarkable as suggested by the second-order rate index. For TCP, 4-NP and DNP, the slower adsorption rates should be ascribed to the steric effects, i.e., the adsorbate molecules have difficulties in moving within pores with size not large enough. In adsorption studies, much attention has been paid in the steric effects. Kasaoka et al. [57] established the molecular sieve behavior of ACFs using compounds of known structure and shape; Pelekani and Snoeyink [58] studied the competitive adsorption between atrazine and methylene blue on ACFs with various pore size distributions. According to their results, the pore size should be above 1.2 times (Pelekani and Snoeyink) or 1.7 times (Kasaoka et al.) of the second widest dimension of the adsorbate molecule to allow effective adsorption.

Adsorption kinetics is more sensitive to the steric effects, which demonstrates their influences during the adsorption process. The similar adsorption kinetics of 2-CP, 4-CP and DCP indicate that their adsorption process is not hindered to an appreciable extent, suggesting that steric effects are negligible if the molecular dimensions are below some limits. Steric effects are involved in TCP, 4-NP and DNP adsorptions. The molecular dimensions of the phenols (Table 1) and the average pore size of ACFs (9.2 Å) are at the same magnitude. TCP has a larger second widest dimension than other chlorophenols and the nitrophenols have larger widest dimensions than other phenols. At the start, the movement of the phenols is restricted by the pore structure; with the proceeding of the adsorption, an increasing amount of molecules are adsorbed, these molecules would occupy the pore entrance and retard the movement of the following ones. As shown by the kinetic curves, nitro group poses much stronger steric effects than chloro group, due to its larger dimension. Steric effects retard the adsorption kinetics, but if they are not too serious, the following molecules still have opportunities to get into the interior part of the pores after a longer time. Hence, the ultimate uptakes of TCP and 4-NP are influenced to a minor extent, as can be deduced from their adsorption isotherms. However, steric effects on DNP are more significant, as a consequence some part of the pores is inaccessible due to the blockage of the adsorbed molecules, which is an important reason for its reduced uptake.

It seems that the steric effects on the adsorption kinetics are closely related to the widest molecular dimension, while the steric effects on the ultimate uptake are mainly related to the second widest molecular dimension. The average pore size of ACFs (9.2 Å) is about 1.35 times of the widest dimension of 4-NP (6.84 Å) and about 1.60 times of the second widest dimension of DNP (5.76 Å), and the adsorption kinetics and isotherm are affected notably at these molecular dimension levels. The results are more consistent with the observations of Pelekani and Snoeyink [58].

4. Conclusions

Characterizations of ACFs demonstrate narrow distribution of the low-size pores and neutral nature of the surface. Redlich–Peterson model gives the best fitting for the adsorption isotherms in most cases, while Langmuir model is reasonably applicable in all cases. Thermodynamic studies demonstrate negative free energy and enthalpy changes and increased entropy change with the increase of substitution degree; based on thermody-

namic parameters, the adsorption is primarily physical in nature enhanced by chemisorption. The uptakes are stable at $\text{pH} < \text{pK}_a$ except for a slight decrease at $\text{pH} 1$, while decreased uptakes are observed at $\text{pH} > \text{pK}_a$. The effects of electron donor–acceptor, π – π interactions, solvent effects, hydrophobic interactions, molecular dimensions and other interactions on the adsorption have been discussed. In kinetic studies, ACFs show high adsorption rate due to their open pore structure. The pseudo-second-order model gives satisfactory fitting, and the intraparticle diffusion model describes the adsorption process well. Steric effects on adsorption kinetics were found for TCP, 4-NP and DNP, due to the limitation of the pore structure and the retardation of the adsorbed molecules. It is proposed that the steric effects are notable on the adsorption kinetics and ultimate uptake when the average pore size is 1.35 times to the widest molecular dimension and 1.60 times to the second widest molecular dimension, respectively.

Acknowledgment

The authors appreciate the financial supports by the National Science Foundation of China (No. 50678045).

