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Competitive adsorption behaviors, characteristics, and dynamics of phenol, cresols, and dihydric phenols onto granular activated carbon

Wei Wang*, Shanglei Pan, Ruijie Xu, Jing Zhang, Shun Wang, Jun Shen

Department of Municipal Engineering, School of Civil and Hydraulic Engineering, Hefei University of Technology, Hefei 230009, China, Tel. +86 13655605619; email: dwhit@126.com (W. Wang), Tel. +86 13721060150; email: 1148838303@qq.com (S. Pan), Tel. +86 15056925389; email: 383946594@qq.com (R. Xu), Tel. +86 13095519780; email: 1014098002@qq.com (J. Zhang), Tel. +86 13637076176; email: 767073806@qq.com (S. Wang), Tel. +86 18505517229; email 821691605@qq.com (J. Shen)

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ABSTRACT

Although activated carbon is an effective tool for adsorbing phenolic compounds, it has not been systematically studied in the adsorption of phenolic compounds in the multi-component solutions. Adsorption characteristics and kinetics of phenol, *o*-, *m*-, *p*-cresol, catechol, hydroquinone, and resorcinol onto granular activated carbon were examined in single- and multi-component solutions. Results indicated that the adsorption rate constants decreased in the order of *p*-cresol > *o*-cresol > catechol > resorcinol > *m*-cresol > hydroquinone > phenol in single-component solutions. The pseudo-second-order model was better than the pseudo-first-order model for fitting the experimental data in the multi-component solutions. The adsorption rate constants of dihydric phenols isomers decreased dramatically when the solutions contained phenol and cresol isomers. Resorcinol exhibited a significant promoting effect on adsorption capacities of cresol isomers. The adsorption capacities almost obeyed the following sequence of (catechol, hydroquinone) > cresol isomers > (resorcinol, phenol) in the multi-component solutions. The distribution constants (b^i) of phenol were 3.169, 3.175, and 3.249, respectively, in the ternary solutions, which were significantly higher than the values of other two components (No. 1, *o*-cresol 2.951, catechol 2.893; No. 2, *o*-cresol 2.864, resorcinol 2.977; No. 3, *o*-cresol 2.918, hydroquinone 2.861). Results also demonstrated the solubility and functional groups of phenolic compounds might play a key role in their competitive adsorption capabilities in multi-component solutions.

Keywords: Phenolic wastewater; Granular activated carbon; Phenol; Cresol; Dihydric phenol

1. Introduction

A group of phenolic compounds including phenol, cresols, and dihydric phenols are the main organic constituents of industrial wastewaters from coal gasification plants, coking plants, and oil refineries [1]. The phenolic compounds have shown hazardous effects in the aquatic environment at relatively low concentrations [2]. Thus, these pollutants need proper treatment prior to being discharged to the water bodies or used for irrigation purposes. Current techniques available for removing phenolic compounds from wastewaters include the methods such as activated carbon adsorption, ion exchange, solvent extraction, biological treatment, and chemical oxidation [3–6]. Among these

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*Corresponding author.

techniques, the activated carbon adsorption is the most widely used method to remove phenolic compounds from the wastewaters [7].

The adsorption properties of phenolic compounds onto activated carbon had been studied in the literatures [7], and the results demonstrated that the adsorption capacity depends mainly on the operational conditions, the characteristics of activated carbon, and the molecular properties of organics [8]. The operational parameters such as adsorbent dose, adsorbate concentration, pH, and temperature are also involved in the adsorption behaviors, which have implications on the interactions between activated carbon and phenolic compounds. Also, the physical properties of activated carbon and the organic molecular properties of phenolic compounds play an important role in its adsorption capacity, as they determine the interactions between organics and activated carbon at the interface [9]. The majority of studies is concerned with the dynamics of activated carbon in single-component solution. The modified Polanyi-based model was proposed to accurately predict the adsorption of phenolic compounds onto polymeric adsorbents [10]. The homogeneous surface diffusion model was developed to describe the dynamic adsorption of *para*-chlorophenol onto activated carbon adsorption columns [11]. The adsorption behaviors of resorcinol and catechol on granular activated carbon (GAC) were fitted with six isotherm models [12]. These experiments provided a good description of the adsorption process of phenolic compounds on activated carbon. Interestingly, the interference and competition adsorption behaviors of phenolic compounds were explored in the multi-component solutions [13–15].

