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Isotherm, Thermodynamics, Desorption, and Disposal Study for the Adsorption of Catechol and Resorcinol onto Granular Activated Carbon

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ABSTRACT: The present paper reports isotherm, thermodynamic, and disposal studies for the adsorption/desorption of catechol (C) and resorcinol (R) from aqueous solution onto/from granular activated carbon (GAC). Isotherm data were generated for C and R solutions having initial concentrations of C and R in the range of (0.18 to 9.08) $\text{mmol}\cdot\text{L}^{-1}$ for the GAC dosage of 10 $\text{g}\cdot\text{L}^{-1}$ at temperatures of (288, 303, and 318) K. The adsorption of C and R onto GAC was favorably influenced by an increase in temperature. Equilibrium data were well-represented by the Tempkin isotherm model. Values of the change in entropy (ΔS_0), heat of adsorption (ΔH_0), and Gibbs energy (ΔG_0) were determined. The desorption of C and R from GAC was studied by various solvents and a thermal desorption method. NaOH was found to be a better eluant for the desorption of C and R with a maximum desorption efficiency of 10.1 % and 11.4 %, respectively. Thermal desorption at 623 K was found to be better as compared to solvent desorption. GAC worked well for at least five adsorption−desorption cycles, with a continuous decrease in adsorption efficiency after each thermal desorption. Owing to its heating value, spent GAC can be used as a cofuel for the production of heat in boiler furnaces.

1. INTRODUCTION

Phenol and substituted phenols are important organic intermediates for the synthesis of various industrial and agricultural products.[1] For example, hydroxy aromatic compounds, such as catechol (C) and resorcinol (R), are used widely as industrial solvents. C (1,2- dihydroxybenzene) is also widely used to produce food additive agents, hair dyes, and antioxidants.[2] Similarly, R (1,3- dihydroxybenzene) is used to produce dyes, plastics, and synthetic fibers.[3−5] As a result, C and R are extensively present in effluents generated from their manufacturing usage units and hence get introduced into water inevitably. If released into the environment, C and R can accumulate in soil, groundwater, and surface water.[6]

R and C have a higher toxicity than phenol,[7] and C is considered more toxic than R.[8] C and R are irritants for the skin, eyes, and mucous membranes. Acute toxicity of R and C occurs mainly by the oral route; symptoms are nausea, vomiting, diarrhea, pulmonary edema, tachypnea, and depression of the central nervous system. Methemoglobinemia and hepatic injury may be noted within a few days after intoxication by R and C.[7] Phenol and associated compounds have been listed as priority pollutants by the Ministry of Environment and Forests (MoEF), Government of India, and Environmental Protection Agency (EPA), USA. MoEF has prescribed that the concentration of phenols should not exceed 1.0 $\text{mg}\cdot\text{L}^{-1}$ for their discharge into surface waters and 5.0 $\text{mg}\cdot\text{L}^{-1}$ for discharge into the public sewers, on land for irrigation, and marine coastal areas. These limits have generally been defined on the basis of the total phenols present in the effluent.

Conventional methods used for remediation/degradation of C and R are biodegradation[9,10] and anaerobic biodegradation,[11−13] anodic oxidation,[14,15] adsorption,[16] photocatalysis,[17] and oxidative catalysis.[18] The adsorption of phenol and substituted phenols from aqueous solution onto activated carbons has been intensively investigated.[16,19−34] Adsorption equilibria information is one the most important pieces of information in understanding an adsorption process. No matter how many components are present in the system, the adsorption equilibria of pure components are the essential ingredients for the understanding of how many components can be accommodated by a solid adsorbent.

Few authors have previously conducted adsorption studies for the removal of C and R onto activated adsorbents.[16,28,31−34] Table 1 shows a comparative assessment of the work reported in the literature with that carried out in the present study. Generally, equilibrization has been studied and reported in the literature. However, the effect of temperature on isotherm parameters and the estimation of thermodynamic parameters were not reported earlier. None of the earlier studies reported on desorption which is very essential considering the high cost of activated carbon. The present paper aims to study and model the isotherms of adsorption of C and R from aqueous solutions onto granular activated carbon (GAC). The effect of temperature for the adsorption of C and R onto GAC has also been investigated. The thermodynamics of the adsorption process have been studied, and the change in Gibbs energy (ΔG_0), entropy (ΔS_0), and enthalpy (ΔH_0), and isosteric heat of adsorption have also been determined. Desorption studies have been carried out using solvent and thermal desorption methods. A method for disposal of spent GAC has also been proposed.

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Table 1. Comparison of Work Reported for Isothermal, Thermodynamic, and Desorption Studies for the Adsorption of Catechol and Resorcinol onto Activated Carbon[a]

	Kumar et al.[28]	Mohamed et al.[16]	Blanco-Martinez et al.[34]	Richard et al.[33]	Mondal and Balomajumder[31]	Rodriguez et al.[32]	present work
types of adsorbent	AC	AC	AC	AC	AC-SAB	AC	granular-AC
compounds	C, R	C, R	C, R	C	R	R	C, R
batch or column study	batch	−	batch	column	batch	batch	batch
Isotherm Study							
Langmuir	x	x	x	x			x
Freundlich	x (best)		x	x (best)	x (best)	x	x
Tempkin							x (best)
Redlich−Peterson	x			x			x
Toth	x			x			
Radke−Prausnitz	x						
Fritz−Schlunder	x						
Thermodynamic Study							
ΔH_0			x				x
ΔS_0							x
ΔG_0							x
isosteric heat							x
Desorption Study							
solvent							x
thermal							x

[a] AC: activated carbon, SAB: simultaneous adsorption biodegradation; C: catechol; R: resocinol. x denotes that particular study has been reported in that paper.

2. MATERIALS AND METHODS

2.1. Chemicals. All of the chemicals used in the study were of analytical reagent (AR) grade. The GAC was manufactured from coconut shells. C and R were purchased from SD Fine Chemicals Ltd. (Mumbai, India). NaOH and H_2SO_4 or HCl were also obtained from SD Fine Chemicals (Mumbai, India). Stock solutions of C and R were made by dissolving exact amounts of C and R in distilled water. Test solutions were prepared by diluting 1 $g\cdot L^{-1}$ of stock solution with double-distilled water. The range of concentration of C and R components prepared from stock solution varied between (0.18 and 9.08) $mmol\cdot L^{-1}$.

