



Modeling studies on simultaneous adsorption of phenol and resorcinol onto granular activated carbon from simulated aqueous solution

Shashi Kumar, Mohd. Zafar, Jitendra K. Prajapati, Surendra Kumar*, Sivaram Kannepalli

Chemical Engineering Department, Indian Institute of Technology Roorkee, Roorkee 247 667, Uttarakhand, India

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ABSTRACT

The modelling study on simultaneous adsorption of phenol and resorcinol onto granular activated carbon (GAC) in multicomponent solution was carried out at 303 K by conducting batch experiments at initial concentration range of 100–1000 mg/l. Three equilibrium isotherm models for multicomponent adsorption studies were considered. In order to determine the parameters of multicomponent adsorption isotherms, individual adsorption studies of phenol and resorcinol on GAC were also carried out. The experimental data of single and multicomponent adsorption were fitted to these models. The parameters of multicomponent models were estimated using error minimization technique on MATLAB R2007a. It has been observed that for low initial concentration of adsorbate (100–200 mg/l), modified Langmuir model represents the data very well with the adsorption constant (Q_0), 216.1, 0.032 and average relative error (ARE) of 8.34, 8.31 for phenol and resorcinol respectively. Whereas, for high initial concentration of adsorbate (400–1000 mg/l), extended Freundlich model represents the data very well with adsorption constant (K_F) of 25.41, 24.25 and ARE of 7.0, 6.46 for phenol and resorcinol respectively. The effect of pH of solution, adsorbent dose and initial concentrations of phenol and resorcinol on adsorption behaviour was also investigated.

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1. Introduction

Water pollution by organic chemicals is a major problem over decades. Owing to this, there is growing public concern over the contamination of groundwater by organic compounds. The removal of organic contaminants from groundwater or separation of contaminants present in polluted water has become a major focus of research and policy debate. The presence of these compounds even at low concentrations can be an obstacle for the reuse of water [1]. These organic compounds constitute a very large group of pollutants in the wastewater. Amongst them aromatic compounds especially phenol and its derivatives such as resorcinol, catechol, and cresols are widely found in the effluent of many industries [2]. These pollutants are harmful and toxic to organisms at low concentrations and considered to be carcinogenic when present in high amounts [3].

Phenol is present in the surface water of industrial effluents such as coal tar, gasoline, plastic, rubber-proofing, coking, pharmaceutical and steel industries, domestic wastewaters and chemical

spillage [4]. Resorcinol is found in the effluents of many industries such as textile, paper and pulp, steel, petrochemical, petroleum refinery, rubber, dyes, plastics, pharmaceutical, cosmetics etc., and in synthetic coal fuel conversion process wastewater. The effluents from the synthetic coal fuel conversion processes may contain high concentrations of resorcinol, which varies in the range from a few mg/l to more than 1000 mg/l [5]. The Ministry of Environment and Forests (MOEF), Government of India and Environmental Protection Agency (EPA), USA, have listed phenol and phenolic compounds on the priority pollutants list. Phenol is highly toxic and difficult to degrade biologically, has led to setting up of rigid limits on the acceptable level of phenol in the environment. The MOEF has set a maximum concentration level of 1.0 mg/l of phenol in the industrial effluents for safe discharge into surface water. World Health Organization (WHO) recommends the permissible phenolic concentration of 0.001 mg/l in potable water [6].

There are many methods to treat phenolic compounds from wastewater such as chemical oxidation, coagulation, aerobic or anaerobic biodegradation, solvent extraction, liquid membrane permeation and adsorption by ion-exchange resin and activated carbon [7]. Amongst these methods, adsorption by activated carbon is a very efficient technology for the removal of contaminants from wastewater and has gained a lot of popularity [3,8–10]. A number of single component adsorption studies have been reported onto various adsorbents from aqueous solutions [1–12]. Since industrial effluents contain several substances, it is necessary to

Abbreviations: MOEF, Ministry of Environment and Forests; EPA, Environmental Protection Agency; GAC, granular activated carbon; WHO, World Health Organization; UV–VIS, Ultraviolet–Visible.

* Corresponding author. Tel.: +91 1332285714; fax: +91 1332273560.

E-mail address: skumar@iitr.ernet.in (S. Kumar).

