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Adsorption Equilibrium Studies of Some Aqueous Aromatic Pollutants on Granular Activated Carbon Samples

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Abstract

Adsorption equilibrium studies of some aromatic organic pollutants in water with some commercially available standard grades of granular activated carbons have been carried out at 35°C. The adsorption equilibrium data for adsorbates such as phenol, aniline, benzoic acid, *o*-cresol, and *p*-methoxyphenol on six grades of granular activated carbons were analyzed for their adherence to Freundlich or Langmuir adsorption isotherms, and the results are discussed.

INTRODUCTION

Increasing environmental awareness and concern are bound to expand the role of activated carbon as a highly effective adsorbent for the removal of organic pollutants from aqueous waste. In recent years the ready availability of a wide variety of granular activated carbon (GAC) samples in several countries has made activated carbon an integral part of day-to-day life and has opened a new realm of science which is fascinating to study and to work with. Recent inroads into the regeneration of spent GAC samples has led to a tremendous reduction in operating and control equipment and has opened new vistas in the recovery of chemicals, holding additional promise that the value of chemicals recovered will outweigh the cost of adsorbent regeneration processes.

Adsorption from the liquid phase onto activated carbons is used primarily for decolorizing and deodorizing aqueous solutions. This is due to the affinity of activated carbons for organic compounds in the presence of water.

Drinking water has been successfully treated since 1930 with activated carbon powders (*1*). During the course of investigations carried out in this laboratory on the removal of some organic pollutants from aqueous wastes, it was found necessary to determine the adsorption isotherms of these pollutants on the grades of GAC used. These isotherms helped in calculating the free pollutant concentration in solution during kinetic studies. Keeping this in view, the adsorption isotherms in the present work are centered around such organic pollutants as phenol, aniline, benzoic acid, *o*-cresol, and *p*-methoxyphenol, and the six grades of GAC which were characterized for their physical properties separately. The choice of employing several grades of carbon was mainly to compare the indigenous activated carbon with some standard grades available elsewhere. The present study gives data on the adsorption isotherms and discusses their possible relation in the removal of a particular pollutant.

EXPERIMENTAL

The adsorbates used in this work were obtained commercially in the purest form available, were subjected to purification tests as and when necessary, and were used as their aqueous solutions for equilibrium studies. In view of differences in solubilities of these pollutants in water, a rough aqueous concentration range of 1×10^{-4} to 20×10^{-4} mol/L was employed to determine the isotherms. This was justified by taking into consideration the concentrations of these pollutants which are generally found in wastewater. All aqueous pollutants were analyzed by their UV absorption. The wavelengths employed and the Beer's law plots for these pollutants are summarized in Table 1 in the form of a mathematical equation:

$$\text{Concentration} = m(\text{optical density}) + b$$

and the values of m, b, and the regression coefficient r are reported.

TABLE 1
UV Absorption Data on Adsorbates

	Expected[a]		Observed				
Adsorbate	λ (nm)	ϵ ($\mathrm{cm^{-1}\cdot mol^{-1}}$)	λ (nm)	ϵ ($\mathrm{cm^{-1}\cdot mol^{-1}}$)	r	$m \times 10^4$	$b \times 10^6$
Phenol	270	1445	270	1452	1.0000	6.8882	−2.28
Aniline	280	1445	280	1350	0.9996	7.4683	−2.33
Benzoic acid	269	794	269	775	0.9995	12.9160	1.36
o-Cresol	270	1549	270	1617	0.9999	6.1850	−8.07
p-Methoxyphenol	288	2530	288	2553	0.9998	3.8987	−1.01

[a] M. J. Kamlet (ed.), *Organic Electronic Spectral Data*, Vols. I to V, Interscience, New York.

Six grades of granular activated carbons (RRL, CAL, KURARE, FILTRASORB 200, FILTRASORB 400, and LCK) were employed in the present work. These samples were sieved for mesh size 12 × 16 (BS Standard) and washed several times with distilled water until the leachate was free from any suspended impurities. The samples were then dried in an oven at 100–110°C and stored in a calcium chloride dessicator until use. The properties (density, N_2-BET surface area, total pore volume) and other pertinent information were supplied along with the GAC samples, and these are reported in Table 2.

