

Adsorption behaviors of some phenolic compounds onto high specific area activated carbon cloth

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Abstract

Adsorption of phenol, hydroquinone, *m*-cresol, *p*-cresol and *p*-nitrophenol from aqueous solutions onto high specific area activated carbon cloth has been studied. The effect of ionization on adsorption of these ionizable phenolic compounds was examined by studying the adsorption from acidic, basic and natural pH solutions. Kinetics of adsorption was followed by in situ UV spectroscopy over a period of 90 min. First-order rate law was found to be valid for the kinetics of adsorption processes and the rate constants were determined. The highest rate constants were obtained for the adsorption from solutions at the natural pH. The lowest rate constants were observed in basic solutions. The rate constants decreased in the order *p*-nitrophenol \sim *m*-cresol $>$ *p*-cresol $>$ hydroquinone \sim phenol. Adsorption isotherms were derived at 30 °C and the isotherm data were treated according to Langmuir, Freundlich and Tempkin isotherm equations. The goodness of fit of experimental data to these isotherm equations was tested and the parameters of equations were determined. The possible interactions of compounds with the carbon surface were discussed considering the charge of the surface and the possible ionization of compounds at acidic, basic and natural pH conditions.

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1. Introduction

Phenolic compounds are considered to be one of the major and most undesirable pollutants in wastewaters. Therefore, removal, destruction or modification to less noxious structures of phenolic compounds is essential for purification of wastewaters as well as raw water. Removal of organic molecules including phenolic compounds from solutions is widely achieved by adsorption onto activated carbon in powder or granular form. Removal of phenol from aqueous solutions by adsorption onto adsorbents such as silica gel, Hi-Siv 3000, activated alumina, activated carbon, Filtrasorb-400 and Hi-Siv 1000, was studied recently by Roostaei and Tezel [1]. It was found from kinetic experiments that Hi-Siv 1000 had the highest adsorption rate and from equilibrium experiments that activated carbon and Filtrasorb-400 had the highest ad-

sorption capacities. The amount of adsorption of commercial dyes, phenol and 4-chlorophenol was studied and the role of microporosity of activated carbons on adsorption was examined by Juang et al. [2]. Adsorption of resorcinol and catechol on granular activated carbon has been reported by Kumar et al. [3]. Adsorption of phenol and 2,3,4-trichlorophenol from aqueous solutions onto granular nanoporous activated carbon was studied by László et al. [4]. Urano et al. [5] reported the equilibria for adsorption of 16 organic aromatic and aliphatic compounds on five commercial granular activated carbon materials. The slow intraparticle diffusion and the handling difficulties in granular adsorbent have led to the development of new adsorbent materials such as activated carbon fibers. These materials in the form of felt or cloth have the advantages of having high specific surface area (as high as 2500 m² g⁻¹), mechanical integrity, easy handling and minimal diffusion limitation to adsorption [6]. In many recent studies carbon fibers have been proven to display good adsorptive capabilities for organic and inorganic species. Lee

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et al. [7] studied the adsorption of Cu(II) by activated carbon fibers. Babić et al. [8] reported the studies on adsorption of some metal ions onto activated carbon cloth. Recently we have studied the adsorption of some organic heterocyclic compounds [9], some anilinic compounds [10,11], adsorption and electrosorption of some sulfur containing oxyanions [12], thiocyanate and ethyl xanthate [13] onto high specific area carbon cloth. The effect of ionization on adsorption of organic compounds having ionizable functional groups is important. This aspect has been studied by Haghseresht et al. [14] on the adsorption of some aromatic acids and phenolic compounds onto activated carbon and by Ayranci and Conway [15] on adsorption and electrosorption of phenol, phenoxide and chlorophenols at high area carbon felt electrodes.

The purpose of the present study is to investigate the adsorption behaviors of structurally related phenolic compounds: phenol, hydroquinone, *m*-cresol, *p*-cresol and *p*-nitrophenol from aqueous solutions, onto high area activated carbon cloth. Examination of ionization effect on adsorption and determination of adsorption isotherms were also aimed. Although there are a number of studies in literature on the adsorption of phenol onto various carbon materials including carbon cloth as mentioned above, this compound was also included in this study to complete the systematically chosen series of compounds. Other four compounds are derivatives of phenol with different substituents at different positions of the aromatic ring.