References

- [1] A.C. Lua, Q.P. Jia, Adsorption of phenol by oil-palm-shell activated carbons in a fixed bed, *Chem. Eng. J.* 150 (2009) 455–461.
- [2] M. Radhika, K. Palanivelu, Adsorptive removal of chlorophenols from aqueous solution by low cost adsorbent—kinetics and isotherm analysis, *J. Hazard. Mater.* B138 (2006) 116–124.
- [3] S. Esplugas, J. Gimenez, S. Contreras, E. Pascual, M. Rodriguez, Comparison of different advanced oxidation processes for phenol degradation, *Water Res.* 36 (2002) 1034–1042.
- [4] K. Rzeszutek, A. Chow, Extraction of phenols using polyurethane membrane, *Talanta* 46 (1998) 507–519.
- [5] A.P. Annachhatre, S.H. Gheewala, Biodegradation of chlorinated phenolic compounds, *Biotechnol. Adv.* 14 (1996) 35–56.
- [6] J.D. Rodgers, W. Jedral, N.J. Bunce, Electrochemical oxidation of chlorinated phenols, *Environ. Sci. Technol.* 33 (1999) 1453–1457.
- [7] Z.F. Guo, R.X. Ma, G.J. Li, Degradation of phenol by nanomaterial TiO_2 in wastewater, *Chem. Eng. J.* 119 (2006) 55–59.
- [8] A. Dabrowski, P. Podkoscielny, Z. Hubicki, M. Barczak, Adsorption of phenolic compounds by activated carbon—a critical review, *Chemosphere* 58 (2005) 1049–1070.
- [9] D.M. Nevskaiia, A. Santianes, V. Munoz, A. Guerrero-Ruiz, Interaction of aqueous solutions of phenol with commercial activated carbons: an adsorption and kinetic study, *Carbon* 37 (1999) 1065–1074.
- [10] S.L. Wang, Y.M. Tzou, Y.H. Lu, G. Sheng, Removal of 3-chlorophenol from water using rice-straw-based carbon, *J. Hazard. Mater.* 147 (2007) 313–318.
- [11] S.J. Park, Y.S. Jang, J.W. Shim, S.K. Ryu, Studies on pore structures and surface functional groups of pitch-based activated carbon fibers, *J. Colloid Interface Sci.* 260 (2003) 259–264.
- [12] L. Ding, V.L. Snoeyink, B.J. Marinas, Z. Yue, J. Economy, Effects of powdered activated carbon pore size distribution on the competitive adsorption of aqueous Atrazine and natural organic matter, *Environ. Sci. Technol.* 42 (2008) 1227–1231.
- [13] I. Martian-Gulloan, R. Font, Dynamic pesticide removal with activated carbon fibers, *Water Res.* 35 (2001) 516–520.
- [14] L. Li, P.A. Quinlivan, D.R.U. Knappe, Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution, *Carbon* 40 (2002) 2085–2100.
- [15] M.Z. Alam, E.S. Ameen, S.A. Muyibi, N.A. Kabbashi, The factors affecting the performance of activated carbon prepared from oil palm empty fruit bunches for adsorption of phenol, *Chem. Eng. J.* 155 (2009) 191–198.
- [16] A.P. Terzyk, Molecular properties and intermolecular forces—factors balancing the effect of carbon surface chemistry in adsorption of organics from dilute aqueous solutions, *J. Colloid Interface Sci.* 275 (2004) 9–29.
- [17] H.B. Li, Y.M. Du, X.J. Wu, H.Y. Zhan, Effect of molecular weight and degree of substitution of quaternary chitosan on its adsorption and flocculation properties for potential retention-aids in alkaline papermaking, *Colloids Surf. A* 242 (2004) 1–8.
- [18] X. Zhang, A.M. Li, Z.M. Jiang, Q.X. Zhang, Adsorption of dyes and phenol from water on resin adsorbents: effect of adsorbate size and pore size distribution, *J. Hazard. Mater.* B137 (2006) 1115–1122.