As the most widely used adsorbent, the activated carbon was applied to remove phenolic compounds from the multi-component solutions [16,17]. These solutions usually have a complicated composition. Until recently, little attention is paid to the differences between the phenolic isomers in the adsorption process. However, the strong nonlinearities of the isotherms and interference effects of other solutes make the adsorption process hard to predict and control. Some studies had indicated that competitive adsorption was very significant in the multi-component solutions [18]. The distribution of the solutes is an important parameter for controlling its absorption and separation processes. The distribution data of phenolic compounds can be used to fit the competitive adsorption equilibrium, but difficulties in selecting an appropriate model have been clearly reported [19]. Phenol possesses one hydroxyl group and cresols and dihydric phenols have another methyl and hydroxyl groups, respectively. The significant differences can be expected in the composition and distribution of phenolic solutions as a function of the adsorption behavior of phenolic compounds in the multi-component solutions. Hence, it has important theoretical and practical values to understand the effect of composition and distribution of phenolic solutions on adsorption behaviors, characteristics, and dynamics of activated carbon in a mixture of phenolic compounds.

The aims of this paper are to conduct experiments on the adsorption characteristics and kinetics of GAC for seven kinds of phenolic compounds (phenol, *o*-, *m*-, *p*-cresol, catechol, hydroquinone, and resorcinol) in single- and multi-component solutions and to propose a distribution constant to fit the competitive adsorption of phenolic compounds onto GAC in the multi-component solutions. For this purpose, we select ternary phenolic compounds as the multi-component system. The possibilities of description of the distribution constants that depend on the composition of multi-component solutions were studied. Further scope of this study is to provide an adequate model to make possible a prediction of adsorption behaviors which dynamics as a function of distribution constant can be used for the optimization of adsorption of phenolic compounds in the multi-component solutions.

2. Materials and methods

2.1. Adsorbent and adsorbate

The thermally activated commercial GAC was supplied by the Sinopharm Chemical Reagent Co., Ltd, China. The physical properties of GAC were as follows: apparent relative density of 0.08–0.45, particle density of 1.9–2.1 kg/L, surface area of 500–1,000 m^2/g, and ash content less than 3%. The GAC was sieved into 16/26 mesh, washed three times in distilled water, and dried at 105℃ for 24 h, before being used as adsorbent. The solutions of phenol, (*o*-, *m*-, and *p*-) cresol, catechol, hydroquinone, and resorcinol were prepared using analytical grade reagents.

2.2. Adsorption isotherms, adsorption rates, and competitive adsorption tests

The adsorption experiments included adsorption isotherms, adsorption rates, and competitive adsorption tests. All adsorption experiments were adjusted at the initial pH of 7.0 for the single- and multi-component of phenolic compounds. The pH values were adjusted with 0.1 mol/L NaOH and 0.1 mol/L HCl. For the determination of adsorption isotherms, 250 mL flasks were filled with 100 mL of known concentration of solutes (approximately 200 mg/L each) and a weight series of GAC (0.25, 0.5, 1, 2, 3, and 4 g/L). The adsorption rate tests in the single-component solutions were obtained by 2 L glass beaker fitted with a magnetic speed mixer. The beaker was filled with 1 L of known concentration solution (approximately 200 mg/L each) and around 4 g/L of GAC. The competitive adsorption tests in the ternary component solutions were carried out in the flasks with 4 g/L of GAC, and the flasks were placed on a shaker and agitated continuously for 25 h at 35℃.