2. Materials and methods

2.1. Materials

The activated carbon cloth (ACC) used in the present work was obtained from Spectra Corp. (MA, USA) coded as Spectracarb 2225, having a specific area of $2500 \text{ m}^2 \text{ g}^{-1}$ determined by the manufacturer by means of Kr-desorption BET procedure. The phenolic compounds: phenol, hydroquinone, *m*-cresol, *p*-cresol and *p*-nitrophenol were obtained from Merck. NaOH, H_2SO_4 , HNO_3 and NaNO_3 were reagent grade. Deionized water was used in adsorption experiments.

2.2. Treatment of carbon cloth

The activated carbon fibers are known to provide spontaneously a small but significant quantity of ions into the conductivity water probably due to its complex structure originating from its somewhat unknown proprietary preparation procedure [12,16]. Therefore, a deionization cleaning procedure was applied to avoid desorption of ions during adsorption studies. This cleaning procedure was described in detailed in our previous reports [9,12]. In this procedure, carbon cloth was washed with lots of warm conductivity water in many successive batch kind operations, until the

out coming washing water has the same conductivity with the deionized conductivity water. The N_2 gas was bubbled through the washing cup to avoid possible CO_2 adsorption. The washed carbon cloth modules were then dried under vacuum at 120°C and kept in a vacuum desiccator for further use.

The specific surface area of the treated carbon cloth was measured as $1464 \text{ m}^2 \text{ g}^{-1}$ by N_2 adsorption isotherm method (this measurement was done by Turkish Scientific and Technical Research Center). Although the methods of measurement of BET surface area of the original and treated carbon cloth samples are different (original is by Kr-desorption, treated is by N_2 adsorption), obviously there is a decrease in specific surface area upon the above treatment. A similar decrease was observed in surface area of granular activated carbon upon aqueous treatment by László et al. [4]. SEM pictures of pretreated (washed) carbon cloth were previously given [13]. The average fiber diameter was measured as $17 \mu\text{m}$ from these SEM pictures.

2.3. Procedure for the determination of pH_{PZC} of carbon cloth

The carbon surface charge is mainly determined by the pH of the adsorbate solution. It is known that [17] the net charge on carbon surface is positive at a solution pH lower than that corresponding to the point of zero charge (pH_{PZC}) of the surface and is negative at a solution pH higher than pH_{PZC} . Therefore, it is very important to determine the pH_{PZC} for the carbon material.

Batch equilibrium method, described by Babić et al. [18], was applied for the determination of pH_{PZC} of the activated carbon cloth used in the present study. The carbon cloth samples of $100 \pm 0.1 \text{ mg}$ were shaken in erlenmeyer flasks for 24 h with 40 mL solutions of 0.1, 0.05 or 0.01 M NaNO_3 at different initial pH values, which were adjusted by adding NaOH or HNO_3 solutions. At the end of 24 h contact period, the amount of H^+ or OH^- ions adsorbed by the carbon cloth was calculated from the difference between the initial and the final concentrations of H^+ or OH^- ions, determined from the initial and the final pH values (pH_i and pH_f , respectively) measured with a Jenway 3040 ion analyzer using glass electrode. pH_f readings for the determination of pH_{PZC} were plotted as a function of pH_i in Fig. 1. It is seen that data points obtained at different concentrations of NaNO_3 fit into one common curve. This shows that pH_{PZC} is independent of ionic strength. Similar conclusion was arrived by Babić et al. [18] after making measurements at 0.1 and 0.01 M NaNO_3 solutions for their carbon cloth. The pH_f value of the plateau observed in Fig. 1 corresponds to the pH at which there is no net OH^- or H^+ adsorption [18]. At this pH, the difference between the initial and the final $[\text{H}^+]$ or $[\text{OH}^-]$ is zero. This pH was determined to be 7.4 and taken as the pH_{PZC} of the carbon cloth used.

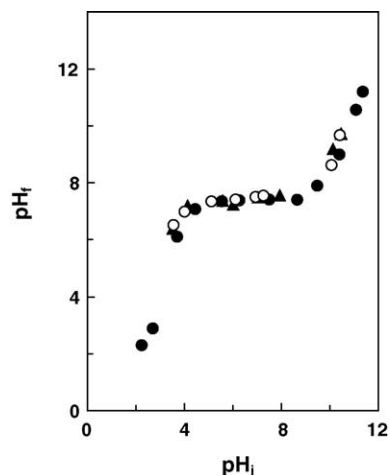


Fig. 1. Plot of pH_f vs. pH_i for the determination of pH_{PZC} of the carbon cloth: (○) in 0.01 M NaNO_3 ; (▲) in 0.05 M NaNO_3 ; and (●) in 0.1 M NaNO_3 .