- [19] T. Vasiljevic, J. Spasojevic, M. Bacic, A. Onjia, M. Lausevic, Adsorption of phenol and 2,4-dinitrophenol on activated carbon cloth: the influence of sorbent surface acidity and pH, *Sep. Sci. Technol.* 41 (2006) 1061–1075.
- [20] Y.S. Al-Degs, M.I. El-Barghouti, A.H. El-Sheikh, G.M. Walker, Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon, *Dyes Pigments* 77 (2008) 16–23.
- [21] J.P. Wang, Y.Z. Chen, H.M. Feng, S.J. Zhang, H.Q. Yu, Removal of 2,4-dichlorophenol from aqueous solution by static-air-activated carbon fibers, *J. Colloid Interface Sci.* 313 (2007) 80–85.
- [22] J.P. Wang, H.M. Feng, H.Q. Yu, Analysis of adsorption characteristics of 2,4-dichlorophenol from aqueous solutions by activated carbon fiber, *J. Hazard. Mater.* 144 (2007) 200–207.
- [23] P.E. Diaz-Flores, R. Leyva-Ramos, R.M. Guerrero-Coronado, J. Mendoza-Barron, Adsorption of pentachlorophenol from aqueous solution onto activated carbon fiber, *Ind. Eng. Chem. Res.* 45 (2006) 330–336.
- [24] D. Tang, Z. Zheng, K. Lin, J. Luan, J. Zhang, Adsorption of *p*-nitrophenol from aqueous solutions onto activated carbon fiber, *J. Hazard. Mater.* 143 (2007) 49–56.
- [25] R.S. Juang, F.C. Wu, R.L. Tseng, Adsorption isotherms of phenolic compounds from aqueous solutions onto activated carbon fibers, *J. Chem. Eng. Data* 41 (1996) 487–492.
- [26] Q. Lu, G.A. Sorial, The effect of functional groups on oligomerization of phenolics on activated carbon, *J. Hazard. Mater.* 148 (2007) 436–445.
- [27] H. Rong, Z. Ryu, J. Zheng, Y. Zhang, Effect of air oxidation of rayon-based activated fibers on the adsorption behavior for formaldehyde, *Carbon* 40 (2002) 2291–2300.
- [28] G. Horvath, K. Kawazoe, Method for the calculation of effective pore size distribution in molecular sieve carbon, *J. Chem. Eng. Jpn.* 16 (1983) 470–475.
- [29] Z. Li, M. Kruk, M. Jaroniec, S.K. Ryu, Characterization of structural and surface properties of activated carbon fibers, *J. Colloid Interface Sci.* 204 (1998) 151–156.
- [30] H.P. Boehm, Some aspects of the surface chemistry of carbon blacks and other carbons, *Carbon* 32 (1994) 759–769.
- [31] J.S. Noh, J.A. Schwarz, Estimation of the point of zero charge of simple oxides by mass titration, *J. Colloid Interface Sci.* 130 (1989) 157–164.
- [32] O. Hamdaoui, E. Naffrechoux, Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon. Part I. Two-parameter models and equations allowing determination of thermodynamic parameters, *J. Hazard. Mater.* 147 (2007) 381–394.
- [33] F.I. Talens-Alession, H. Adamczak, J. Szymanski, Micellar-enhanced ultrafiltration of phenol by means of oxyethylated fatty acid methyl esters, *J. Membr. Sci.* 192 (2001) 155–163.
- [34] C.H. Giles, D. Smith, A. Huitson, A general treatment and classification of the solute adsorption isotherm. I. Theoretical, *J. Colloid Interface Sci.* 47 (1974) 755–765.
- [35] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, *Chem. Eng. J.* (2009), doi:10.1016/j.ces.2009.09.013.
- [36] Y. Yu, Y.Y. Zhuang, Z.H. Wang, M.Q. Qiu, Adsorption of water-soluble dyes onto modified resin, *Chemosphere* 54 (2004) 425–430.
- [37] Y. Liu, Is the free energy change of adsorption correctly calculated? *J. Chem. Eng. Data* 54 (2009) 1981–1985.
- [38] Y.H. Li, Z. Di, J. Ding, D. Wu, Z. Luan, Y. Zhu, Adsorption thermodynamic, kinetic and desorption studies of Pb^{2+} on carbon nanotubes, *Water Res.* 39 (2005) 605–609.