The adsorption isotherms are given in Figs. 1–6. Each experimental point in these isotherms is an average of two independent determinations and was obtained by stirring 0.500 ± 0.0005 g of the GAC with 1 L of the adsorbate solution taken in a 2-L round-bottom flask fitted with a paddle-type stirrer and maintained at 35°C. The stirring was continued for about 5 h, and it was separately verified that prolonging the time of stirring did not bring about any change in the residual adsorbate concentration in the experiment. The adsorption isotherms have been treated both by Freundlich and Langmuir adsorption isotherms, and the results are given in Table 3 and discussed below.

The adsorption isotherms for all the systems are summarized in Figs. 1–6. These figures, which show a plot of q_e versus the equilibrium concentration of the adsorbate in solution c_e, fairly indicate typical Type I favorable isotherms as generally referred to in the literature (*2*). It is possible to conclude that practically all the isotherms obtained in the present investigation fall under this category. The Langmuir treatment is based on the assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface. The equation can be expressed as

$$q_e = Q^\circ bc_e/(1 + bc_e) \tag{1}$$

Rearranging Eq. (1):

$$1/q_e = 1/Q^\circ bc_e + 1/Q^\circ \tag{2}$$

Thus a plot of $1/q_e$ versus $1/c_e$ should be linear if Langmuir adsorption were operative, permitting calculation of Q°. Knowledge of Q° leads to determination of the surface area of the adsorbent. However, it must be cautioned that the Langmuir equation may not always be strictly valid over the range of concentrations employed in an investigation. A mathematical analysis of the data would validate this point.

TABLE 2
Properties of GAC

GAC	Origin	Surface area of N_2-BET (m^2/g)	Particle density (g/cm^3)	Apparent density (g/cm^3)	True density (g/cm^3)	Pore volume (cm^3/g)	Porosity
RRL	Coconut shell	900	0.749	—	—	—	—
CAL	Coal	1090	0.820	—	—	0.750	0.62
KURARE	—	1020	0.722	—	—	0.926	0.67
F 200	Bituminous coal	825	0.858	0.530	2.267	0.724	0.53
F 400	Bituminous coal	998	0.795	0.480	2.308	0.825	0.65
LCK	Coconut shell	1025	0.753	0.464	—	—	—

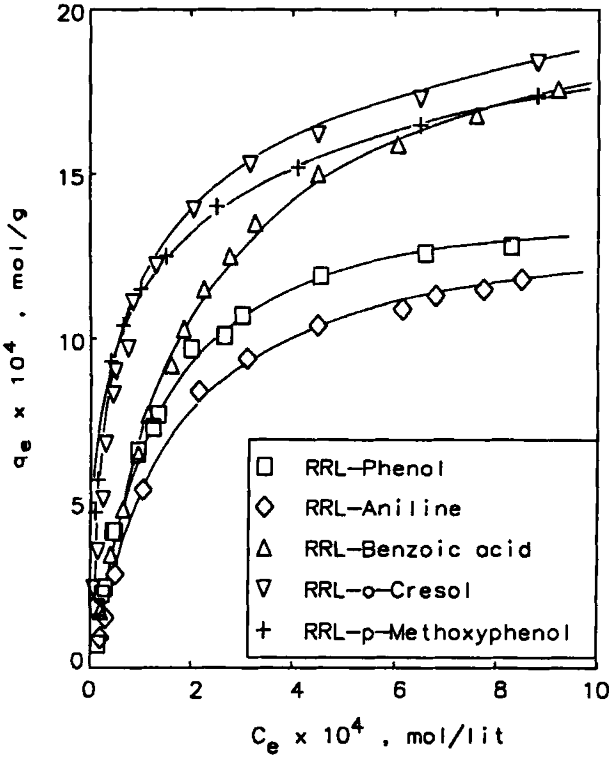

FIG. 1. Adsorption isotherms.

The Freundlich equation is basically empirical but is often useful as a means for data description. It generally agrees quite well with the Langmuir equation and experimental data over a moderate range of adsorbate concentrations. The equation is

$$q_e = k(c_e)^{\beta} \tag{3}$$

where q_e and c_e have the same significance, and k and β are constants. The relation is merely indicative of the adsorption capacity and intensity. It can easily be verified by using the relation in the form

$$\log q_e = \log k + \beta \log c_e \tag{4}$$

whereby a plot of log q_e versus log c_e should be linear, bringing out the validity of the equation.