2.3. Analytical methods

The concentrations of phenol, (*o*-, *m*-, and *p*-) cresol, catechol, hydroquinone, and resorcinol were determined by UV spectrophotometer (2600 UV/VIS, UNIC) and bromide titration in the single-component solutions and by liquid chromatography (SPD-20A, Shimadzu) in the multi-component solutions [20]. Elution was operated at a flow rate of 1.0 mL/min, using as mobile phase a mixture of water/acetonitrile/ acetic acid (50:49:1, v/v). The sampling times of the experiments were set up to be: 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, and 140 min in the adsorption rates; 0, 5, 15, 30, 90, 120, 900, and 1,500 min in the competitive adsorption tests. The experiment was independently repeated twice. The surface groups of GAC were analyzed by FTIR spectroscopy (iS10, Nicolet) and Boehm titration results [21]. The infrared spectra of organic fractions of GAC were obtained using dried powders lyophilized in potassium bromide pellets. The FTIR spectrometer was scanned from 4,000 to 400 cm^{-1}. The amount adsorbed at time $t(q_t)$ was calculated by the following equations:

$$q_t = \frac{C_0 - C_t}{X} \tag{1}$$

where C_0 and C_t are the concentrations of adsorbate at time zero and t in the solution, X is the dose of the adsorbent.

3. Theories

3.1. Adsorption isotherms

The Langmuir and Freundlich models (Eqs. 2 and 3) were used to describe the adsorption equilibrium.

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{2}$$

$$q_e = K_f C_e^{\frac{1}{n}} \tag{3}$$

where q_e and C_e are equilibrium concentrations of the adsorbate in the solid and liquid phases, respectively, K_L and $q_{\max}$ are the Langmuir adsorption constant and the maximum adsorption capacity of the adsorbent in Eq. (2), K_f and $1/n$ in Eq. (3) are the Freundlich equation constants.

3.2. Adsorption kinetic models

According to the developed transformed Langmuir kinetics [22], the rate equation can be written as:

$$\frac{\mathrm{d}\theta_\mathrm{t}}{\mathrm{d}t} = k_1(\theta_e - \theta_t) + k_2(\theta_e - \theta_t)^2 \tag{4}$$

The proportion of the surface occupied by the adsorbate $i(\theta_t^i)$ is defined as:

$$\theta_t^i = \frac{q_t^i}{q_{\max}^0} = \frac{C_0^i - C_t^i}{Xq_{\max}^0} \tag{5}$$

and then,

$$C_t^i = C_0^i - \theta_t^i X q_{\max}^0 \tag{6}$$

where q_t^i and $q_{\max}^0$ represent the adsorption capacity of the adsorbent for the solute i at time t and the maximum value for total solutes, C_0^i and C_t^i are the concentrations of solute i in the multi-component solutions at time zero and time t, respectively, while X is the dosage of GAC. The $q_{\max}^0$ is defined as:

$$q_{\max}^0 = \sum_{i=1}^{n} \frac{q_{\max}^i}{b^i} \tag{7}$$

where $q_{\max}^i$ is the maximum adsorption capacity of solute i and b^i is the distribution constant of solute i in the multi-component solutions. The distribution constant b^i relates to the ratio of maximum adsorption capacity of solute i in single-component system to its adsorption capacity in multi-component system. It is directly linked to the interaction of solutes in the multi-component solutions. If b^i value is larger than the reciprocal of mass proportion of solute i, it means that other solutes have a negative effect on adsorption of solute i in the multi-component solutions.

It is assumed that $b^i\theta_t^i$ equaled to $\sum_{i=1}^{n}\theta_t^i$, and can deduce Eq. (9).

$$\sum_{i=1}^{n}\theta_t^i = b^1\theta_t^1 = b^2\theta_t^2 = b^3\theta_t^3 = \cdots b^i\theta_t^i \cdots = b^n\theta_t^n \tag{8}$$

$$\frac{1}{b^1}+\frac{1}{b^2}+\frac{1}{b^3}+\cdots\cdots\frac{1}{b^n}=1 \tag{9}$$

According to the previous derivation [22], the rate adsorption equation for all solutes can be further written as:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t}=\sum_{i=1}^{n}k_2^i(q_t^i-q_e^i)^2+\sum_{i=1}^{n}k_1^i(q_t^i-q_e^i) \tag{10}$$

in which

$k_2^i=\frac{b^ik_a^iX}{q_{\max}^0}, k_1^i=\frac{\sqrt{\Delta}}{q_{\max}^0}, \Delta=(k_a^i)^2({C_0}^ib^i-Xq_{\max}^0)^2+2k_a^ik_d^i({C_0}^ib^i+Xq_{\max}^0)+(k_d^i)^2$, where ${k_a}^i$ and ${k_d}^i$ are the adsorption and desorption rate constants of solute i, respectively. Eq. (10) represents that the adsorption kinetic terms are governed by the weight of k_1^i and k_2^i in the multi-component solutions, and the difference of adsorption capacity q_t^i at time t and equilibrium adsorption capacity of q_e^i. Obviously, b_i is an important factor for determining the values of k_1^i and k_2^i in the multi-component system.

