Removal of Phenol and *o*-Cresol by Adsorption onto Activated Carbon

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Abstract: A commercial activated carbon was utilized for the adsorptive removal of phenol and *o*-cresol from dilute aqueous solutions. Batch mode adsorption studies were performed by varying parameters such as concentration of phenol solution, time, pH and temperature. The well known Freundlich, Langmuir and Redlich-Peterson isotherm equations were applied for the equilibrium adsorption data and the various isotherm parameters were evaluated. The Langmuir monolayer adsorption capacities were found to be 0.7877 and 0.5936 mmole/g, respectively, for phenol and *o*-cresol. Kinetic studies performed indicate that the sorption processes can be better represented by the pseudo-second order kinetics. The processes were found to be endothermic and the thermodynamic parameters were evaluated. Desorption studies performed indicate that the sorbed phenol molecules can be desorbed with dil. HCl.

Keywords: Adsorption, Activated carbon, Phenol, *o*-Cresol, Adsorption kinetics, Isotherm

Introduction

Phenols and their derivatives are invariably present in the effluents from industries engaged in the manufacture of a variety of chemicals such as plastics, dyes, and in plants used for thermal processing of coal. Many of these phenols are carcinogens even when present in low concentrations. The presence of phenols in water also produces foul smelling chlorophenols during chlorination treatment of water for domestic supply.

Exposures to phenol can occur in workplace, from environmental media, from contaminated drinking water or foodstuff or from use of consumer products containing phenol¹. All routes readily absorb phenol: oral, inhalation, and dermal². Phenol is a strong eye and respiratory irritant. It is corrosive to the eyes and skin upon direct contact. Human deaths have occurred following internal ingestion of large areas of skin (>25% of total)¹. The minimum reported lethal dose in humans³ was 4.8g or approximately 70mg/Kg.

The worldwide production of *o*-cresol is approximately 37000-38000 tones/annum. It is mainly used as an intermediate for the production of pesticides, herbicides, rubber and plastics, antioxidants, deodourizing and fragrances, epoxy resins, dyes, and pharmaceuticals and also as a component of disinfectants and cleaning agents. *o*-Cresol is toxic to fish, aquatic plants, microorganisms, soil dwelling organisms, terrestrial plants and also to humans.

The Indian Standard specifications⁴ for drinking water has set the maximum allowable limit of 0.001 ppm for phenols. It is therefore necessary to reduce or eliminate phenols from water and wastewater. Though bioaccumulation and biosorption are mainly preferred for this task as the phenols are easily biodegradable, adsorption onto activated carbon is also effective. Many works have been reported in the adsorptive removal of phenolics from aqueous solutions⁵⁻¹¹. The removal efficiency of a commercial activated carbon (M/s. Loba Company, Mumbai) towards phenol and *o*-cresol was attempted in the present study. The effects of adsorbate dose, pH, time and temperature were studied.

Experimental

Adsorbent

The granular activated carbon supplied by M/s. Loba Company, Mumbai was used in this study. The carbon was ground and the portion retained between 150 and 250 μ m sieves was used for study. The adsorbent was named as CC. The characteristics of the carbon were reported elsewhere¹².

Analysis of phenol and o-cresol

Both phenol and *o*-cresol were analyzed spectrophotometrically by monitoring their absorption at 270 nm.

Equilibrium adsorption experiments

All the equilibrium adsorption experiments comprised three replicate 100mL glass-stoppered bottles containing selected amount of adsorbent and 50mL of adsorbate solutions of selected concentrations. Control flasks without the adsorbents are also prepared simultaneously. Mixtures were maintained in a rotary shaker (Orbitek, Chennai, India) at constant temperature (30, 45 or 60°C). After the attainment of equilibrium the contents of each flask were filtered through Whatmann No.41 filter paper, with the first 10mL discarded. The filtered samples were then analyzed for unadsorbed phenols.

pH variation studies

In order to find out the optimum pH for maximum removal of phenols, experiments were carried out with solutions of same phenol concentration but adjusted to different initial pH values (with HNO₃ or NaOH).