2.2. Analysis of C and R. The initial and residual concentration of C and R were determined by finding out the absorbance of the respective solution at a wavelength of (275 and 273) nm, respectively, using UV−vis (ultraviolet−visible) spectrophotometry (Lambada 35; PerkinElmer, MA 02451, USA). The calibration plot of absorbance versus concentration for C and R showed a linear variation up to 0.91 $mmol\cdot L^{-1}$. Before the analysis, the samples were diluted to below 0.91 $mmol\cdot L^{-1}$ with double-distilled water whenever necessary.

2.3. Batch Adsorption Equilibrium Study. For each experimental run, 100 mL of aqueous solution of known concentrations of C and R, as the case may be, was taken in 250 mL conical flasks containing 1 g of GAC. These flasks were agitated at a constant shaking rate of 150 rpm in a temperature-controlled orbital shaker (Metrex Scientific Instruments, New Delhi) maintained at (288, 303, or 318) K for 24 h. The initial concentrations were (0.18 to 9.08) $mmol\cdot L^{-1}$ for both C and R. Preliminary tests showed that the concentration of adsorbate solutions remained unchanged after (18 to 24) h contact time with GAC depending on the type of adsorbate. So, the allowed contact time of 24 h ensured equilibration for the two adsorbates with GAC. The samples were withdrawn from the flasks after 24 h and centrifuged using a research centrifuge (Remi Instruments, Mumbai) at 10 000 rpm for 5 min, and then the supernatant liquid was analyzed for residual concentrations of C and R.

The percentage removal of C and R from the solution and the equilibrium adsorption uptake on the solid phase (q_e) were calculated using the following relationships:

$$\text{percentage C or R removal} = 100(C_0 - C_e)/C_0 \qquad (1)$$

$$\text{amount of C or R adsorbed per g of solid,} \quad q_e = (C_0 - C_e)V/w \qquad (2)$$

where C_0 is the initial C and R concentration ($mmol\cdot L^{-1}$), C_e is the equilibrium C and R concentration ($mmol\cdot L^{-1}$), V is the volume of the solution (L), and w is the mass of the adsorbent (g).

2.4. Desorption. For the batch desorption study, two different studies were performed. One was a solvent desorption study and the other a thermal desorption study. In the solvent desorption study, the GAC utilized for the adsorption was separated from the solution. The C- and R-loaded GAC (0.2 g) was then agitated at 150 rpm in a series of 250 mL conical flasks containing 50 mL of aqueous solutions (0.1 N) of HCl, H_2SO_4, HNO_3, distilled water, CH_3COOH, C_2H_5OH, acetone, and NaOH at 303 K for 24 h in the orbital shaker.[35]

In the thermal desorption study, the GAC utilized for the adsorption was separated from the solution, and it was dried in an oven at 378 K for 2 h. After that it was placed in a furnace at 623 K for 4 h. The samples were taken from the furnace and kept in the desiccator. At this condition it was assumed that the GAC had been thermally cleaned of C and R. After this, the GAC was again used as an adsorbent for the removal of C and R (C_0 = 9.18 mmol·L^{-1}) at 303 K. This adsorption−desorption procedure was repeated five times.

Thermogravimetric analysis (TGA) of the samples was done using a DuPont Hi-Res TGA 2950, USA. To determine the TGA, the sample was uniformly spread over the crucible base in all of the experiments, and the quantity of sample taken was ∼10 mg in all runs. Oxidation runs were taken at a heating rate of 10 °C·min^{-1} under an oxidizing atmosphere (flowing moisture-free air) for gasification. The tests were conducted over a range of temperature from ambient to 1000 °C. The flow rate of air was maintained at 200 mL·min^{-1}. The weight loss during thermal heating was continuously recorded and downloaded using the software, Muse, Pyris Diamond. The instrument also provided the continuous recording of differential thermal gravimetry (DTG) and differential thermal analysis (DTA) traces as a function of sample temperature and time.

2.5. Theory. *2.5.1. Adsorption Equilibrium Study.* Equilibrium adsorption equations are required in the design of an adsorption system and their subsequent optimization. Therefore, it is important to establish the most appropriate correlation for the equilibrium isotherm curves. Srivastava et al.[36] have discussed the theory associated with the most commonly used isotherm models.

Four isotherm equations, namely, Freundlich,[37] Langmuir,[38] Redlich−Peterson (R-P),[39] and Tempkin[40] have been used in the present study to fit the experimental data for C and R adsorption onto GAC at various temperatures. The sum of squares of errors (SSE) was used as a criterion in finding the best isotherm model to fit the experimental data. The SSE is given by following equation:

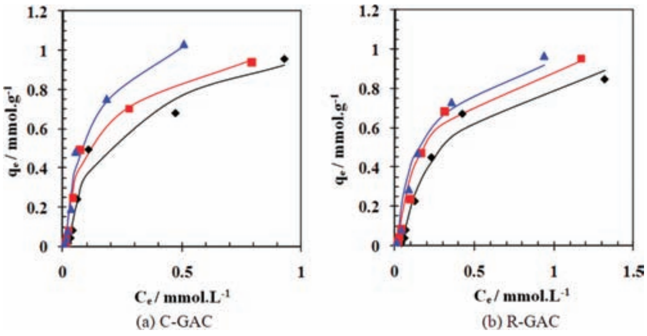
$$\mathrm{SSE} = \sum_{i=1}^{n} (q_{\mathrm{e,\,exp}} - q_{\mathrm{e,\,cal}})_i^2 \qquad (3)$$

where, $q_{\mathrm{e,exp}}$ and $q_{\mathrm{e,cal}}$ are the experimental and calculated equilibrium adsorbate uptake, respectively, and n is the number of data points.