2.4. The adsorption cell and optical absorbance measurements

A specially designed cell was used to carry out the adsorption and simultaneously to perform in situ concentration measurements by means of UV absorption spectrophotometry. It was described in detail in our earlier reports [9,10,13].

Solutions of phenolic compounds were prepared in water, in 1 M H_2SO_4 or in 0.1 M NaOH. The initial concentrations of phenolic compounds and the amount of carbon cloth were kept as constant as possible for kinetic studies of adsorption in order to make an easy comparison; concentration: 1×10^{-4} M, mass of carbon cloth: 15 mg. The carbon cloth pieces were pre-wetted by leaving in water for 24 h before dipping into the actual adsorbate solution. The idea of using pre-wetted carbon cloth originates from our previous findings that pre-wetting enhances the adsorption process by increasing the rate [12,13]. This effect can be attributed to possible changes in internal structure of the carbon cloth during pre-wetting. For example, pores may expand and surfaces may become more accessible or active toward adsorption during long contact with water.

The procedure for the optical absorbance measurement was as described earlier [9,10,13]. Absorbance data was recorded in programmed time intervals of 1 min over a period of 90 min while the adsorption process is taking place. Absorbance data were converted into concentration data using calibration relations pre-determined at the wavelength of maximum absorbance for each phenolic species: neutral or anionic.

2.5. Determination of adsorption isotherms

The adsorption isotherms of phenolic compounds on the carbon cloth were determined on the basis of batch analysis. Carbon cloth pieces of varying masses were allowed to equilibrate with solutions of phenolic compounds at acidic, basic or

natural pH with known initial concentrations at 30 °C for 48 h. Preliminary tests showed that the concentration of phenolic compounds remained unchanged after 8–10 h contact with the carbon cloth. So, the allowed contact time of 48 h ensures the equilibration. The equilibration was allowed in 100 mL erlenmeyer flasks kept in Nüve ST 402 shaking waterbath at a constant shaking speed of 150 rpm. The concentrations after the equilibration period were measured spectrophotometrically. The amount of phenolic compound adsorbed per unit mass of carbon cloth, q_e , was calculated by Eq. (1)

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where V is the volume of the solution of phenolic compound in L, C_0 and C_e are the initial and equilibrium concentrations, respectively, in mmol L^{-1} and m is the mass of carbon cloth in g. Then Eq. (1) gives q_e in $\text{mmol adsorbate adsorbed per g carbon cloth}$.

3. Results and discussion

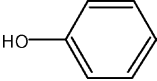
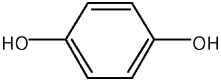
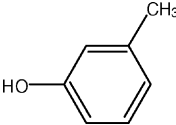
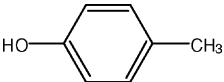
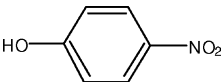
3.1. Absorption characteristics and calibration data of the phenolic compounds

Phenolic compounds in aqueous solutions can become hydrolyzed to phenolate ions depending on the pH of the solution. Conversion of phenol to phenolate anion makes an additional pair of nonbonding electrons available to the conjugated system so that both the band intensities and their wavelengths are increased, as reported in the literature [19].

At the concentrations studied (on the order of 10^{-4} M or higher) the hydrolysis of phenol is negligible in water solutions considering its acid dissociation constant (Table 1). The same is true for hydroquinone, *m*-cresol, *p*-cresol and *p*-nitrophenol as their acidic dissociation constants are also small (Table 1). The major species in water and in acid (in 1 M H_2SO_4) solutions of all phenolic compounds is, therefore, the neutral molecule with negligible amount of hydrolysis product. On the other hand, calculations show that in 0.1 M NaOH the phenolic compounds dissociate almost completely into anionic forms leaving negligible amount of neutral molecules.