Desorption Studies

After equilibrium adsorption, the phenols loaded carbons were separated and washed gently with several portions of distilled water to remove any unadsorbed species. The samples were then air-dried and agitated with 0.1M solutions of HCl, AcOH or water for a period of 10 hours and the amounts of desorbed species were determined in the usual way.

Results and Discussion

Equilibrium studies

The isotherm plots obtained for the adsorption of phenol and *o*-cresol are shown in Figure 1. The isotherms were of L2 type under Giles¹³ classification.

Figure 1. Isotherm plots for adsorption of phenol and *o*-cresol on activated carbon

The equilibrium adsorption data obtained were then fitted to Freundlich, Langmuir and Redlich-Peterson isotherm¹⁴ equations:

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

$$\text{Langmuir} \quad q_e = K_L C_e / (1 + b C_e) = q_m b C_e / (1 + b C_e)$$

$$\text{Redlich-Peterson} \quad q_e = K_R C_e / (1 + b_R C_e^\beta)$$

Where q_e is the adsorption capacity in mg/g; C_e is the equilibrium concentration of adsorbate (mg/L); K_F and n are Freundlich constants; K_L and b are Langmuir constants; q_m is the Langmuir monolayer adsorption capacity and K_R , b_R and β are Redlich-Peterson isotherm constants. The equilibrium data obtained were fitted to the above three isotherm equations separately and the parameters evaluated are presented in Table 1 along with the correlation coefficient values for each fit.

Table 1. Isotherm parameters for the adsorption of phenols on CC at 30°C

Adsorbate	Model	Model parameters				
		K_F		$1/n$	n	r^2
		mmol/g	mg/g			
Phenol	Freundlich	0.8201	14.2430	0.3719	2.6889	0.9594
<i>o</i> -Cresol		0.5733	8.9307	0.4137	2.4172	0.9991
Adsorbate	Model	Model parameters				
		K_L	b	q_m		r^2
Phenol	Langmuir	7.7014	9.7773	0.7877		0.9965
<i>o</i> -Cresol		3.6658	6.1756	0.5936		0.9852
Adsorbate	Model	Model parameters				
		K_R	b_R	β		r^2
Phenol	Redlich-Peterson	6.8139	8.8798	1.0858		0.9976
<i>o</i> -Cresol		17.8209	30.6469	0.6472		0.9999

It is evident from Table 1 that of the three isotherm models used it is the three-parameter Redlich-Peterson model that fits the experimental data with best correlation coefficient values. This is expected as the Redlich-Peterson equation has three fitting parameters, especially with β being a more direct parameter for adsorbate-adsorbent interaction strength.

The Langmuir monolayer capacity, K_L was higher for phenol than *o*-cresol. A possible explanation can be given by invoking a 'bottle-neck' model for the pores present on the adsorbents' surface. According to this model, the pores resemble bottles in that they have very small openings like bottlenecks. After an appropriate monolayer outer surface coverage, there will be a certain population of phenol molecules at the pore entrance and as there are no substituents on the benzene ring of phenol, the pore entrance is relatively free for the movement of other unadsorbed phenol molecules into the pores. Therefore, more and more of phenol molecules can diffuse and subsequently be adsorbed in pores. But the situation for the adsorption of *o*-cresol is somewhat different in that the methyl groups of adsorbed *o*-cresol molecules may block the pore openings. Transport of unadsorbed cresol molecules from solution into the pores, therefore, is hindered which leads to lesser filling of pores. The overall amount of adsorbed cresol is thus less than that of phenol.

The Langmuir b values determined are further used to calculate the dimensionless separation factor, R_L ^{15, 16}, defined as

$$R_L = 1/(1 + bC_i)$$

where C_i is the initial solute concentration. The R_L values calculated are listed in Table 2.

Table 2. R_L values for the adsorption of phenols on CC at 30°C

Adsorbate	C_i mg/L	R_L value
Phenol	25	0.0041
	50	0.0020
	100	0.0010
	150	0.0007
	200	0.0005
<i>o</i> -Cresol	25	0.0064
	50	0.0032
	100	0.0016
	150	0.0011
	200	0.0008

The magnitude of R_L value gives an idea about the nature of adsorption equilibrium: the process is non-spontaneous when R_L is greater than one; favorable when R_L lies between 0 and 1; and irreversible when R_L is zero. In all the systems studied, R_L values were comprised between 0 and 1 indicating favorable on the activated carbon.