2.5.2. Adsorption Thermodynamics. Classical thermodynamics of the adsorption process gives the following relationship among ΔG_0, ΔH_0, ΔS_0, and the equilibrium adsorption constant (K_D):

$$\ln K_D = \frac{-\Delta G_0}{RT} = \frac{\Delta S_0}{RT} - \frac{\Delta H_0}{R}\frac{1}{T} \qquad (4)$$

where T is the absolute temperature (K), R is the universal gas constant (8.314·10^{-3} kJ·mol^{-1}·K^{-1}), and K_D (= q_e/C_e) is the single point or linear sorption distribution coefficient. Thus, ΔH_0, which is the enthalpy change (kJ·mol^{-1}), can be determined from the slope of the linear van't Hoff plot, that is, lnK_D versus (T^{-1}). This ΔH_0 corresponds to the isosteric heat of adsorption ($\Delta H_{\mathrm{st},0}$) with zero surface coverage (i.e., $q_e = 0$).[41] K_D at $q_e = 0$ can be obtained from the intercept of the ln q_e/C_e versus q_e plot.[42] Recently Chakrabarty et al.[43] have reported on the thermodynamic modeling of the isosteric heat of adsorption for gaseous adsorbate−adsorbent systems. For the liquid adsorbate−adsorbent system, their model reduces to the classical Clausius−Clapeyron equation.



(a) C-GAC (b) R-GAC

Figure 1. Equilibrium adsorption isotherms at different temperatures for C and R-GAC systems, t = 24 h, C_0 = (0.18 to 9.08) mmol·L^{-1}, m = 10 g·L^{-1}, T = ◆, 293 K; ■, 303 K; and ▲, 318 K. Experimental data points given by the symbols and the lines predicted by Tempkin equation.

3. RESULTS AND DISCUSSION

3.1. Effect of Temperature. Figure 1 shows the plots of adsorption isotherms, q_e versus C_e, for C-and R-GAC systems at different temperatures ranging from (288 to 318) K. At low C_e, the rise in q_e is sharp which becomes gradual at higher C_e. Similar trends were observed for the adsorption of R. As seen in Figure 1, the equilibrium adsorption capacity of C and R increased with increasing temperature from (1.09 and 1.21) mmol·g^{-1} at 288 K to (1.11 and 1.24) mmol·g^{-1} at 303 K and (1.41 and 1.27 mmol·g^{-1}) at 318 K, indicating that C and R adsorption onto GAC was favored at higher temperatures. This indicated that the adsorption of C and R onto GAC was controlled by an endothermic process. Many investigators have given different reasons for the endothermic nature of phenolic compound adsorption onto activated carbons. The increase of adsorption capacity with increasing temperature may be due to an increase in the chemical potential of the organic molecules to penetrate to the surface of GAC, thereby increasing the possibility of bonding between the C and the R and the functional groups present on the adsorption sites of GAC. Also, adsorption processes which are diffusion (intraparticle transport-pore diffusion) controlled show an increase in adsorption capacity with an increase in temperature due to the endothermicity of the diffusion process. This is due to the increased mobility of the adsorbates and decreased retarding forces acting on the diffusing adsorbates at higher temperatures. This results in the enhancement in the adsorptive capacity of the GAC at higher temperatures.[30] However, the diffusion of C and R into the pores of the adsorbent is not the only rate-controlling step (details not given here), and the diffusion resistance can be ignored with adequate contact time. Therefore, the increase in adsorptive uptake of C and R with an increase in temperature can be attributed to chemisorption. In later sections of the present paper, it is shown that the desorption of C and R from the spent (C-and R-loaded) GAC using various solvents (acids, bases, and water) is not significant, confirming some degree of chemisorptive nature of the adsorption process. It is also known that the rise in adsorption temperature weakens the hydrogen bonds among water molecules and between water molecules and solute or adsorbent[44] and also increases pore diffusion.[45,46] Therefore, the increase in temperature favors dehydration of the C and R molecules, which makes them more planar and gives them a larger dipolar moment. The increase in planarity gives C and R molecules greater access

Table 2. Isotherm Parameters for the Removal of C and R by GAC at Different Temperatures (t = 24.0 h, C_0 = (0.18 to 9.08) mmol·L^{-1}, m = 10 g·L^{-1}, T = 303 K)

Freundlich: $q_e = K_F C_e^{1/n}$

temp. K	K_F (mmol·g^{-1})(L·mmol·g^{-1})$^{-1/n}$	$1/n$	R^2	SSE	K_F (mmol·g^{-1})(L·mmol·g^{-1})$^{-1/n}$	$1/n$	R^2	SSE
	C-GAC				R-GAC			
288	1.02	0.57	0.912	0.072	0.79	0.57	0.876	0.088
303	1.12	0.48	0.900	0.081	0.93	0.52	0.912	0.075
318	0.59	0.55	0.915	0.089	0.49	0.99	0.948	0.045

Langmuir: $q_e = (q_m K_L C_e)/(1 + K_L C_e)$

temp. K	q_m mmol·g^{-1}	K_L L·mmol^{-1}	R^2	SSE	q_m mmol·g^{-1}	K_L L·mmol^{-1}	R^2	SSE
		C-GAC				R-GAC		
288	1.09	4.48	0.947	0.053	1.21	2.09	0.960	0.037
303	1.11	6.81	0.966	0.031	1.24	3.14	0.984	0.019
318	1.41	5.83	0.962	0.042	1.27	3.56	0.990	0.009

Tempkin: $q_e = B_T \ln K_T + B_T \ln C_e$

temp. K	K_T L·mmol^{-1}	B_1 mmol·g^{-1}	R^2	SSE	K_T L·mmol^{-1}	B_1 mmol·g^{-1}	R^2	SSE
		C-GAC				R-GAC		
288	41.68	0.25	0.968	0.025	21.75	0.27	0.978	0.014
303	76.60	0.23	0.980	0.015	42.81	0.24	0.970	0.023
318	78.00	0.27	0.966	0.032	56.96	0.23	0.950	0.035