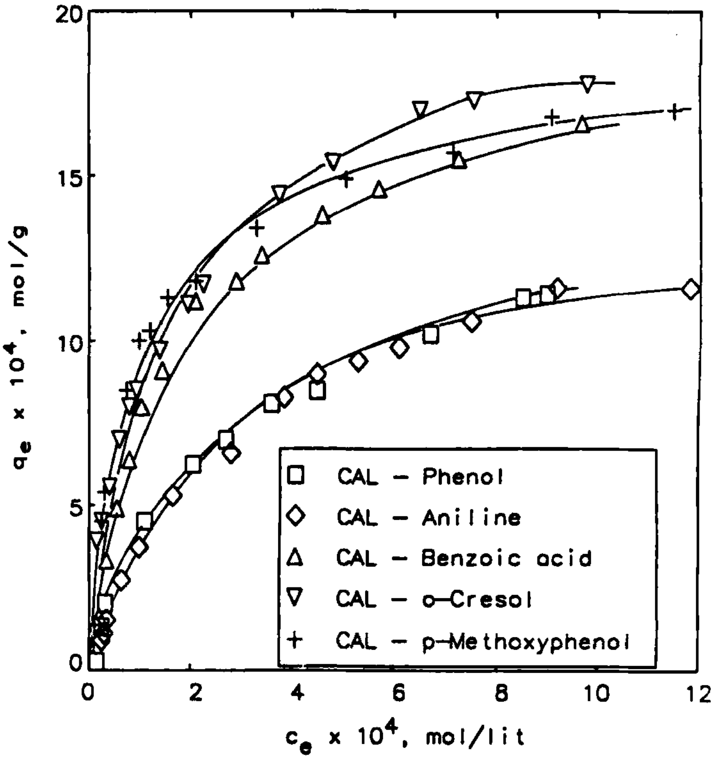

FIG. 2. Adsorption isotherms.

Data on treatment of the adsorption isotherms according to both the Langmuir equation and the Freundlich equation are given in Table 3 for all combinations of adsorbate and adsorbent. The equations were obtained by the method of linear regression of the data, which obeyed the linearity fairly satisfactorily. This table also gives the c_e range over which a given system adheres to the linearity of the relations. The values of the regression coefficients, r, are all mostly around 0.99, indicating a very good mathematical fit. The Langmuir equations for these systems also help in determining the surface area of the adsorbent under the present conditions of the experiment. Estimation of the specific surface areas of the GAC are conventionally based upon measurements of the capacity of the adsorbent for a selected solute having a well-accepted molecular cross-sectional area. This is usually done by using the isothermal equilibrium data for determining the monolayer capacity of the adsorbent, expressed in mol/g of

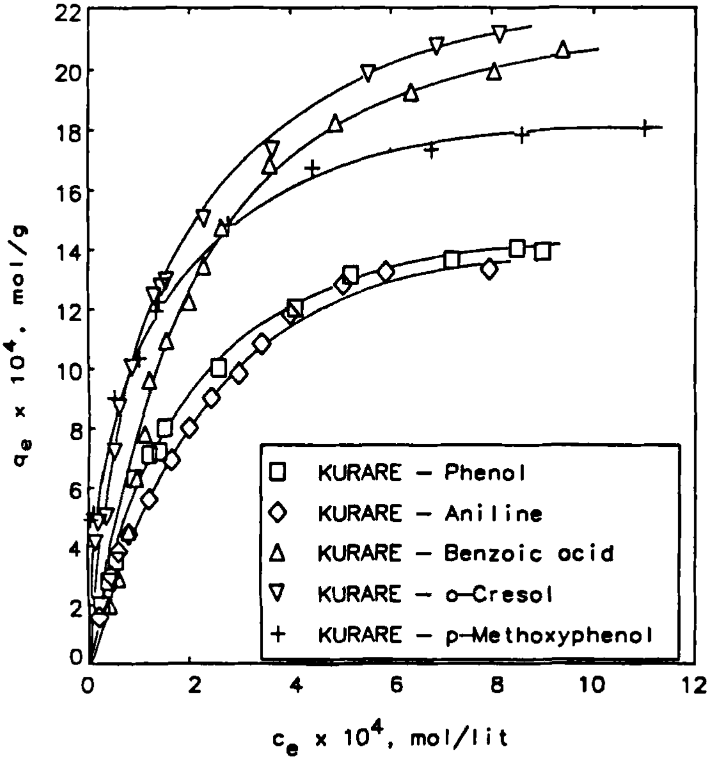

FIG. 3. Adsorption isotherms.