4. Results and discussion

4.1. Adsorption isotherm of phenolic compounds in the single-component solution

The experimental data for the adsorption of phenol, (*o*-, *m*-, and *p*-) cresol, catechol, hydroquinone, and resorcinol, respectively, onto GAC are fitted to the Langmuir and Freundlich isotherm models and the calculated parameters are listed in Table 1. The experimental data of C_e and q_e were treated with the models in order to determine the parameters of $q_{\max}$ and K_L of the Langmuir model (Eq. (1)), n and K_f of Freundlich model (Eq. (2)). The correlation coefficients (R^2) showed the fit between experimental values and isotherm models. The Langmuir isotherm and Freundlich isotherm fitted quite well with the experimental data of phenol, *o*-cresol, *m*-cresol, *p*-cresol, and catechol ($R^2 > 0.925$ and 0.941). However, resorcinol and hydroquinone were not well fitted by these two models [23]. In terms of $q_{\max}$ in Langmuir model, it was found that the maximum and minimum adsorption capacities of the phenolic compounds were 156.250 mg/g GAC for resorcinol and 116.279 mg/g GAC for catechol. The maximum adsorption capacity of phenolic compounds decreased in the order: resorcinol > *o*-cresol > phenol > *p*-cresol > hydroquinone > *m*-cresol > catechol. Obviously, the substitution position of functional groups caused great differences in the maximum adsorption capacity of isomers [23]. The different substituent groups and their relative position could affect the electron density and the torsion angle in the phenyl ring relating attraction with the surface of carbon [24].

4.2. Adsorption kinetics of phenolic compounds in the single-component solution

Fig. 1 shows that the adsorption kinetics of seven phenolic compounds in the single-component solutions. Similar adsorption trends were observed for the seven phenolic compounds with time. It was found that the q_t of each phenolic compound reached around 30 mg/g GAC after 10 min at initial phenolic concentration of 200 mg/L and GAC concentration of 4 g/L, while the adsorption approached equilibrium of 45–50 mg/g GAC after 40 min. In Fig. 1, the adsorption amounts of *p*-cresol and phenol reached the highest value of 43.745 mg/L and the lowest value of 37.883 mg/L among the seven phenolic compounds during the initial 20 min, respectively. After 40 min adsorption, the adsorption capacities exhibited some

Table 1
Calculated parameters of phenolic compounds onto GAC for the Langmuir and Freundlich adsorption isotherm equations

	Langmuir			Freundlich		
Phenolic compounds	$q_{\max}$ (mg/g)	K_L (L/mg)	R^2	n	K_f (mg/g)(L/mg)1/n	R^2
Phenol	140.845	0.059	0.9781	3.263	28.022	0.9333
o-cresol	151.515	0.200	0.9530	3.392	40.841	0.9830
m-cresol	123.457	0.240	0.9411	4.087	41.039	0.9810
p-cresol	128.205	0.120	0.9737	3.582	33.335	0.9769
Catechol	116.279	0.075	0.9259	3.008	22.809	0.9417
Resorcinol	156.250	0.021	0.8923	2.030	10.877	0.8565
Hydroquinone	126.582	0.058	0.8402	2.624	19.320	0.8680

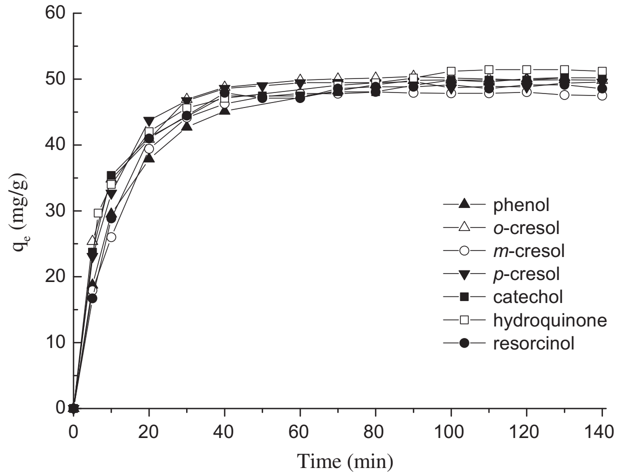

Fig. 1. Adsorption kinetics of the phenolic compounds in the single-component solutions.

changes in the seven phenolic compounds, in which the amounts adsorbed of hydroquinone and *m*-cresol reached the highest value of 51.422 mg/L and the lowest value of 47.489 mg/L among seven phenolic compounds, respectively.