R-P: $q_e = (K_R C_e)/(1 + a_R C_e^{\beta})$

temp. K	K_R L·g^{-1}	a_R L·mmol^{-1}	β	R^2	SSE	K_R L·g^{-1}	a_R L·mmol^{-1}	β	R^2	SSE
		C-GAC					R-GAC			
288	4.45	3.75	0.975	0.942	0.0495	2.55	2.10	0.999	0.960	0.037
303	7.58	6.82	0.999	0.966	0.0311	3.92	3.15	0.999	0.982	0.019
318	5.83	8.22	0.999	0.962	0.0424	4.55	3.56	0.999	0.990	0.009

to the micropores of the GAC, while the increase in dipolar moment leads to enhanced adsorbent—adsorbate interactions. In addition, the adsorption potential within the micropores increases the planarity of C and R molecules, so that at high temperature (318 K) the entire carbon surface is covered by at least one layer of C and R molecules. As a result of this process, C and R adsorption is apparently endothermic due to the endothermicity of C and R molecule dehydration. However, among the two adsorbates C and R, hydration of the R molecules in solution does not have such a large effect on their size and polarity because R molecules lack the urea type chain, which gets twisted after hydration. This causes a lesser increase in adsorption capacity of GAC for R as compared to that for C.[47] The increase in phenol sorption capacity of the carbonaceous adsorbents with the increase in temperature has also been reported by other investigators.[48,49]

3.2. Adsorption Isotherm Modeling. The Langmuir, Freundlich, Tempkin, and R-P isotherm parameters along with coefficient of determination (R^2) and SSE values for the fit of the adsorption of C and R onto GAC at various temperatures are given in Table 1. The R^2 values alone are insufficient in determining the best isotherm model to represent the experimental data because they are mostly greater than 0.90 for all four models. The SSE values, for C, are smaller for the Tempkin model as compared to that for the other models. So, it can be concluded that the Tempkin model is the best among the four models for representing the adsorption isotherm data of the C-GAC system. Similarly, either of the Tempkin and Langmuir isotherms could be used to represent the isotherm data for the R-GAC system.

The most important parameter to compare in Table 1 is the q_{max} value of the Langmuir model, because this measures the adsorption capacity of the GAC for the adsorbates. By comparing the results for adsorption capacity of GAC for C or R, it is seen that the q_{max} value is clearly greater for C at higher temperature (318 K), whereas it is greater for R at lower temperatures (288 and 303 K). Thus, it is difficult to establish a relation between the chemical structure of C and R which are similar types of compounds and their adsorption behavior onto GAC. The amount of C and R adsorbed onto GAC depends on many factors including the size of the substrate molecule. In this regard, C tends to be larger than R, thus leading to a higher adsorption capacity of R at lower temperature. A similar trend was reported by Garcia-Araya et al.[45] for the adsorption of gallic, syringic, and *p*-hydroxy benzoic acids onto an active charcoal. They argued that, at higher temperatures, the discrepancy observed between the expected order and the one observed for adsorption of compounds of similar size may be due to differences in solubility rather than to differences in chemical structure. The q_{max} value of C is higher than R at higher temperatures (318 K). It may be related to the planarity of C and R molecules. The reasons have been explained in the previous section.

Huang et al.[50] found that the adsorption capacity of C is a little larger than that of R at the same temperature and equilibrium concentration. This difference in absorbability was explained in terms of the solubility and the polarity of the two adsorbates.[48] The solubility of R in water is larger than that of C [(110 and 43) g/100 mL H_2O at 298 K for C and R, respectively], thus it shows stronger affinity toward water. This may be one of the reasons for its smaller adsorption capacity. That is, hydrophobic interaction may be one of the driving forces. In addition, the matching of the polarity between the adsorbent and the adsorbate is also an important factor affecting adsorption.

The formation of hydrogen bonds between solute and solvent, favored at low temperatures, can modify the shape and size of solute molecules such that they cannot access the micropores of the adsorbent. In addition, temperature variations may possibly affect the equilibrium among different conformers when a solute has various molecular conformations, which could affect solute uptake on the adsorbent.[51]

Several authors have reported Freundlich and Langmuir constants for the adsorption of phenols and related compounds onto various adsorbents. The Freundlich and Langmuir constant values obtained in some of these studies are compared with the values obtained in the present work in Table 2. It may be seen

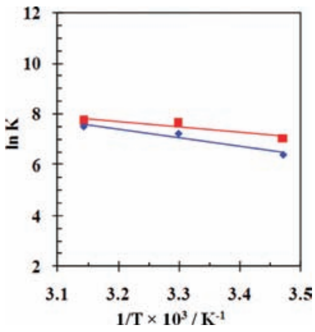


Figure 2. van't Hoff plot of adsorption equilibrium constant *K* for C (red ■) and R (blue ◆).

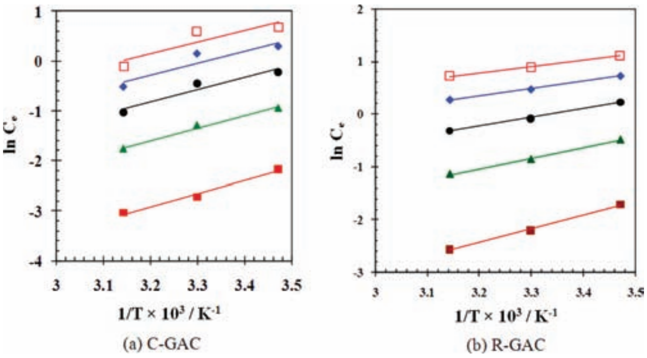
Table 4. Thermodynamics Parameters for the Adsorption of C by GAC (t = 24 h, C_0 = (0.18 to 9.08) mmol·L^{-1}, m = 10 g·L^{-1})

temp. K	K_d L·g^{-1}	ΔG_0 kJ·mol^{-1}	ΔH_0 kJ·mol^{-1}	ΔS_0 J·mol^{-1}·K^{-1}
		C-GAC		
288	1.13	−16.84	17.99	121.63
303	2.13	−19.32		
318	2.28	−20.45		
		R-GAC		
288	0.59	−15.29	28.32	152.04
303	1.35	−18.18		
318	1.79	−19.81		

Table 3. Literature Review of Freundlich and Langmuir Constants for the Adsorption of C and R onto Various Activated Carbons[a]