All the spectral and calibration data for the species studied are given in Table 1 together with their respective regression coefficients. The data are for neutral molecules when the solvent is water or 1 M H_2SO_4 and for anionic dissociation product when the solvent is 0.1 M NaOH. There are two absorption bands having significantly different λ_{max} (wavelength of maximum absorption) values. Although the calibration data were derived at both λ_{max} values for each compound, only one of them was utilized in the actual adsorption experiment depending on the intensities of absorption bands. When the intensity at one λ_{max} value is too strong (>1.5 absorbance unit) deviation from Lambert–Beer law occurs or when it is too weak the sensitivity of absorbance

Table 1
Spectral and calibration data for phenolic compounds

Phenolic compound	Molecular structure	Solvent	λ_{\max} (nm)	ϵ ($M^{-1} \text{ cm}^{-1}$)	K_a [20,21]
Phenol		H ₂ O	211	5500	1.0×10^{-10}
		H ₂ O	270	1450	
		1 M H ₂ SO ₄	211	5450	
		1 M H ₂ SO ₄	270	1450	
		0.1 M NaOH	235	8750	
		0.1 M NaOH	287	2500	
Hydroquinone		H ₂ O	222	4800	4.5×10^{-11}
		H ₂ O	290	2450	
		1 M H ₂ SO ₄	222	4850	
		1 M H ₂ SO ₄	289	2470	
<i>m</i> -Cresol		H ₂ O	272	1580	8.1×10^{-11}
		1 M H ₂ SO ₄	272	1610	
		0.1 M NaOH	238	9750	
		0.1 M NaOH	289	3000	
<i>p</i> -Cresol		H ₂ O	220	7250	5.5×10^{-11}
		H ₂ O	277	2100	
		1 M H ₂ SO ₄	220	7290	
		1 M H ₂ SO ₄	277	2100	
		0.1 M NaOH	237	10900	
		0.1 M NaOH	296	3200	
<i>p</i> -Nitrophenol		H ₂ O	227	6500	7.0×10^{-8}
		H ₂ O	317	9330	
		1 M H ₂ SO ₄	227	6400	
		1 M H ₂ SO ₄	318	9450	
		0.1 M NaOH	230	5400	
		0.1 M NaOH	399	17400	

measurement becomes too low. In such cases absorbance measurements were made at the other λ_{\max} value and the corresponding calibration data in Table 1 was utilized.

One further point to note is that hydroquinone may oxidize to 1,4-benzoquinone. Its stability depends on the pH of the solution. Oxidation occurs slowly in neutral, very slowly in acidic but very rapidly even in slightly alkaline solutions. Therefore, the solutions of hydroquinone in neutral or acidic solutions were freshly prepared prior to experiments for calibration or for adsorption. However, it could not be studied at all in alkaline solution due its rapid oxidation.

3.2. Adsorption behaviors of phenolic compounds over 90 min

A typical concentration versus time plot for the adsorption of *m*-cresol from solutions in water, in 1 M H₂SO₄ and in 0.1 M NaOH onto activated carbon cloth is shown in Fig. 2.

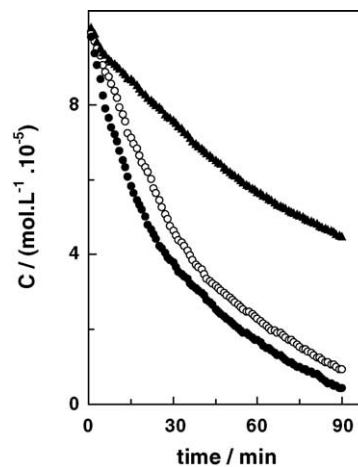


Fig. 2. Adsorption behavior of *m*-cresol: (●) in water; (○) in 1 M H₂SO₄; and (▲) in 0.1 M NaOH solutions.

Similar adsorption behaviors and plots (not shown) were observed for the other adsorbates studied. The first striking feature that all these figures reveal is that the extents of adsorption are the highest from water solutions and the lowest from basic solutions. The extents of adsorption from acidic solutions are slightly lower than those from water solutions. In water and in acid solutions all the phenolic species are in neutral form (with negligible dissociation in water). On the other hand net charge on the surface of carbon cloth is close to zero in water solution and positive in acidic solution since the pH_{pZC} was found to be 7.4. So, interactions between the phenolic species and the carbon cloth in water or in acid solutions are expected to be mainly due to dispersion forces with small contribution of electrostatic forces in acid solution. In basic solutions all the phenolic species dissociate into anionic forms and the net charge on the surface of carbon cloth is negative. So, electrostatic repulsions play an important role in interactions between the surface and the phenolic species. This explains the lower extents of adsorption observed in basic solutions than in water or in acid solutions.