Nomenclature

a	constant in Toth model (mg/l) ⁿ
A_F	accuracy factor (–)
b	constant in Langmuir model (l/mg)
B_F	bias factor (–)
C_e	concentration of adsorbate in solution at equilibrium (mg/l)
$C_{e,i}$	concentration of <i>i</i> th component in the binary mixture at equilibrium (mg/l)
C_0	initial concentration of adsorbate in solution (mg/l)
k	constant in Radke–Prausnitz model (mg/g)/(mg/l) ^{1/p}
K_F	constant in Freundlich model (mg/g)/(mg/l) ^{1/n}
$K_{F,i}$	constant in extended Freundlich model for <i>i</i> th component (mg/g)/(mg/l) ^{1/n}
K	constant in Radke–Prausnitz model (l/g)
K_1	constant in Redlich–Peterson model (l/g)
K_2	constant in Redlich–Peterson model (l/mg)
m	constant in Redlich–Peterson model (–)
n	constant in Freundlich model and in Toth model (–)
n_i	constant in extended Freundlich model for <i>i</i> th component (–)
N	number of data points in the experimental run (–)
ND	normalised deviation (–)
NSD	normalised Standard deviation (–)
p	constant in Radke–Prausnitz model (–)
q_e	amount of adsorbate adsorbed per gram of adsorbent at equilibrium (mg/g)
$q_{e,i}$	amount of <i>i</i> th component adsorbed per gram of adsorbent at equilibrium (mg/g)
q_e^∞	constant in Toth model (mg/g)
Q_0	constant in Langmuir model (mg/g)
$Q_{0,i}$	constant in modified Langmuir model for <i>i</i> th component (mg/g)
$q_{e,exp}$	experimental value of q_e (mg/g)
$q_{e,cal}$	predicted value of q_e (mg/g)
RMSE	root mean square error (–)
SEP	standard error of prediction (–)
t	time (h)
V	volume of solution (l)
W	weight of adsorbent (g)
x_i	constant in extended Freundlich model for <i>i</i> th component (–)
y_i	constant in extended Freundlich model for <i>i</i> th component (–)
z_i	constant in extended Freundlich model for <i>i</i> th component (–)
Greek letters	
α_1	constant in Fritz–Schlunder model (mg/g)/(mg/l) ^{β_1}
α_2	constant in Fritz–Schlunder model (mg/g)/(mg/l) ^{β_2}
β_1, β_2	constants in Fritz–Schlunder model (–)
η_i	correction parameter of <i>i</i> th component in modified Langmuir model (–)
η_{ij}	correction parameter of <i>i</i> th component in <i>j</i> th experiment in modified Langmuir model (–)

study the simultaneous adsorption of two or more compounds. Simultaneous adsorption experiments provide a wide range of information such as the fraction of sites being shared with each solute tested, their affinities towards these sites, and the lateral interaction between the solutes in the mixture solution. Thus, the study on equilibrium adsorption of organic compounds in binary

and ternary systems is very important. Very little amount of literature is available on the multicomponent adsorption of phenolic compounds onto activated carbon [13–22]. Kim et al. [21] studied the adsorption of phenol, p-chlorophenol (PCP) and p-nitrophenol (PNP) on activated carbon for single and multi-component systems. Srivastava and Tyagi [13] experimentally investigated the simultaneous adsorption equilibria of 4-nitrophenol, 2,4,6-trinitrophenol, 4-chlorophenol and 1,3-dihydroxybenzene onto activated carbon developed from fertilizer waste slurry in binary and multicomponent systems. Adsorption of p-cresol and p-nitrophenol by activated carbon in single and multi-component systems was also studied by Nouri [18]. Leitao and Serrao [20] studied the single and binary components adsorption studies of phenol and m-cresol on activated carbon. However, no information is available in literature for the simultaneous adsorption of phenol and resorcinol.