			T	C_0	m	t	K_F		q_m	K_L	
adsorbent	adsorbate	pH	K	mmol·L^{-1}	g·L^{-1}	h	(mmol·g^{-1})·(L· mmol·g^{-1})$^{-1/n}$	1/n	mmol·g^{-1}	L·mmol^{-1}	ref
GAC	C	7.1	303	4.54−9.08	5	48	42.40	0.205	1.302	8.808	28
CZ	C	-	298	0.45	5	48	-	-	0.006	-	16
CS	C	-	298	0.45	5	48	-	-	0.026	-	16
AC	C	6.25	293	-	2−15	48	-	0.134	2.91	10.42	33
GAC	C	7	298	0.18−18.16	10	48	1.49	0.81	2.162	0.462	34
CAR	C	-	-	-	-	48	1.39	0.74	1.651	0.627	34
CAO	C	-	-	-	-	48	1.62	0.70	1.621	0.429	34
GAC	C	5.8	318	0.18−9.08	10	24	-	0.55	1.41	5.83	present study
GAC	R	7.1	303	4.54−9.08	5	48	34.83	0.226	1.297	5.175	28
CZ	R	-	298	0.45	5	48	-	-	0.008	-	16
CS	R	-	298	0.45	5	48	-	-	0.033	-	16
GAC	R	6.24	301	0.09−1.82	10	10	34.52	0.236	1.277	5.065	31
GAC-SAB	R	-		-	-	-	23.43	0.877	0.452	8.148	31
GAC	R	-	-	-	-	48	2.70	0.70	1.621	0.660	34
CAR	R	-	-	-	-	48	2.00	0.73	2.112	0.605	34
CAO	R	-		-	-	48	2.09	0.66	1.488	0.528	34
GAC	R	6	318	0.18−9.08	10	24	-	0.99	1.27	3.56	present study

[a] GAC, granular activated carbon; CZ, non-activated carbon; CS, sulfuric acid activated carbons; SAB, simultaneous adsorption biodegradation; CAR, reduced activated carbon; CAO, oxidized activated carbon.



(a) C-GAC (b) R-GAC

Figure 3. Adsorption isosteres for determining the isosteric heat of adsorption for C and R adsorption onto GAC at various loadings, q_e (mmol·g^{-1}) = red ■, 0.3; green ▲, 0.6; ●, 0.9; blue ◆, 1.2; and red □, 1.5.

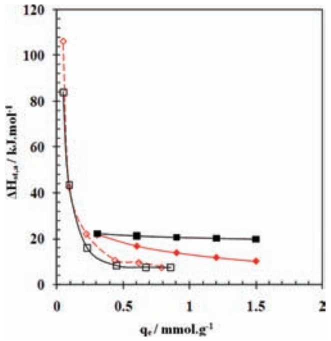


Figure 4. Variation of $\Delta H_{st,a}$ with respect to surface loading. $\Delta H_{st,a}$ calculated theoretically: R (red —◆—) and C (—■—). $\Delta H_{st,a}$ calculated calorimetrically: R (red —◇—) and C (—□—).

that the isotherm parameters differ widely in their values for activated carbons of different origin. This difference in values is due to the variation in the parametric conditions under which the isotherm study was performed. It is also due to the difference in nature of the studied activated carbon. Considering the variation reported for isotherm values, one should be cautious while using these values in the design of adsorption systems.

3.3. Adsorption Thermodynamics. Figure 2 shows the van't Hoff plots for C and R, from which ΔH_0 and ΔS_0 values have been estimated (Tables 3 and 4). The positive value of ΔS_0 (121.6 J·mol^{-1}·K^{-1} and 152.0 J·mol^{-1}·K^{-1} for C and R, respectively) suggests increased randomness at the solid−solution interface with some structural changes in the adsorbates and the GAC and an affinity of the GAC toward C and R.[30] The positive ΔS_0 value also corresponds to an increase in the degree of freedom of the adsorbed species.[52] ΔG_0 values were negative indicating that the adsorption process led to a decrease in ΔG_0 and that the adsorption process is feasible and spontaneous.[53]

The positive values of ΔH_0 (17.9 kJ·mol^{-1} and 28.3 kJ·mol^{-1} for C and R, respectively) indicate the endothermic nature of the adsorption process. The ΔH_0 of R is greater than C, displaying that the interaction of the GAC with R is a little stronger.[47] The enthalpy of adsorption of organic molecules from aqueous solution onto activated carbon is usually within the range (8 to 65) kJ·mol^{-1}.[54] The values obtained in the present study are within the same range. In physiosorption, the bond between adsorbent and adsorbate is van der Waals interactions, and ΔH_0 is typically in the range of (5 to 10) kJ·mol^{-1} for liquid phase adsorption. In case of chemisorption, a chemical bond is formed between adsorbate molecules and the surface, and the chemisorption energy is, generally, in the range of (30 to 70) kJ·mol^{-1}.[55] The values of ΔH_0 for the present study show that the adsorption of C and R onto GAC is neither fully physical nor fully chemical and some complex mechanism dictates the adsorption process. Some researchers have suggested that adsorption of some organic compounds from aqueous solution onto activated carbon is by a different adsorption mechanism, which may not be described as either physical adsorption or chemisorption.[54]

3.3.1. Isosteric Heat of Adsorption. The apparent isosteric heat of adsorption ($\Delta H_{st,a}$) at constant surface coverage (q_e = (0.3 to 1.5) mmol·g^{-1}) was calculated using the Clausius−Clapeyron equation:[56]

$$\frac{d \ln C_e}{dT} = \frac{-\Delta H_{st,a}}{RT^2} \qquad (5)$$

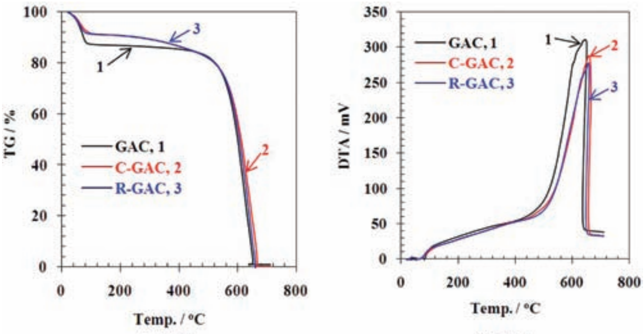
$$\Delta H_{st,a} = R\frac{d \ln C_e}{d(1/T)}\bigg|_{q_e} \qquad (6)$$

For this purpose, C_e at a constant amount of adsorbed C or R is obtained from the adsorption isotherm data at different temperatures. $\Delta H_{st,a}$ is calculated from the slope of the ln C_e versus T^{-1} plot for different amounts of C and R adsorbed onto GAC. The isosteres corresponding to different equilibrium adsorption uptake of C and R by GAC are shown in Figure 3. The linear regression coefficients of determination of the isosteres and the corresponding isosteric enthalpies for C or R adsorption onto GAC are presented in Table 2.