Adsorption data of the phenolic compounds over a 90 min period were treated according to the first-order kinetics by plotting $\ln[C_0/C_t]$ as a function of time, t , according to the following equation:

$$\ln \left[\frac{C_0}{C_t} \right] = kt \quad (2)$$

and applying linear regression analysis. Here C_0 and C_t are the initial concentration and the concentration at any time of the phenolic compound and k is the first-order rate constant. The slopes of the lines provided the first-order rate constants for the adsorption processes and are given in Table 2 together with the regression coefficients. Closeness of regression coefficients to one supports the assumption of first-order kinetics for the adsorption processes. It is clearly seen that the highest adsorption rate constants are obtained in water solutions and the lowest ones in 0.1 M NaOH solutions. Adsorption rate constants decrease three to five times in going from water to 0.1 M NaOH solutions. The order of rate constants for the five phenolic species in H₂O and in 1 M H₂SO₄ solutions is: p -nitrophenol \sim m -cresol $>$ p -cresol $>$ hydroquinone \sim phenol. The rate constants are too small and close to each other in 0.1 M NaOH solution to make any comparison and thus to give an order.

Another quantitative comparison for the adsorption of phenolic compounds onto the carbon cloth can be made on the basis of the amount of adsorbate adsorbed per unit mass of carbon cloth, M , at the end of 90 min adsorption calculated by the following equation:

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

where C_0 and C_t are the concentrations of the solutions at the beginning and at 90 min of adsorption, respectively. V is the volume of the solution and m the mass of carbon cloth module. The calculated M values are given in the last column of

Table 2

First-order rate constants, regression coefficients, M and θ values at 90 min for the adsorption of phenolic compounds

Phenolic compound	Solvent	k^a	r^b	M^c
Phenol	H ₂ O	0.0204	0.9978	1.13
	1 M H ₂ SO ₄	0.0177	0.9960	1.11
	0.1 M NaOH	0.0044	0.9938	0.43
Hydroquinone	H ₂ O	0.0219	0.9957	1.14
	1 M H ₂ SO ₄	0.0167	0.9910	1.04
	0.1 M NaOH ^d	–	–	–
m -Cresol	H ₂ O	0.0319	0.9936	1.32
	1 M H ₂ SO ₄	0.0253	0.9983	1.22
	0.1 M NaOH	0.0096	0.9996	0.76
p -Cresol	H ₂ O	0.0259	0.9966	1.22
	1 M H ₂ SO ₄	0.0236	0.9999	1.20
	0.1 M NaOH	0.0085	0.9966	0.70
p -Nitrophenol	H ₂ O	0.0323	0.9885	1.28
	1 M H ₂ SO ₄	0.0265	0.9959	1.26
	0.1 M NaOH	0.0099	0.9849	0.76

^a First-order rate constant in min⁻¹.

^b Regression coefficient for linear regression analysis.

^c The amount of adsorbate adsorbed over a period of 90 min per unit mass of carbon cloth in units of [10⁻⁴ mol (g C-cloth)⁻¹].

^d Hydroquinone oxidizes in basic solutions.

Table 2. Examination of these values shows that the amounts of adsorption at the end of 90 min for the five phenolic species follow the same order observed for the rate constants given above. The pore size distribution of the carbon cloth used in the present work [22] indicated an average pore radius of approximately 2.3 \pm 0.3 nm and an overall pore volume of 1.2 mL g⁻¹. The adsorbates studied in this work have average molecular radii of 0.29–0.41 nm [23–25]. They seem to fit well to the pores of the carbon cloth whether they are adsorbed parallel or perpendicular conformation on the surface.

The order of rate constants or the extents of adsorption observed for the species studied can be explained on the basis of structural effects. The π electrons are expected to delocalize over the whole molecule including the substituents in the case of p -nitrophenol. Therefore, dispersion forces between the carbon cloth surface and the phenolic compound are expected to be the strongest for p -nitrophenol. Thus, the highest rate constant and extent of adsorption are observed with this compound. The decrease in the strength of dispersion forces due to lowering of π electron delocalization resulting from the absence of –NO₂ group in m -cresol compared to p -nitrophenol is partly compensated by the hydrophobic interactions due to the presence of hydrophobic methyl substituent. Therefore, the rate constant and the extent of adsorption of m -cresol are observed to be almost the same as those of p -nitrophenol. The methyl group in m -position to –OH does not have much effect in π electron delocalization over the ring but in p -position (as in p -cresol) have negative effect in delocalization. Thus lower rate constant and extent of adsorption are observed in the case of p -cresol compared to m -cresol. The absence of hydrophobic methyl substituent in hydroquinone and phenol cause their rate constants and extents of adsorption to be even