In order to investigate the adsorption kinetics, the pseudo-first-order and pseudo-second-order adsorption equations were used to analyze the adsorption process by nonlinear regression. However, the pseudo-first-order rate constant having negative values indicated clearly that the pseudo-first-order kinetic model cannot be accepted. Table 2 shows the results of adsorption rate constant (k_2), amount adsorbed at equilibrium (q_e), and the coefficient of determination (R^2) for seven phenolic compounds by the pseudo-second-order equations. Considering both q_e and R^2, for all the phenolic compounds, the pseudo-second-order model fitted very well ($R^2 \geq 0.9973$). The sorption process obeyed pseudo-second-order kinetics at initial phenolic concentration of 200 mg/L. The highest and lowest equilibrium adsorption capacities were 53.763 mg/g GAC for phenol and 49.751 mg/g GAC for *m*-cresol, respectively. According the pseudo-second-order kinetic constants, the adsorption rate constants of seven phenolic compounds were in the order of: *p*-cresol > *o*-cresol > catechol > resorcinol > *m*-cresol > hydroquinone > phenol in the single-component solutions. The above order of *p*-cresol, hydroquinone, and phenol obtained in this work was similar to the reported results in previous literature [25].

Table 2
Parameters of pseudo-second-order kinetic models calculated from experimental data for seven phenolic compounds in single-component solutions ($X = 4$ g/L for GAC, $T = 308$ K, and pH 7)

	Pseudo second-order kinetics		
Phenolic compounds	q_e (mg/g)	k_2 (g/mg h)	R^2
Phenol	53.763	0.137	0.9997
o-cresol	51.282	0.401	0.9990
m-cresol	49.751	0.278	0.9973
p-cresol	50.505	0.439	0.9988
Catechol	51.546	0.285	0.9991
Resorcinol	52.910	0.280	0.9991
Hydroquinone	51.020	0.250	0.9976

4.3. *Adsorption kinetics of phenolic compounds in the multi-component solutions*

Three kinds of phenolic compounds, phenol, one of cresols, and one of dihydric phenols were chosen for the ternary solutes. Each phenolic compound was at the initial concentration of 200 mg/L in the ternary solutions. The GAC addition employed the same dose of 4 g/L. Fig. 2 shows adsorption kinetics of the phenolic compounds in the ternary solutions. Results of the adsorption kinetics show a rapid uptake of phenolic compounds within the first 120 min to achieve the equilibrium condition. Therefore, an optimum agitation time of 25 h was chosen for further experiment. Table 3 shows the comparison of pseudo-second-order models fitting with the experimental data of phenolic compounds in ternary solutions. Similarly, the pseudo-first-order kinetic model did not fit the experimental data well. The equilibrium adsorption capacities and the kinetic rate constants of K_2 to the pseudo-second-order models are shown in Table 3. Obviously, the pseudo-second-order model fitted well for phenolic compounds in the ternary solutions ($R^2 \geq 0.996$). Thus, the adsorption kinetics tended to obey the pseudo-second-order model and indicated $K_2^i(q_t^i - q_e^i) >> K_1^i$ which was the sufficient and necessary condition for Eq. (10) to be simplified to the pseudo-second-order rate expression, and it could be further rearranged to:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = \sum_{i=1}^{n} \frac{\partial \theta_t^i}{\partial t} \approx \sum_{i=1}^{n} \frac{b^i k_a^i X}{q_{\max}^0} (q_t^i - q_e^i)^2 = \sum_{i=1}^{n} K_2^i (q_t^i - q_e^i)^2 \tag{11}$$