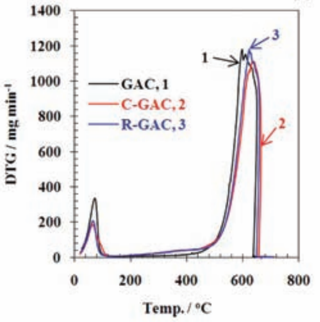
The variation of $\Delta H_{st,a}$ as calculated using the Clausius−Clapeyron equation for the two adsorbate−adsorbent systems with the surface loading is presented in Figure 4. Values of $\Delta H_{st,a}$ were also calculated calorimetrically for various loadings. It may be seen in Figure 4 that these values show similar trends as shown by $\Delta H_{st,a}$ calculated using the Clausius−Clapeyron equation. At higher surface coverage, the $\Delta H_{st,a}$ calculated using the Clausius−Clapeyron formula matches well with the calorimetric measured $\Delta H_{st,a}$ values. The $\Delta H_{st,a}$ is high at low coverage and decreases steadily with an increase in q_e indicating that the GAC has energetically heterogeneous surfaces. The dependence of ΔH_0 with surface coverage is usually observed to display adsorbent−adsorbate interaction followed by adsorbate−adsorbate interaction. The adsorbent−adsorbate interaction takes place initially at lower q_e values resulting in high ΔH_0. On the other hand, adsorbate−adsorbate interaction occurs with an increase in the surface coverage. The variation in $\Delta H_{st,a}$ with surface loading can also be attributed to the lateral interactions between adsorbed adsorbates.

3.4. Desorption Study. Various solvents, namely, ethanol, HNO_3, HCl, NaOH, CH_3COOH, acetone, and water, were used in the elution of C or R from the GAC.[35] However, NaOH showed some desorption efficiency with C (10.1 %) and R (11.4 %).

Spent GAC was thermally desorbed as described in Section 2.4. Thermally desorbed GAC was again used for adsorption. This cycle of adsorption−desorption was repeated five times. Thermal desorption was carried out in the absence of air or gas at 350 °C. Successive adsorption−desorption cycles showed continuous decreasing desorption efficiencies. This, however, can be overcome by using air and sweeping the desorbed R or C.



(a) TG (b) DTA



(c) DTG

Figure 5. TGA-DTA graphs of blank and C- and R-loaded GAC under oxidizing atmosphere.

3.5. Thermal Oxidation and Disposal of the Spent GAC. It is necessary to properly dispose of the spent GAC and/or utilize it for some beneficial purpose if possible. The dried spent GAC can be used directly or by making fire briquettes for furnace combustors or incinerators to recover its energy value. C and R loaded adsorbents were studied for their thermal degradation characteristics by a thermogravimetric instrument. The TGA, DTA, and DTG curves of the blank and C- and R-loaded GAC at a heating rate of 10 K·min^{-1} are shown in Figure 5. The TG traces (Figure 5a) show the loss of moisture and the evolution of some lightweight molecules including water up to 500 °C. The weight loss was 18 % for blank GAC, 18.2 % for C-GAC, and 18.1 % for R-GAC. Higher temperature drying (> 100 °C) occurs because of the loss of the surface tension bound water of the particles. Blank and C- and R-GAC do not show any endothermic transition between room temperature and 400 °C, indicating the lack of any crystalline or other phase change during the heating process.[57] The rate of weight loss was found to increase between (~500 and ~637) °C (81 % weight loss), (~501 and ~657) °C (80 %), and (~500 and ~650) °C (78.3 %) for blank and C- and R-GAC, respectively. In these temperature ranges, the C-and R-loaded GAC oxidize and completely lose their weight. The strong exothermic peak centered between (~500 and 680) °C is due to the oxidative degradation of the samples (Figure 5b). This broad peak as that observed from the first derivative loss curve (DTG) may be due to the combustion of carbon species (Figure 5c). The TGA and DTA curves could be used to deduce drying and thermal degradation characteristics.

Blank GAC has a heating value of about 8.26 MJ·kg^{-1}. Thus, the GAC along with the adsorbed C and R can be dried and used as a fuel in boilers or incinerators or can be used for the production of fuel briquettes. The bottom ash may be blended with clay to make fire bricks or with a cement−concrete mixture to make colored building blocks, thus disposing of C and R through chemical and physical fixation. Thus, not only spent GAC could be safely disposed, but also its energy value can be recovered.

4. CONCLUSION

Adsorption isotherms of C and R on GAC were studied and modeled using different isotherm models. The Freundlich equation is not appropriate for the experimental results. The model of Langmuir is more suitable than that of the Freundlich model, but it slightly diverges from the experimental results for the higher values of equilibrium concentrations. The Tempkin model best fitted the experimental values compared to other models which are studied in this work. The adsorption of C and R onto GAC is endothermic in nature. C- and R-loaded GAC regeneration was studied using various solvents as well as by heating the spent GAC at 623 K. Solvent-aided regeneration of GAC was found to be very low with maximum desorption efficiencies of 10.1 % and 11.4 %, respectively, shown by the C- and R-GAC systems. Thermal desorption of GAC worked well for at least five adsorption−desorption cycles with a continuous decrease in adsorption efficiency after each cycle. Spent GAC can be used as a cofuel in boiler furnaces or incinerators.

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■ REFERENCES

(1) Korbahti, B. K.; Tanyolac, A. Continuous electrochemical treatment of phenolic wastewater in a tubular reactor. *Water Res.* **2003**, *37*, 1505–1514.