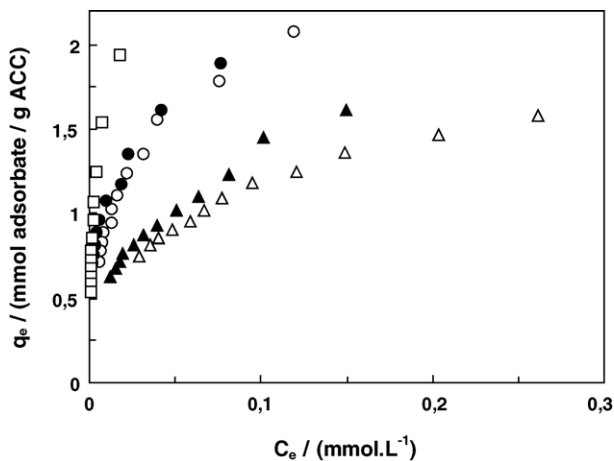


Fig. 3. Adsorption isotherms at 30°C for phenolic compounds in water: (Δ) phenol; (\blacktriangle) hydroquinone; (\circ) *m*-cresol; (\bullet) *p*-cresol; and (\square) *p*-nitrophenol.

lower than *p*-cresol. The order of adsorption rate constants observed in this study is in agreement with the order reported by Baudu et al. [26] for the adsorption of *p*-nitrophenol, *m*-cresol and phenol onto activated carbon in granular or powder form, with the order reported by Juang et al. [27] for the adsorption of *p*-nitrophenol and phenol onto activated carbon fibers.

3.3. Adsorption isotherms

Adsorption isotherms at 30°C, derived for the phenolic compounds in water, in 1 M H₂SO₄ and in 0.1 M NaOH are shown in Figs. 3–5, respectively. The isotherm data were treated according to three well known isotherm equations: Langmuir, Freundlich and Tempkin.

The linearized forms of Langmuir, Freundlich and Tempkin isotherm equations can be given in Eqs. (4)–(6),

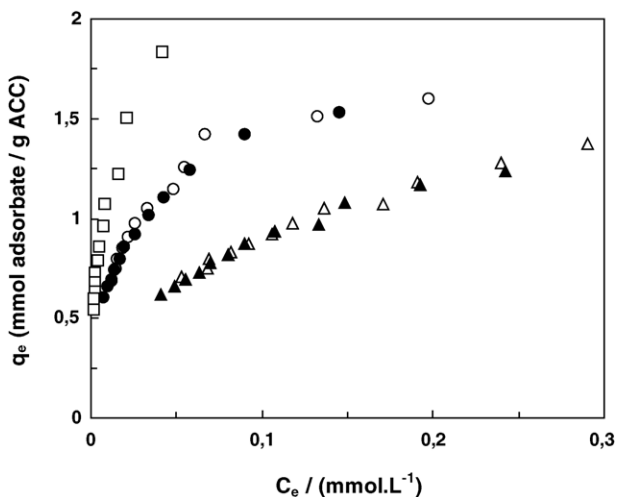


Fig. 4. Adsorption isotherms at 30°C for phenolic compounds in 1M H₂SO₄: (Δ) phenol; (\blacktriangle) hydroquinone; (\circ) *m*-cresol; (\bullet) *p*-cresol; and (\square) *p*-nitrophenol.