- [39] C. Moreno-Castilla, Adsorption of organic molecules from aqueous solutions on carbon materials, *Carbon* 42 (2004) 83–94.
- [40] J.S. Mattson, H.B. Mark Jr., M.D. Malbin, W.J. Weber Jr., J.C. Crittenden, Surface chemistry of active carbon: specific adsorption of phenols, *J. Colloid Interface Sci.* 31 (1969) 116–130.
- [41] S. Haydar, M.A. Ferro-Garcia, J. Rivera-Utrilla, J.P. Joly, Adsorption of *p*-nitrophenol on an activated carbon with different oxidations, *Carbon* 41 (2003) 387–395.
- [42] M.W. Jung, K.H. Ahn, Y. Lee, K.P. Kim, J.S. Rhee, J.T. Park, K.J. Paeng, Adsorption characteristics of phenol and chlorophenols on granular activated carbons (GAC), *Microchem. J.* 70 (2001) 123–131.
- [43] C.A. Hunter, J.K.M. Sanders, The nature of π – π interactions, *J. Am. Chem. Soc.* 112 (1990) 5525–5534.
- [44] F. Cozzi, M. Cinquini, R. Annuziata, J.S. Siegel, Dominance of polar/ π over charge-transfer effects in stacked phenyl interactions, *J. Am. Chem. Soc.* 115 (1993) 5330–5331.
- [45] D. Pan, M. Jaroniec, Adsorption and thermogravimetric studies of unmodified and oxidized active carbons, *Langmuir* 12 (1996) 3657–3665.
- [46] A.A.M. Daifallah, B.S. Girgis, Removal of some substituted phenols by activated carbon obtained from agricultural waste, *Water Res.* 32 (1998) 1169–1177.
- [47] M.A. Fontecha-Camara, M.V. Lopez-Ramon, M.A. Alvarez-Merino, C. Moreno-Castilla, Temperature dependence of herbicide adsorption from aqueous solutions on activated carbon fiber and cloth, *Langmuir* 22 (2006) 9586–9590.
- [48] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, *Chem. Eng. J.* 70 (1998) 115–124.
- [49] E. Tutem, R. Apak, C.F. Unal, Adsorption removal of chlorophenols from water by bituminous shale, *Water Res.* 32 (1998) 2315–2324.
- [50] G. McKay, Y.S. Ho, Pseudo-second-order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.
- [51] X. Yang, B. Al-Duri, Kinetic modeling of liquid-phase adsorption of reactive dyes on activated carbon, *J. Colloid Interface Sci.* 287 (2005) 25–34.
- [52] F.C. Wu, R.L. Tseng, S.C. Huang, R.S. Juang, Characteristics of pseudo-second-order kinetic model for liquid-phase adsorption: a mini-review, *Chem. Eng. J.* 151 (2009) 1–9.
- [53] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* 89 (1963) 31–59.
- [54] E. Lorenc-Grabowska, G. Gryglewicz, Adsorption characteristics of Congo Red on coal-based mesoporous activated carbon, *Dyes Pigments* 74 (2007) 34–40.

- [55] W.H. Cheung, Y.S. Szeto, G. McKay, Intraparticle diffusion processes during acid dye adsorption onto chitosan, *Bioresour. Technol.* 98 (2007) 2897–2904.
- [56] K. Mohanty, D. Das, M.N. Biswas, Adsorption of phenol from aqueous solutions using activated carbons prepared from *Tectona grandis* sawdust by $ZnCl_2$ activation, *Chem. Eng. J.* 115 (2005) 121–131.
- [57] S. Kasaoka, Y. Sakata, E. Tanaka, R. Naitoh, Design of molecular-sieve carbon. Studies on the adsorption of various dyes in the liquid phase, *Int. Chem. Eng.* 29 (1989) 734–742.
- [58] C. Pelekani, V.L. Snoeyink, Competitive adsorption between atrazine and methylene blue on activated carbon: the importance of pore size distribution, *Carbon* 38 (2000) 1423–1436.