(2) Dellinger, B.; Pryor, W. A.; Cueto, R.; Squadrito, G. L.; Hegde, V.; Deutsch, W. A. Role of free radicals in the toxicity of airborne fine particulate matter. *Chem. Res. Toxicol.* **2001**, *14*, 1371–1377.

(3) *The Merck Index*, 11th ed.; Merck: Rahway, NJ, 1989.

(4) Milligan, P. W.; Haggblom, M. M. Biodegradation of resorcinol and catechol by denitrifying enrichment cultures. *Environ. Toxicol. Chem.* **1998**, *17*, 1456–1461.

(5) Hays, M. D.; Fine, P. M.; Geron, C. D.; Kleeman, M. J.; Gullett, B. K. Open burning of agricultural biomass: physical and chemical properties of particle-phase emissions. *Atmos. Environ.* **2005**, *39*, 6747–6764.

(6) Freeman, H. M.; Harry, E. S. *Hazardous Waste Remediation: Innovative Treatment Technologies*; Technomic Publishing Co., Inc.: Lancaster, PA, 1995.

(7) Othmer, K. Hydroquinone, resorcinol, and catechol. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., Vol. 13; John Wiley & Sons: New York, NY, 1981.

(8) Prager, J. C. In *Environmental Contaminant Reference Data Book*; Van Nostrand Reinhold: New York, 1997.

(9) Kumar, A.; Kumar, S.; Kumar, S. Biodegradation Kinetics of phenol and Resorcinol Using *Pseudomonas putida MTCC* 1194. *Biochem. Eng. J.* **2005**, *22*, 151–159.

(10) Stoilova, I.; Krastanov, A.; Stanchev, V.; Daniel, D.; Gerginova, M.; Alexieva, Z. Biodegradation of high amounts of phenol, resorcinol, 2,4-dichlorophenol and 2,6-dimethoxyphenol by *Aspergillus awamori* cells. *Enzyme Microb. Technol.* **2006**, *39*, 1036–1041.

(11) Latkar, M.; Swaminathan, K.; Chakrabarti, T. Kinetics of anaerobic biodegradation of resorcinol and hydroquinone in upflow fixed film-fixed bed reactors. *Bioresour. Technol.* **2003**, *88*, 69–74.

(12) Subramanyam, R.; Mishra, I. M. Biodegradation of catechol (2-hydroxy phenol) bearing wastewater in an UASB reactor. *Chemosphere* **2007**, *69*, 816–824.

(13) Subramanyam, R.; Mishra, I. M. Co-degradation of resorcinol and catechol in an UASB reactor. *Bioresour. Technol.* **2008**, *99*, 4147–4157.

(14) Nasr, B.; Abdellatif, G.; Canizares, P.; Saez, C.; Lobato, J.; Rodrigo, M. A. Electrochemical oxidation of hydroquinone, resorcinol, and catechol on boron doped diamond anodes. *Environ. Sci. Technol.* **2005**, *39*, 7234–7239.

(15) Chien, S. W. C.; Chen, H. L.; Wang, M. C.; Seshaiah, K. Oxidative degradation and associated mineralization of R, hydroquinone and resorcinol catalyzed by birnessite. *Chemosphere* **2009**, *74*, 1125–1133.

(16) Mohamed, F. S.; Khater, W. A.; Mostafa, M. R. Characterization and phenols sorptive properties of carbons activated by sulphuric acid. *Chem. Eng. J.* **2006**, *116*, 47–52.

(17) Arana, J.; Rodriguez, J. M. D.; Diaz, O. G.; Melian, J. A. H.; Rodriguez, C. F.; Pena, J. P. The effect of acetic acid on the photocatalytic degradation of catechol and resorcinol. *Appl. Catal., A* **2006**, *299*, 274–284.

(18) Ahn, M. Y.; Martinez, C. E.; Archibald, D. D.; Zimmerman, A. R.; Bollag, J.-M.; Dec, J. Transformation of resorcinol in the presence of a laccase and birnessite. *Soil Biol. Biochem.* **2006**, *38*, 1015–1020.

(19) Zogorski, J. S. M.; Faust, S. D.; Haas, J. H., Jr. The kinetics of adsorption of phenols by granular activated carbon. *J. Colloid Interface Sci.* **1976**, *55*, 329–341.

(20) Ten Hulscher, Th. E. M.; Cornelissen, G. Effect of temperature on sorption equilibrium and sorption kinetics of organic micropollutants-a review. *Chemosphere* **1996**, *32*, 609–626.

(21) Scaroni, W. An experimental and theoretical study of the adsorption of aromatics possessing electron-donating functional groups by chemically modified activated carbons. *Carbon* **1997**, *35*, 1339–1348.

(22) Khan, A. R.; Al-Bahri, T. A.; Al-Haddad, A. Adsorption of phenol based organic pollutants on activated carbon from multi-component dilute aqueous solutions. *Water Res.* **1997**, *31*, 2102–2112.

(23) Streat, M.; Patrick, J. W.; Perez, M. J. C. Sorption of phenol and para-chlorophenol from water using conventional and novel activated carbons. *Water Res.* **1995**, *29*, 467–472.

(24) Hsieh, C. T.; Teng, H. Liquid-phase adsorption of phenol onto activated carbons prepared with different activation levels. *J. Colloid Interface Sci.* **2000**, *230*, 171–175.

(25) Dabrowski, A. Adsorption-from theory to practice. *Adv. Colloid Interface Sci.* **2001**, *93*, 135–224.

(26) Terzyk, A. P. Further insights into the role of carbon surface functionalities in the mechanism of phenol adsorption. *J. Colloid Interface Sci.* **2003**, *268*, 301–329.

(27) Salame, I. I.; Bandosz, T. J. Role of surface chemistry in adsorption of phenol on activated carbons. *J. Colloid Interface Sci.* **2003**, *264*, 307–312.

(28) Kumar, A.; Shashi, A.; Kumar, S. Adsorption of resorcinol and catechol on activated carbon: Equilibrium and kinetics. *Carbon* **2003**, *41*, 3015–3025.

(29) Ayranci, E.; Bayram, E. Adsorption of phthalic acid and its esters onto high-area activated carbon-cloth studied by in situ UV-spectroscopy. *J. Hazard. Mater.* **2005**, *122*, 147–153.