GAC, and related to the surface area by using either the Langmuir equation for monomolecular adsorption or the BET equation for multimolecular adsorption.

RESULTS AND DISCUSSION

A glance at the isotherms, Figs. 1–6, shows the phenol is adsorbed to a maximum extent by both KURARE and RRL–GAC while all other GAC samples show fairly similar lower value. In all GAC samples it is found that *o*-cresol is adsorbed to a larger extent as compared to the other adsorbates under the same conditions. Strikingly, it is found that while phenol and aniline class themselves into one category in terms of adsorption isotherms, benzoic acid, *o*-cresol, and *p*-methoxyphenol can be classified into a different one in all GAC samples. In terms of relative adsorption trends in practically all GAC samples, the increase of adsorption follows the trend:

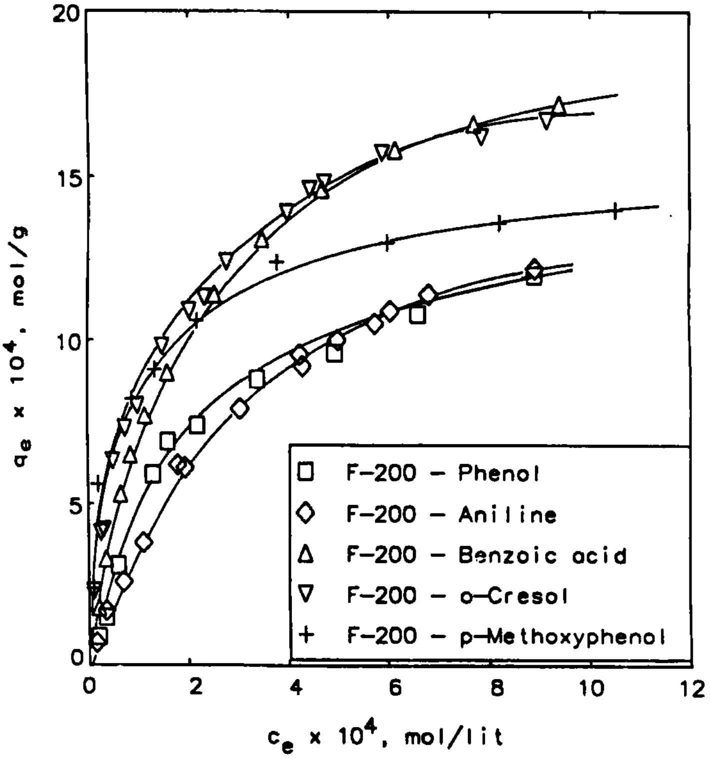

FIG. 4. Adsorption isotherms.

aniline < phenol < benzoic acid < *p*-methoxyphenol < *o*-cresol at lower values of equilibrium concentration, while for higher equilibrium concentration values the benzoic acid interchanges its position with *p*-methoxyphenol and *o*-cresol in some systems. Since the solubility of the adsorbate is a measure of the adsorbate solvent forces of attraction, any change in solubility of a molecule will influence adsorbate adsorbent forces of attraction. If we consider the solubility of the adsorbates used in the present work, the trend is benzoic acid < *o*-cresol < aniline < *p*-methoxyphenol < phenol, which is in accordance with the literature (*3*) that a hydrophobic substance will be more likely adsorbed from aqueous solution. This is explained by the trend of adsorption of phenol and aniline, which are less adsorbed compared to the other three solutes. The near coincidence of the isotherms for phenol and aniline suggests that these compounds may have similar energies of interaction at the carbon surface. The monolayer