The competitive adsorption experiments of phenolic compounds were conducted at a dose of 4 g GAC/L, while the initial concentration of phenolic compounds was 200 mg/L in the ternary-component solutions. When the competitive adsorption reaches equilibrium state in the ternary solutions, θ_t^i become θ_e^i and substituting θ_e^i into Eq. (8), yields:

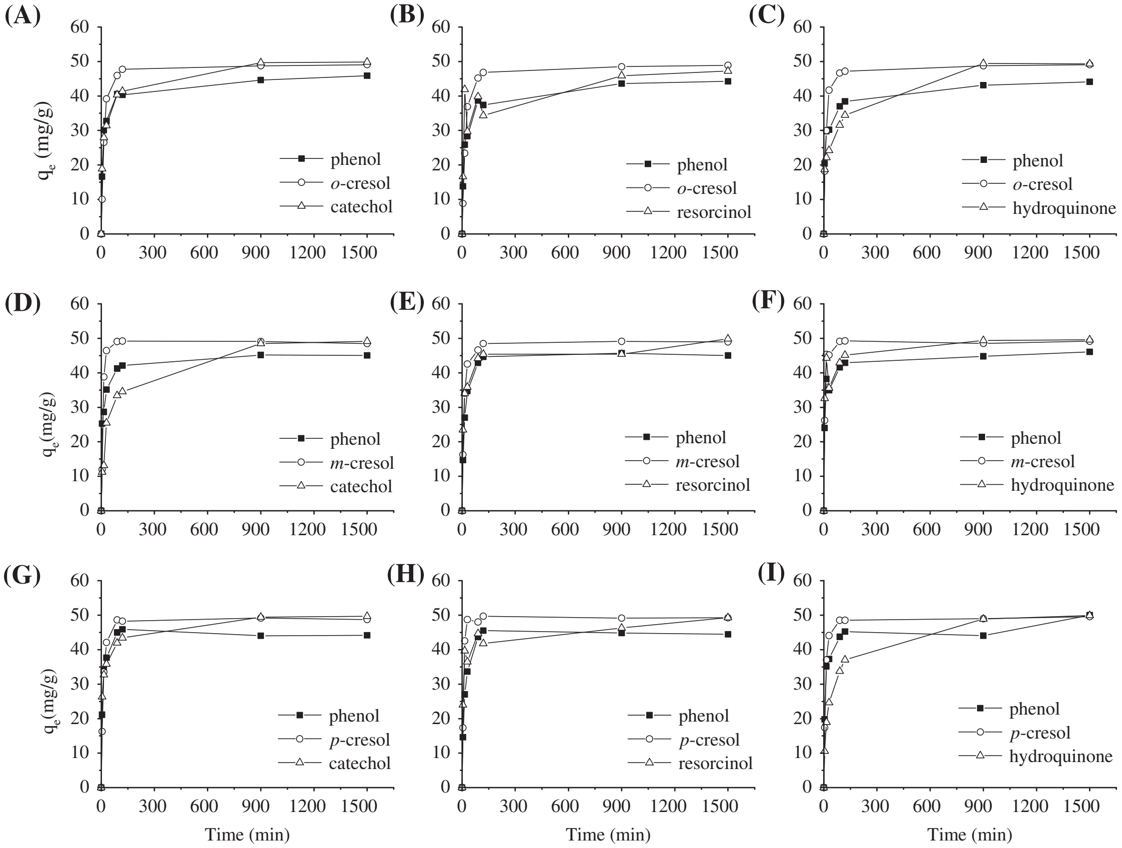

Fig. 2. Adsorption kinetics of the phenolic compounds in the ternary solutions ((A) phenol, *o*-cresol, catechol; (B) phenol, *o*-cresol, resorcinol; (C) phenol, *o*-cresol, hydroquinone; (D) phenol, *m*-cresol, catechol; (E) phenol, *m*-cresol, resorcinol; (F) phenol, *m*-cresol, hydroquinone; (G) phenol, *p*-cresol, catechol; (H) phenol, *p*-cresol, resorcinol; (I) phenol, *p*-cresol, hydroquinone).

$$\sum_{i=1}^{3}\theta_e^i = b^1\theta_e^1 = b^2\theta_e^2 = b^3\theta_e^3 \tag{12}$$

Here, it is assumed that the maximum adsorption capacity of GAC is certain in the specific ternary solutions. Using Eq. (5) and eliminating $q^0_{\max}$, Eq. (12) becomes:

$$\sum_{i=1}^{3}q_e^i = b^1q_e^1 = b^2q_e^2 = b^3q_e^3 \tag{13}$$

q_e^1, q_e^2, q_e^3, and k_2 are obtained from the fitting of second-order rate equations in the experimental data (Table 3). In this work, b^i is calculated using Eq. (13), and their values are shown in Table 4.