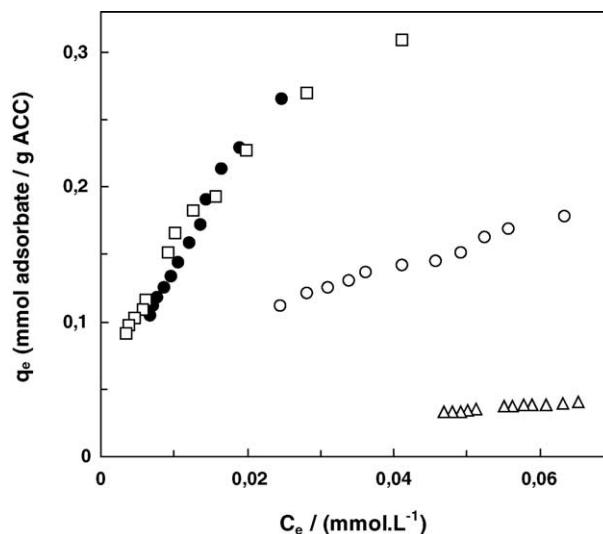


Fig. 5. Adsorption isotherms at 30°C for phenolic compounds in 0.1 M NaOH: (Δ) phenol; (\circ) *m*-cresol; (\bullet) *p*-cresol; and (\square) *p*-nitrophenol.

respectively [28–30];

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{bq_{\max}} \quad (4)$$

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (5)$$

$$q_e = k_1 \ln k_2 + k_1 \ln C_e \quad (6)$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium in mmol g^{-1} ; C_e the final concentration at equilibrium in mmol L^{-1} ; q_{\max} the maximum adsorption at monolayer coverage in mmol g^{-1} ; b the adsorption equilibrium constant related to the energy of adsorption in L mmol^{-1} ; K_F a Freundlich constant representing the adsorption capacity in $(\text{mmol g}^{-1})(\text{L mmol}^{-1})^{1/n}$; n a constant depicting the adsorption intensity; k_1 the Tempkin isotherm energy constant in L mmol^{-1} and k_2 the Tempkin isotherm constant. The main difference between these three isotherm models is in the variation of heat of adsorption with the surface coverage. Langmuir model assumes uniformity, Freundlich model assumes logarithmic decrease and Tempkin model assumes linear decrease in heat of adsorption with surface coverage.

The experimental isotherm data were fitted to these equations (Eqs. (4)–(6)) by applying linear regression analysis. The parameters of the equations are given in Table 3. One way to assess the goodness of fit of experimental isotherm data to these equations is to check the regression coefficients obtained during the regression analysis. However, the regression coefficients or their squares (both are not given) were very close to each other and they were mostly >0.98 . Thus, it was very difficult to decide which model represents the experimental data best on the basis of regression coefficient. This result is not surprising on the basis of just regression coefficients. For example, the regression coefficients for

Table 3

Parameters of Langmuir, Freundlich and Tempkin adsorption isotherm equations, normalized percent deviations (P) and R_L values for phenolic compounds at 30 °C

Phenolic compound	Solvent	Langmuir parameters			Freundlich parameters			Tempkin parameters			
		q_{\max} (mmol g ⁻¹)	b (L mmol ⁻¹)	P	K_F (mmol g ⁻¹) (L mmol ⁻¹) ^{1/n}	$1/n$	P	k_1 (L mmol ⁻¹)	k_2	P	R_L
Phenol	H ₂ O	1.84	20.0	3.41	2.56	0.342	1.25	0.382	229	1.53	0.083
	1 M H ₂ SO ₄	1.76	10.9	2.51	2.25	0.398	1.43	0.397	101	2.31	0.144
	0.1 M NaOH	0.100	10.4	0.812	0.232	0.638	0.720	0.0232	87.8	0.690	0.586
Hydroquinone	H ₂ O	1.86	30.7	8.62	3.19	0.371	2.35	0.378	362	5.83	0.068
	1 M H ₂ SO ₄	1.59	13.9	2.37	2.26	0.404	1.54	0.361	125	1.76	
<i>m</i> -Cresol	H ₂ O	2.26	64.2	7.85	4.47	0.344	3.15	0.433	860	3.41	0.030
	1 M H ₂ SO ₄	1.75	50.0	2.86	2.91	0.308	4.42	0.340	680	2.35	0.039
	0.1 M NaOH	0.299	23.0	2.28	0.679	0.487	1.52	0.0719	184	2.19	0.311
<i>p</i> -Cresol	H ₂ O	1.92	186	20.6	3.46	0.250	3.02	0.274	7100	7.33	0.012
	1 M H ₂ SO ₄	1.70	53.3	5.94	3.08	0.330	1.92	0.329	721	2.64	0.042
	0.1 M NaOH	0.648	28.3	2.92	4.05	0.728	2.49	0.123	331	4.84	0.323
<i>p</i> -Nitrophenol	H ₂ O	2.10	530	13.2	8.44	0.353	2.38	0.372	7790	7.08	0.005
	1 M H ₂ SO ₄	1.99	173	11.0	5.89	0.363	2.79	0.375	2340	5.58	0.015
	0.1 M NaOH	0.405	69.6	5.83	1.66	0.514	3.23	0.0880	684	7.18	0.188