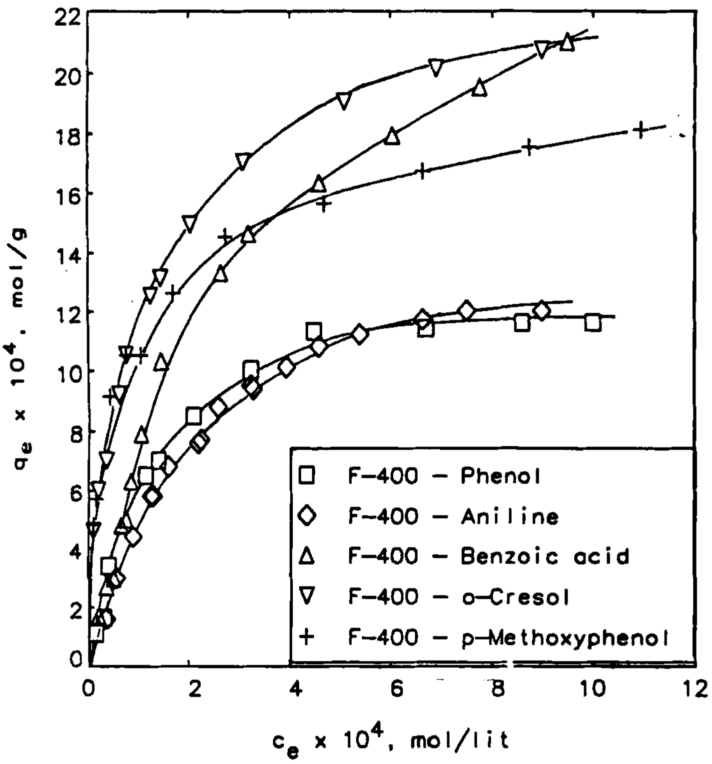

FIG. 5. Adsorption isotherms.

capacity, Q°, as seen from Table 3, is higher for benzoic acid for all the GAC–benzoic acid systems as compared to the other systems. This may also be attributed to the fact that benzoic acid is the most hydrophobic (least soluble) of the adsorbates studied in this work.

The alkyl-substituted phenols are more strongly adsorbed (*4*) as compared to phenol itself, and adsorption increases as the length of the alkyl chain increases, which explains the larger extent of adsorption of *o*-cresol in spite of its high solubility and *p*-methoxyphenol as compared to phenol. The large extent of adsorption of *p*-methoxyphenol may also be because it can effectively desorb (*5*) phenol from the adsorbent surface, indicating preferential adsorption of *p*-methoxyphenol compared to phenol.

A pure carbon surface is considered to be nonpolar, but in actual practice some carbon–oxygen complexes are usually present, which render the surface slightly polar. Since there is no satisfactory method for determining

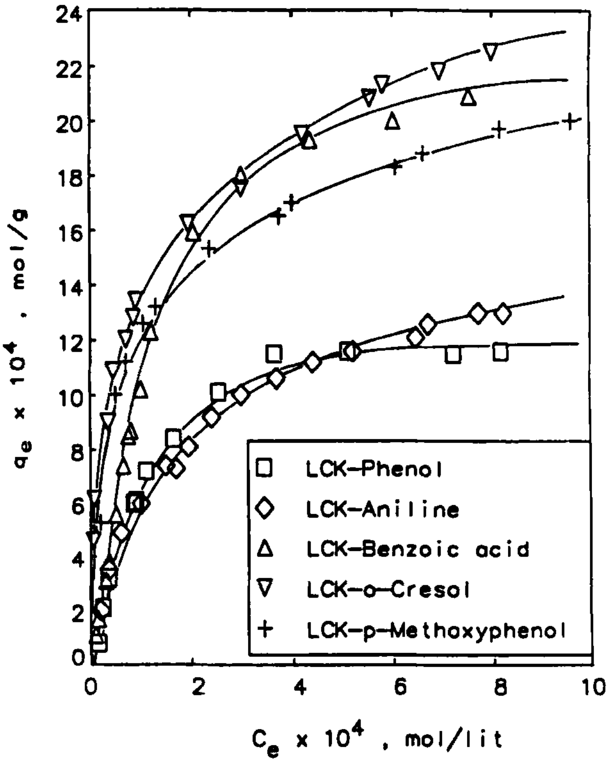

FIG. 6. Adsorption isotherms.