Obviously, the adsorption rate constants of dihydric phenols isomers were in the order of catechol (0.086) > resorcinol (0.080) > hydroquinone (0.045) in No. 1, No. 2, and No. 3 ternary solutions. Interestingly, the sequence was consistent with the previous order in the single-component solutions, but the adsorption rate constants of dihydric phenols isomers and *o*-cresol had significantly decreased. This showed the antagonistic sorption interaction between dihydric phenols isomers and *o*-cresol. In No. 4–6 ternary solutions, both adsorption rate constants of phenol and *m*-cresol were larger than the constants of single-component solutions, except *m*-cresol in No. 5, which resulted in a decrease in the constants of dihydric phenols isomers and presented a significant promoting effect between phenol and *m*-cresol. This result of *p*-cresol could not be concluded from No. 7–9. However, the adsorption rate constants of dihydric phenols isomers could dramatically decrease when the solutions contained phenol and cresol isomers.

In addition, the b^i values of phenol were 3.169, 3.175, and 3.249 in the ternary solutions of No. 1, 2, and 3, respectively. Obviously, the b^i values of phenol

Table 3
Parameters of pseudo-second-order kinetic models calculated from experimental data for nine ternary solutions of phenolic compounds ($X = 4$ g/L for GAC, $T = 308$ K and pH 7)

		Pseudo second-order kinetic		
No	Phenolic compounds	q_e (mg/g)	k_2 (g/mg·h)	R^2
1	phenol	45.872	0.125	0.9998
	o-cresol	49.261	0.142	0.9999
	catechol	50.251	0.086	0.9998
2	phenol	44.444	0.105	0.9998
	o-cresol	49.261	0.114	0.9999
	resorcinol	47.393	0.080	0.9992
3	phenol	44.248	0.125	0.9998
	o-cresol	49.261	0.217	1
	hydroquinone	50.251	0.045	0.9987
4	phenol	45.249	0.212	1
	m-cresol	48.780	0.467	0.9999
	catechol	50	0.039	0.9991
5	phenol	45.454	0.242	0.9999
	m-cresol	49.261	0.275	1
	resorcinol	49.020	0.110	0.9976
6	phenol	46.083	0.188	0.9998
	m-cresol	49.020	0.694	1
	hydroquinone	49.751	0.176	0.9999
7	phenol	44.248	0.851	1
	p-cresol	49.019	0.347	0.9999
	catechol	50	0.125	0.9999
8	phenol	44.643	0.295	0.999
	p-cresol	49.261	0.515	1
	resorcinol	48.780	0.117	0.9989
9	phenol	48.780	0.098	0.9956
	p-cresol	49.505	0.291	0.9999
	hydroquinone	50.505	0.044	0.9993