The aim of the present research work is to carryout modeling studies on the simultaneous adsorption of phenol and resorcinol from simulated aqueous solution onto granular activated carbon (GAC). In the process, the batch adsorption experiments for the simultaneous removal of phenol and resorcinol have been carried out at temperature 303 K and initial concentration range of 100–1000 mg/l. Using the experimental data, parameters of various available multicomponent adsorption isotherms have been estimated. The equilibrium adsorption isotherm equations proposed for single component adsorption have been extended and modified to represent the binary and multicomponent adsorption equilibria. Therefore, in order to fit the data for the multicomponent isotherms models, it is necessary to obtain the parameters of single component adsorption isotherm models. Thus, single component experimental studies have also been carried out prior to multicomponent adsorption studies and are briefly described in the present work. In addition, the effect of pH, adsorbent dose and initial concentration of phenol and resorcinol on adsorption behaviour, have been studied.

2. Materials and methods

2.1. Adsorbent and adsorbates

The commercially available activated carbon was granular LR grade in the size range of 2–5 mm supplied by S.D. Fine Chemicals, Boisar, India. It was partially grinded and sieved through 18–44 BS mesh to get average particle size of 0.536 mm. The sieved carbon was further washed many times with distilled water to remove any attached fines and leachable matter. After washing, it was dried in an oven at 105 °C for 72 h and stored in an air tight bottle. The phenol and resorcinol were of AR grade supplied by Qualigens, Fisher Scientific, Mumbai. The characteristics of this GAC are as follows: BET surface area = 686 m²/g; pH = 7.2 (1% solution); moisture content = 5.5%; ash content = 3.1%; bulk density = 0.977 g/ml; average particle size = 0.536 mm; average pore diameter = 18.60 Å; water soluble matter = 2.26%; acid soluble matter = 3.23%.

2.2. Batch adsorption experiments

Stock solutions of phenol and resorcinol were prepared by dissolving pure samples of the solute in the distilled water. For single solute system, batch adsorption studies were carried out in 250 ml stoppered conical flask in which 50 ml solution of known concentration of phenol or resorcinol was taken to study equilibrium isotherms and, the effect of different parameters like pH, initial concentration and adsorbent dose on the adsorption of phenol and resorcinol on to GAC.

In the present study, the concentrations of phenol and resorcinol were chosen to be in the range of 100–1000 mg/l (100, 200,

400, 600, 800, and 1000 mg/l). In each flask a fixed adsorbent dose in the range (1–10 g/l) was added. The pH was maintained in the range of 2–10 by adding HCl or NaOH as per requirement. The flasks were then transferred to a thermostat controlled shaking assembly (Metrex Scientific Instruments, New Delhi) at a temperature of 303 K and shaken at 150 rpm for 24 h to ensure that the adsorption process reached equilibrium.

Adsorption of binary component systems were conducted by following the above procedure except that the initial concentrations of phenol and resorcinol in the aqueous solutions were varied from 100 to 1000 mg/l (100, 200, 400, 600, 800, and 1000 mg/l) with a 1:1 molar ratio of phenol and resorcinol mixtures. Residual solution concentrations of phenol and resorcinol in single and binary component systems were analysed by UV–VIS spectrophotometer (DR 5000™, HACH, Germany) at wavelengths of 269 and 273 nm respectively. The absorbance obtained was used to calculate the equilibrium concentration based on a standard calibration curve prepared for both phenol and resorcinol with correlation coefficient (R^2) equal to 0.99. The amounts of phenol and resorcinol adsorbed onto the adsorbent at equilibrium q_e (mg/g) were calculated according to Eq. (1).

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

where V is the volume of the solution (l), and W is the weight of the adsorbent (g).

2.3. Modeling studies

2.3.1. Single component adsorption isotherm models

In single component adsorption, dynamic phase equilibrium is established in between adsorbate and adsorbent surface. An adsorption equilibrium isotherm relates the adsorbate loading on the adsorbent (q_e) and liquid phase concentration of adsorbate (C_e) at equilibrium condition keeping temperature constant. Thus, adsorption isotherm describes the interaction between adsorbate and adsorbent which is critical in optimizing the use of adsorbent amount. The models used to describe the experimental isotherm data are either theoretical or empirical equations based on the shape of the isotherm curve. The isotherm curve between q_e and C_e predicts the behaviour of the experimental data of phenol and resorcinol adsorption on activated carbon which is concave downwards. The slope is always positive and it decreases steadily as concentrations of phenol and resorcinol increase [2]. Out of several isotherm models available in the literature, six isotherm models have been chosen for the present study to correlate the data, namely Langmuir model [2,3,8,10], Freundlich model [2,3,8,10], Redlich–Peterson model [2,3,9,10], Toth model [2,3,9,10,23], Radke–Prausnitz model [2,10,24] and Fritz–Schlunder models [2,10,25,26]. The model equations are as follows:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e}; \quad \text{Langmuir model}$$