Effect of pH

The effect of pH of solution on the adsorption percentage of phenol and *o*-cresol is shown in Figure 2. There is no significant change in the amount of adsorption with respect to change in the solution pH. But the very slight decrease in the adsorption extent is noted with respect to increase in solution pH. This could be due to the increased solubility of phenol molecules at alkaline conditions, which results in greater affinity for the phenol molecules to remain in solution rather than to get adsorbed onto the carbon surface.

Figure 2. Effect of pH on the adsorption of phenols on CC

Adsorption kinetics

The kinetic behavior as shown in Figure 3 is fitted to the following three rate equations reported in the literature, namely, first order model¹⁷, pseudo-second order model¹⁸⁻²⁰ and the Elovic model²¹⁻²².

$$\text{First order rate equation} \quad \log(q_{e(1)} - q_t) = \log q_{e(1)} - k_1 t$$

$$\text{Second order rate equation} \quad t/q_t = (1/h) + (1/q_{e(2)})t$$

$$\text{Elovic equation} \quad q_e = (1/\beta_E) \ln(\alpha\beta_E) + (1/\beta_E) \ln t$$

where, q_t = amount adsorbed at time t , mg/g

q_e = amount adsorbed at equilibrium, mg/g

$q_{e(1)}$ = adsorption capacity predicted by the I order model, mg/g

k_1 = first order rate constant (min^{-1})

k_2 = second order rate constant ($\text{gmg}^{-1}\text{min}^{-1}$) = $h/q_{e(2)}^2$

$q_{e(2)}$ = adsorption capacity predicted by the II order model, mg/g

α (Elovic model) = h (II order model) = initial sorption rate ($\text{mgg}^{-1}\text{min}^{-1}$)

β = desorption constant (gmg^{-1})

t = contact time, min

The parameters evaluated for the three rate models were shown in Tables 3, 4 and 5. It is observed that both the first order and the Elovic model are quite inefficient than the pseudo-second order rate equation (inferred from the r^2 values) in predicting correctly the sorption dynamics. It is to be noted that the q_e values predicted by the second order model agree very closely to the experimental values.

Table 3. First order parameters for the adsorption of phenols on CC

Adsorbate	Equilibrium uptake		k_l min ⁻¹	r ²
	mg/g			
	$q_{e(1)}$	$q_{e(exp)}$		
Phenol	35.6041	43.8300	0.0048	0.9848
<i>o</i> -Cresol	25.6035	35.9800	0.0074	0.9721

Figure 3. Kinetic curves for adsorption of phenols on CC

Table 4. Pseudo-second order parameters for the adsorption of phenols on CC

Adsorbate	Equilibrium uptake, mg/g		k_2 $\text{gmg}^{-1}\text{min}^{-1}$	h $\text{mgg}^{-1}\text{min}^{-1}$	r^2
	$q_{e(2)}$	$q_{e(exp)}$			
Phenol	46.5116	43.8300	4.88×10^{-4}	1.0337	0.9999
<i>o</i> -Cresol	43.1034	35.9800	7.32×10^{-4}	1.3600	0.9899

Figure 4. Adsorption of phenol on CC: Effect of temperature

Table 5. Elovic parameters for the adsorption of phenols on CC

Adsorbate	α	$\alpha\beta_E$	β_E	r^2
Phenol	0.8654	6.3199	7.3029	0.9936
<i>o</i> -Cresol	0.1192	0.3376	2.8322	0.9866

Effect of temperature

The adsorption of phenols on CC increased with increase in temperature (Figure 4), suggesting that these processes are endothermic. The isotherm parameters for the equilibrium at temperatures of 45 and 60°C are presented in Tables 6 and 7. It can be seen from Tables 6 and 7 that the value of q_m decreases and K_L increases for the adsorption of phenols on CC with increase in adsorption temperature.