(30) Srivastava, V. C.; Swamy, M. M.; Mall, I. D.; Prasad, B.; Mishra, I. M. Adsorptive removal of phenol by bagasse fly ash and activated carbon: equilibrium, kinetics and thermodynamics. *Colloid Surf., A* **2006**, *272*, 89–104.

(31) Mondal, P.; Balomajumder, C. Treatment of resorcinol and phenol bearing wastewater by simultaneous adsorption biodegradation (SAB): optimization of process parameters. *Int. J. Chem. React. Eng.* **2007**, *5*, S1.

(32) Rodriguez, E.; Encinas, A.; Masa, F. J.; Beltran, F. J. Influence of resorcinol chemical oxidation on the removal of resulting organic carbon by activated carbon adsorption. *Chemosphere* **2008**, *70*, 1366–1374.

(33) Richard, D.; Delgado, M. L.; Schweich, D. Adsorption of complex phenolic compounds on activated charcoal: adsorption capacity and isotherms. *Chem. Eng. J.* **2009**, *48*, 1–7.

(34) Blanco-Martinez, D. A.; Giraldo, L.; Moreno-Pirajan, J. C. Effect of the pH in the adsorption and in the immersion enthalpy of monohydroxylated phenols from aqueous solutions on activated carbons. *J. Hazard. Mater.* **2009**, *169*, 291–296.

(35) Mall, I. D.; Srivastava, V. C.; Kumar, G. V. A.; Mishra, I. M. Characterization and utilization of mesoporous fertilizer plant waste carbon for adsorptive removal of dyes from aqueous solution. *Colloids Surf., A* **2006**, *278*, 175–187.

(36) Srivastava, V. C.; Mall, I. D.; Mishra, I. M. Modelling individual and competitive adsorption of cadmium (II) and zinc(II) metal ions from aqueous solution onto bagasse fly ash. *Sep. Sci. Technol.* **2006**, *41*, 2685–2710.

(37) Freundlich, H. M. F. Over the adsorption in solution. *J. Phys. Chem.* **1906**, *57*, 385–471.

(38) Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **1918**, *40*, 1361–1403.

(39) Redlich, O.; Peterson, D. L. A useful adsorption isotherm. *J. Phys. Chem.* **1959**, *63*, 1024–1026.

(40) Tempkin, M. I.; Pyzhev, V. Kinetics of ammonia synthesis on promoted iron catalysts. *Acta Phys. Chim. Sin.* **1940**, *12*, 327–356.

(41) Suzuki, M.; Fujii, T. Concentration dependence of surface diffusion coefficient of propionic acid in activated carbon particles. *AIChE J.* **1982**, *28*, 380–385.

(42) Srivastava, V. C.; Mall, I. D.; Mishra, I. M. Adsorption thermodynamics and isosteric heat of adsorption of toxic metal ions onto bagasse fly ash (BFA) and rice husk ash (RHA). *Chem. Eng. J.* **2007**, *132*, 267–278.

(43) Chakrabarty, A.; Saha, B. B.; Koyama, S. On the thermodynamic modelling of the isosteric heat of adsorption and comparision with experiments. *Appl. Phys. Lett.* **2006**, *89*, 171901-(1-3).

(44) Costa, E.; Calleja, G.; Marijuan, L. Comparative adsorption of phenol, p-nitrophenol and p-hydroxybenzoic acid on activated carbon. *Adsorpt. Sci. Technol.* **1988**, *5*, 213–228.

(45) Garcia-Araya, J.; Beltrn de Heredia, J.; Alvarez, P.; Masa, F. J. Activated carbon adsorption of some phenolic compounds present in agroindustrial wastewater. *Adsorption* **2003**, *9*, 107–115.

(46) Terzyk, A. P. 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.* **2004**, *275*, 9–29.

(47) Sun, Y.; Chen, J.; Li, A.; Liu, F.; Zhang, Q. Adsorption of resorcinol and catechol from aqueous solution by aminated hypercross-linked polymers. *React. Funct. Polym.* **2005**, *64*, 63–73.

(48) Vijayalakshmi, P. R.; Jasra, R. V.; Thirumaleswara, S. G. B. Adsorption of phenol, cresol isomers and benzyl alcohol from aqueous solution on activated carbon at 278, 298 and 323 K. *J. Chem. Technol. Biotechnol.* **1998**, *71*, 173–179.

(49) Banat, F.; Sameer, A. A.; Leema, A. M. Utilization of raw and activated date pits for the removal of phenol from aqueous solutions. *Chem. Eng. Technol.* **2004**, *27*, 80–86.

(50) Huang, J.; Huang, K.; Yan, C. Application of an easily water-compatible hypercrosslinked polymeric adsorbent for efficient removal of catechol and resorcinol in aqueous solution. *J. Hazard. Mater.* **2009**, *167*, 69–74.

(51) Sun, Y.; Li, X. T.; Xu, C.; Chen, J. L.; Li, A. M.; Zhang, Q. X. Adsorption of catechol from aqueous solution by aminated hypercross-linked polymers. *J. Environ. Sci.* **2005**, *17*, 584–588.

(52) Raymon, C. *Chemistry: Thermodynamics*; McGraw-Hill: Boston, 1998.

(53) Sabah, E.; Çinar, M.; Çelik, M. S. Decolorization of vegetable oils: Adsorption mechanism of β-carotene on acid-activated sepiolite. *Food Chem.* **2007**, *100*, 1661–1668.

(54) Mattson, J.; Mark, H. *Activated carbon: surface chemistry and adsorption from solution*; Marcel Dekker, Inc.: New York, 1971.

(55) Murzin, D.; Salami, T. *Chemical kinetics*; Elsevier: Amsterdam, 2005.

(56) Young, D. M.; Crowell, A. D. *Physical adsorption of gases*; Butterworths: London, 1962.

(57) Ng, J. C. Y.; Cheung, W. H.; McKay, G. Equilibrium Studies of the Sorption of Cu(II) Ions onto Chitosan. *J. Colloid Interface Sci.* **2002**, *255*, 64–74.