fitting adsorption data of aqueous aromatic pollutants on various granular activated carbon samples to both Langmuir and Freundlich equations were also found to be mostly >0.98 by Yenkie and Natarajan [31]. A similar result can be seen in the work of Leboda et al. [32]. A better criterion to test the goodness of fit of isotherm data to Langmuir, Freundlich and Tempkin equations is a parameter known as normalized percent deviation [27] or in some literature percent relative deviation modulus, P , [33,34] given by the following equation:

$$P = \left(\frac{100}{N} \right) \sum \left(\frac{|q_{e(\text{exp})} - q_{e(\text{pred})}|}{q_{e(\text{exp})}} \right) \quad (7)$$

where $q_{e(\text{expt})}$ is the experimental q_e at any C_e , $q_{e(\text{pred})}$ is the corresponding predicted q_e according to the equation under study with best fitted parameters, N is the number of observations. It is clear that the lower the percent deviations (P)-value, the better is the fit. The P -values calculated for the fit of isotherm data of the five phenolic species to the three isotherm equations are given in Table 3. It is generally accepted that when the P -value is less than 5, the fit is considered to be excellent [33]. Here, all the P -values for Freundlich model are well below 5 and they are mostly the lowest of the three models. It should be recognized that the goodness of fit of isotherm data to Langmuir, Freundlich and Tempkin equations depends on the range of equilibrium concentration studied.

The parameters of the isotherm equations given in Table 3 are difficult to compare with the literature values because the isotherm data are collected under different conditions; pH, temperature, type of adsorbent and the form of adsorbate species. The most important parameter to compare is probably the Langmuir q_{\max} value since it is a measure of adsorption capacity of the adsorbent. Juang et al. [27] reported q_{\max} values as 1.65 and 1.89 mmol g⁻¹ for the adsorption of phenol and *p*-nitrophenol, respectively, onto activated car-

bon fibers at 30 °C. Haghseresht et al. [14] reported q_{\max} values as, approximately, 1.6 mmol g⁻¹ for the adsorption of *p*-cresol at pH values of 7 and 2, at 28 °C onto a commercial activated carbon. Yenkie and Natarajan [31] reported q_{\max} values varying from 1.19 to 1.94 mmol g⁻¹ for the adsorption of phenol onto six different granular activated carbon at 35 °C. The comparison of these literature values with the values we reported in Table 3 shows that the carbon cloth used in our work has adsorption capacities higher than or comparable to those carbon materials used in other works.

The efficiency of adsorption process can be predicted by the dimensionless equilibrium parameter R_L , which is defined by the following equation [35,36]:

$$R_L = \frac{1}{1 + bC_0} \quad (8)$$

where b is the Langmuir constant (L mmol⁻¹), C_0 the initial concentration of phenolic compounds (mmol L⁻¹). Isotherm is considered to be unfavorable when $R_L > 1$, linear when $R_L = 1$, favorable when $0 < R_L < 1$ or irreversible when $R_L = 0$. The R_L values calculated for the adsorption of phenolic species studied are given in the last column of Table 3. Since all the R_L values are between 0 and 1, the adsorption processes in all cases are favorable.

4. Conclusions

Adsorption of phenol, hydroquinone, *m*-cresol, *p*-cresol and *p*-nitrophenol from aqueous solutions was found to be fastest at the natural pH of solutions of these phenolic compounds. The first-order rate law was observed to be valid for the kinetics of adsorption processes. The decreasing order of rate constants for the adsorption of phenolic compounds studied was determined as *p*-nitrophenol \sim *m*-cresol $>$ *p*-

cresol > hydroquinone ~ phenol. The extent and rate of adsorption were found to be dependent on the charge of carbon cloth surface determined by pH_{PZC} and on the form of phenolic species; ionic or molecular, determined by the pH of the solution. The adsorption isotherms derived at 30 °C were found to be well-represented by Freundlich model. The substituents on phenolic ring were found to present positive or negative effects on both the adsorption rate and the extent of adsorption depending on their hydrophobicity and contribution to the π electron delocalization over the ring.

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