Table 6. Isotherm parameters for adsorption of phenols on CC at 45°C

Adsorbate	Model	Model parameters			
		K_F	$1/n$	n	r^2
Phenol	Freundlich	0.9071	0.3662	2.7307	0.9579
<i>o</i> -Cresol		0.7427	0.4161	2.4033	0.9920
Adsorbate	Model	Model parameters			
		K_L	b	q_m	r^2
Phenol	Langmuir	9.9407	12.0777	0.8321	0.9932
<i>o</i> -Cresol		5.6187	8.0904	0.6945	0.9964
Adsorbate	Model	Model parameters			
		K_R	b_R	β	r^2
Phenol	Redlich-Peterson	9.2157	11.4545	1.0499	0.9936
<i>o</i> -Cresol		0.6074	11.8087	0.8112	1.000

Table 7. Isotherm parameters for adsorption of phenols on CC at 60°C

Adsorbate	Model	Model parameters			
		K_F	$1/n$	n	r^2
Phenol	Freundlich	0.9429	0.3344	2.9904	0.9745
<i>o</i> -Cresol		0.9511	0.4025	2.4847	0.9800
Adsorbate	Model	Model parameters			
		K_L	b	q_m	r^2
Phenol	Langmuir	14.8373	18.4473	0.8043	0.9979
<i>o</i> -Cresol		9.3251	11.8616	0.7862	0.9952
Adsorbate	Model	Model parameters			
		K_R	b_R	β	r^2
Phenol	Redlich-Peterson	17.7603	21.1440	0.9256	0.9993
<i>o</i> -Cresol		11.5808	13.8700	0.8945	0.9966

Van't Hoff equation, in the following form, was used to calculate the thermodynamic parameters such as Gibbs's free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS):

$$\log K_C = \left[\frac{\Delta S}{2.303R} \right] - \left[\frac{\Delta H}{2.303RT} \right]$$

Where K_C is the equilibrium constant for the distribution of phenols between the liquid and solid phases; T is absolute temperature, °K and R the gas constant. Van't Hoff plots were constructed for each system and ΔH and ΔS were calculated from the slope and intercept of the plots, respectively (Table 8)

Table 8. Thermodynamic parameters for the adsorption of phenols on CC

Adsorbate	C_i , mg/L	$-\Delta G$, kJ mol ⁻¹			ΔH kJmol ⁻¹	ΔS JK ⁻¹ mol ⁻¹
		30°C	45°C	60°C		
Phenol	25	5.7554	6.3862	8.8305	25.0063	100.6221
	50	5.9992	7.2935	8.6441	20.7088	88.1209
	100	4.9391	5.8894	6.6618	12.4918	57.6195
	150	3.0146	3.7106	4.2484	9.4749	41.3004
	200	1.5384	2.1068	2.5174	8.3764	32.8029
<i>o</i> -Cresol	25	5.8861	6.5299	7.7657	13.0020	62.0444
	50	4.2388	5.6767	7.7481	31.1052	116.3342
	100	2.3741	4.0396	5.5903	30.1346	107.3485
	150	1.3876	2.6637	4.5603	30.5582	105.1236
	200	0.6172	1.6221	2.7803	21.2088	71.9569

Desorption studies

The results with water, 0.1 M acetic acid and 0.1 M hydrochloric acid are presented in Table 9. We are to understand that desorption increases with increase in the acidity of the desorbing medium; desorption is higher in hydrochloric acid than in acetic acid. This does not imply that the phenol molecules are adsorbed by an ion-exchange mechanism, but rather could be due to the increased solubility of the phenol molecules in the acidic media.

Table 9. Desorption of phenols

Adsorbate	% Desorption with		
	Water	AcOH	HCl
Phenol	25.49	55.28	71.25
<i>o</i> -Cresol	24.05	51.29	70.28

Conclusions

The work presented in this work has shown that the commercial activated carbon can be successfully used for the adsorptive removal of phenolic pollutants from water. The three-parameter Redlich-Peterson isotherm equation better represented the equilibrium adsorption data. Kinetic studies point to the fact that the sorption dynamics of phenols are predicted more accurately by the pseudo-second order rate model. pH has no significant role to play in the adsorptions and are found to be endothermic in nature. The thermodynamic parameters were evaluated.

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