the polar character of the surface quantitatively, the above statement is relative. Previous investigations (*6*) indicated that adsorption of phenol from dilute aqueous solutions by carbon black was enhanced considerably when an acidic CO_2-surface complex was eliminated and the CO-complex predominated. As phenol is slightly acidic in nature, the acidic surface complex may reduce the adsorption of phenol and increase the adsorption of aniline which is basic in character. Since the extent of adsorption of aniline and phenol is nearly the same, as observed from the adsorption isotherms, it may be said that the acidic surface oxides are absent on the surface of the adsorbents used in this work. Since all the adsorbents were procured from various sources and were used after preliminary treatment without our knowing the details of the manufacturing and activation processes, this aspect cannot be discussed in detail because the activation process determines the nature of the carbon surface. However, the chem-

TABLE 3
Adsorption Isotherm Data

		Freundlich isotherm			Langmuir isotherm			
Adsorbent	Adsorbate	Equation	r	$c_e \times 10^4$ (mol/L)	Equation	r	$Q^\circ \times 10^4$ (mol/L)	$c_e \times 10^4$ (mol/L)
RRL	Phenol	$q_e = 122.70c_e^{0.3771}$	0.98	1.25–4.55	$q_e = \frac{11.950c_e}{1 + 7936c_e}$	0.99	15.0579	0.45–8.30
CAL	Phenol	$q_e = 33.45c_e^{0.5370}$	0.99	0.32–6.70	$q_e = \frac{5.7636c_e}{1 + 3985c_e}$	0.98	14.4632	1.00–9.00
KURARE	Phenol	$q_e = 91.68c_e^{0.4268}$	0.99	0.90–5.20	$q_e = \frac{8.4388c_e}{1 + 4357c_e}$	0.98	19.3684	0.55–8.50
F 200	Phenol	$q_e = 113.70c_e^{0.3471}$	0.99	1.30–8.90	$q_e = \frac{6.7159c_e}{1 + 4439c_e}$	0.99	15.1293	0.60–8.90
F 400	Phenol	$q_e = 92.34c_e^{0.3972}$	0.96	0.40–8.60	$q_e = \frac{11.3417c_e}{1 + 8517c_e}$	0.99	13.3165	0.40–10.00
LCK	Phenol	$q_e = 89.43c_e^{0.4359}$	0.99	0.90–3.65	$q_e = \frac{13.1527c_e}{1 + 11009c_e}$	0.92	11.9472	0.35–7.20
RRL	Aniline	$q_e = 39.79c_e^{0.5448}$	0.96	1.05–8.50	$q_e = \frac{7.0077c_e}{1 + 4443c_e}$	0.99	15.7724	0.50–8.50
CAL	Aniline	$q_e = 38.05c_e^{0.5081}$	0.99	1.00–9.20	$q_e = \frac{4.8262c_e}{1 + 3200c_e}$	0.99	15.0819	0.35–11.80
KURARE	Aniline	$q_e = 31.00c_e^{0.6064}$	0.99	0.45–5.05	$q_e = \frac{7.9302c_e}{1 + 4726c_e}$	0.99	16.7799	0.45–7.95
F 200	Aniline	$q_e = 60.97c_e^{0.4496}$	0.99	3.05–6.80	$q_e = \frac{4.3687c_e}{1 + 2272c_e}$	0.99	19.2284	0.50–9.00
F 400	Aniline	$q_e = 61.42c_e^{0.4685}$	0.99	1.25–5.40	$q_e = \frac{6.7935c_e}{1 + 4178c_e}$	0.99	16.2602	0.50–9.00

(*continued*)

TABLE 3 (*continued*)