were significantly higher than the values of the other two components (No. 1, *o*-cresol 2.951, catechol 2.893; No. 2, *o*-cresol 2.864, resorcinol 2.977; No. 3, *o*-cresol 2.918, hydroquinone 2.861). Also, this similar result could be obtained from other ternary solutions. When the value of $b^i$was higher, the adsorption capacity of solute i was lower in the total adsorption capacity. The distribution constant b^i could indirectly reflect the competitive adsorption capacities of phenolic compounds. The physical and chemical properties of phenolic compounds, including primarily organic polarity, molecular size, solubility, and so on, had a significant effect on adsorption capability of phenolic compounds onto GAC [26]. The main adsorption factors were pointed to be the dispersion force between the activated carbon Π-electrons of double bonds and Π-electrons in phenols [27]. As an electron-withdrawing group, the hydroxyl group could decrease the Π-electrons of phenols, thus the affinity to activated carbon surface was stronger. On the contrary, the presence of methyl group increased electron density in the phenyl ring, thus the affinity to activated carbon surface was weaker. The spectrum of FITR indicated a number of stronger bands centered at 3,426 and 1,578 cm^{-1} which were ascribable in turn to stretching (v) (O–H and C=O) vibrations. Specifically, the carbonyl groups were the dominant functional group on the surface of GAC. So, the existence of hydroxyl group made catechol and hydroquinone more absorbable in GAC than cresol isomers. At higher adsorbate concentrations, the interactions between the adsorbate molecules were thought to affect the adsorption process more than the adsorbent–adsorbate forces [28]. The adsorption capacities of methyl phenols and dihydric-substituted phenols were higher than phenol. The adsorption capacities obeyed the following sequence: dihydric phenols > cresols > phenol, except the solutions of phenol, *o*-cresol, and resorcinol (No. 2), phenol, *m*-cresol, and resorcinol (No. 5), and phenol, *p*-cresol, and resorcinol (No. 8). It could find that

Table 4
Comparison of pseudo-second-order kinetic parameters and distribution constants calculated from experimental data for nine ternary solutions of phenolic compounds ($X = 4$ g/L for GAC, $T = 308$ K, and pH 7)

No.	Phenol		*o*-cresol		*m*-cresol		*p*-cresol		Catechol		Resorcinol		Hydroquinone	
	k_2 (g/mg h)	b_i	k_2 (g/mg h)	b_i	k_2 (g/mg h)	b_i	k_2 (g/mg h)	b_i	k_2 (g/mg h)	b_i	k_2 (g/mg h)	b_i	k_2 (g/mg h)	b_i
Control	0.137	1	0.401	1	0.278	1	0.439	1	0.285	1	0.280	1	0.250	1
1	0.125	3.169	0.142	2.951					0.086	2.893				
2	0.105	3.175	0.114	2.864							0.080	2.977		
3	0.125	3.249	0.217	2.918									0.045	2.861
4	0.212	3.183			0.467	2.918			0.039	2.881				
5	0.242	3.162			0.275	2.918					0.110	2.932		
6	0.188	3.143			0.694	2.955							0.176	2.912
7	0.851	3.238					0.347	2.923	0.125	2.865				
8	0.295	3.196					0.515	2.896			0.117	2.925		
9	0.098	3.050					0.291	3.006					0.044	2.946

resorcinol exhibited a significant promoting effect on the adsorption capacities of cresol isomers in No. 2, 5, and 8. However, the solubility in water of seven compounds was in the order: resorcinol > catechol > hydroquinone ≈ phenol > *m*-cresol > *o*-cresol > *p*-cresol [7,24,29,30]. Because the nature of activated carbon was substantially non-polar or slightly polar, the phenolic compounds have a greater solubility and a stronger hydrophilicity, and their adsorption capacities were worse in the similar molecular weight; whereas, the poor solubility and hydrophilicity, and weakly polar organic compounds had a strong adsorption capacity [31]. Then, it could explain the reason why the adsorption capacities of cresol isomers were higher than resorcinol and phenol by their lower solubility in the multi-component solutions. Consequently, both the solubility and functional groups of phenolic compounds might play an important role in their competitive adsorption capabilities in the multi-component solutions.

5. Conclusion

Adsorption characteristics and dynamics of phenol, *o*-, *m*-, and *p*-cresol, catechol, hydroquinone, and resorcinol onto GAC were investigated in single- and multi-component solutions. The pseudo-second-order model fitted well for the experimental data in the multi-component solutions. The adsorption rate constants obeyed the following order of: *p*-cresol > *o*-cresol > catechol > resorcinol > *m*-cresol > hydroquinone > phenol in single-component solutions. In the ternary solutions, the adsorption capacities of catechol and hydroquinone were higher than cresol isomers; the adsorption capacities of cresol isomers were higher than resorcinol and phenol. The dihydric phenols isomers and *o*-cresol exhibited the antagonistic sorption interaction, and the phenol and *m*-cresol presented a significant synergistic effect. The adsorption rate constants of dihydric phenols isomers could dramatically decrease when the solutions contained phenol and cresol isomers. The competitive adsorption capacity of phenolic compounds might correlate with their solubility distribution and functional groups.

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