		Freundlich isotherm			Langmuir isotherm			
Adsorbent	Adsorbate	Equation	r	$c_e \times 10^4$ (mol/L)	Equation	r	$Q^\circ \times 10^4$ (mol/L)	$c_e \times 10^4$ (mol/L)
LCK	Aniline	$q_e = 85.20c_e^{0.4195}$	0.99	0.35–6.70	$q_e = \frac{9.4697c_e}{1 + 6231c_e}$	0.99	15.1977	1.00–8.20
RRL	Benzoic acid	$q_e = 30.27c_e^{0.6681}$	0.99	0.40–3.25	$q_e = \frac{10.4493c_e}{1 + 4702c_e}$	0.98	22.2089	0.20–9.20
CAL	Benzoic acid	$q_e = 171.04c_e^{0.3394}$	0.99	1.05–7.25	$q_e = \frac{11.6198c_e}{1 + 5960c_e}$	0.99	19.4963	0.20–9.70
KURARE	Benzoic acid	$q_e = 100.51c_e^{0.4740}$	0.99	1.20–4.90	$q_e = \frac{11.1607c_e}{1 + 4107c_e}$	0.98	27.1748	0.95–9.40
F 200	Benzoic acid	$q_e = 61.64c_e^{0.5257}$	0.99	0.65–3.50	$q_e = \frac{11.0375c_e}{1 + 5497c_e}$	0.99	20.0791	0.35–9.40
F 400	Benzoic acid	$q_e = 166.01c_e^{0.3716}$	0.99	1.45–9.50	$q_e = \frac{8.6058c_e}{1 + 2633c_e}$	0.99	32.6844	0.20–9.50
LCK	Benzoic acid	$q_e = 11.64c_e^{0.9819}$	0.99	0.10–1.20	$q_e = \frac{14.9254c_e}{1 + 5015c_e}$	0.99	29.7615	0.50–7.55
RRL	*o*-Cresol	$q_e = 350.90c_e^{0.2498}$	0.98	0.50–8.40	$q_e = \frac{31.2500c_e}{1 + 16750c_e}$	0.98	18.6567	0.25–6.50

CAL	*o*-Cresol	$q_e = 137.60c_e^{0.4005}$	0.98	0.15–6.50	$q_e = \frac{20.4918c_e}{1 + 12701c_e}$	0.98	16.1340	0.40–4.80
KURARE	*o*-Cresol	$q_e = 213.80c_e^{0.3521}$	0.99	0.60–6.90	$q_e = \frac{19.2641c_e}{1 + 7898c_e}$	0.99	24.3911	0.35–8.15
F 200	*o*-Cresol	$q_e = 141.30c_e^{0.3821}$	0.99	0.50–5.90	$q_e = \frac{19.3050c_e}{1 + 12896c_e}$	0.99	14.9697	0.30–2.80
F 400	*o*-Cresol	$q_e = 195.16c_e^{0.3769}$	0.99	0.10–5.00	$q_e = \frac{25.1889c_e}{1 + 11511c_e}$	0.98	21.8825	0.75–9.00
LCK	*o*-Cresol	$q_e = 346.70c_e^{0.2922}$	0.99	0.07–6.95	$q_e = \frac{32.5733c_e}{1 + 13909c_e}$	0.98	23.4189	0.45–8.00
RRL	*p*-Methoxyphenol	$q_e = 449.80c_e^{0.2018}$	0.99	0.40–8.80	$q_e = \frac{37.5940c_e}{1 + 21955c_e}$	0.98	17.1232	0.65–8.80
CAL	*p*-Methoxyphenol	$q_e = 333.50c_e^{0.2382}$	0.99	1.00–7.15	$q_e = \frac{21.8962c_e}{1 + 12656c_e}$	0.99	17.3010	0.75–11.50
KURARE	*p*-Methoxyphenol	$q_e = 321.70c_e^{0.2661}$	0.99	0.20–3.80	$q_e = \frac{22.0945c_e}{1 + 12228c_e}$	0.99	18.0688	1.00–11.00
F 200	*p*-Methoxyphenol	$q_e = 259.70c_e^{0.2573}$	0.99	0.20–6.00	$q_e = \frac{19.3274c_e}{1 + 13104c_e}$	0.99	14.7492	1.00–12.80
F 400	*p*-Methoxyphenol	$q_e = 387.30c_e^{0.2272}$	0.99	0.42–6.65	$q_e = \frac{28.8267c_e}{1 + 15967c_e}$	0.97	18.0539	0.75–10.95
LCK	*p*-Methoxyphenol	$q_e = 421.01c_e^{0.2305}$	0.99	0.50–9.60	$q_e = \frac{28.4171c_e}{1 + 13811c_e}$	0.98	20.5757	1.00–9.60

ical nature of the surface is considered secondary in significance in relation to the major factor, the magnitude of the surface area.

It is quite evident from the performance of all GAC samples used in the present investigation that indigenous RRL is worthy of finding a place in the several commercial standard grades of GAC available.

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NOMENCLATURE

b	constant in Eq. (1)
c_e	equilibrium concentration of adsorbate (mol/L)
q_e	adsorbent phase concentration at equilibrium (mol/g)
Q°	monolayer capacity of the adsorbent (mol/g)
k	constant in Eq. (3)
β	constant in Eq. (3)

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