$$q_e = K_F C_e^{1/n}; \quad \text{Freundlich model}$$

$$q_e = \frac{K_1 C_e}{1 + K_2 C_e^m}; \quad \text{Redlich–Peterson model}$$

$$q_e = \frac{q_e^\infty C_e}{[a + C_e^n]^{1/n}}; \quad \text{Toth model}$$

$$\frac{1}{q_e} = \frac{1}{K C_e} + \frac{1}{k C_e^{1/p}}; \quad \text{Radke–Prausnitz model}$$

$$q_e = \frac{\alpha_1 C_e^{\beta_1}}{1 + \alpha_2 C_e^{\beta_2}}; \quad \text{Fritz–Schlunder model}$$

The main purpose to carry out single component adsorption studies is to evaluate the best model among the above mentioned models and to estimate the parameters of the models used in multi-component adsorption studies. The best isotherm model is selected on the basis of correlation coefficient (R^2), accuracy factor (A_F) and bias factor (B_F) closer to unity and at the same time low values of statistical indices such as normalised deviation (ND), normalised standard deviation (NSD), root mean square error (RMSE), and standard error of prediction (SEP).

2.3.2. Multicomponent adsorption equilibrium isotherm models

The presence of more than one component in an aqueous solution causes interference and competition for adsorption sites which leads to a more complex mathematical formulation of the equilibrium. Therefore, the relationships between the adsorbed quantity of one component and the concentrations of all other components present in the aqueous solution are described by multicomponent adsorption isotherms [27]. To analyse the multicomponent adsorption behaviour, many isotherm models have been proposed. These models are non-modified and modified models. Non-modified models use parameters derived from single component models; whereas modified models use single component model parameters with correction factors [15,20].

2.3.2.1. Non-modified Langmuir model. One of the most widely used models in multicomponent systems is the non-modified Langmuir model [13,15,16,18–20,27]. This model predicts the amount of component ‘ i ’ adsorbed per unit weight of adsorbent ($q_{e,i}$) in the presence of other components at equilibrium which is given by Eq. (2).

$$q_{e,i} = \frac{Q_{0,i} b_i C_{e,i}}{1 + \sum_{j=1}^N b_j C_{e,j}} \quad (2)$$

where $C_{e,i}$ is the equilibrium concentration of component ‘ i ’ in a mixture consisting of N components and the constants $Q_{0,i}$ and b_i are the model parameters determined by fitting the single component adsorption equilibrium data of component ‘ i ’ alone to Langmuir model.

2.3.2.2. Modified Langmuir model. In many cases, single component adsorption isotherm model parameters fail to describe exactly the interaction between individual components in the mixture. In that case, addition of a correction factor to the non-modified model may make the model capable to depict the complexity of the adsorption process. The modified Langmuir model [20,27] is given by Eq. (3).

$$q_{e,i} = \frac{Q_{0,i} b_i (C_{e,i} / \eta_i)}{1 + \sum_{j=1}^N b_j (C_{e,j} / \eta_j)} \quad (3)$$

where $Q_{0,i}$ and b_i are derived from corresponding single component Langmuir model and η_i is the correction parameter of component ‘ i ’, which is the characteristic of each species and depends upon the concentrations of all other components in the solution. The values of the correction parameters (η_i) can be determined from the experimental data on multicomponent system.

2.3.2.3. Extended Freundlich model. The extended Freundlich model [17,28] equations for binary system are given by Eqs. (4) and (5).

$$q_{e,1} = \frac{K_{F,1} C_{e,1}^{n_1+x_1}}{C_{e,1}^{x_1} + Y_1 C_{e,2}^{z_1}} \quad (4)$$

$$q_{e,2} = \frac{K_{F,2} C_{e,2}^{n_2+x_2}}{C_{e,2}^{x_2} + y_2 C_{e,1}^{z_2}} \quad (5)$$

where $K_{F,1}$, $K_{F,2}$, n_1 and n_2 are the constants of single component Freundlich isotherm model and x_1 , y_1 , z_1 , x_2 , y_2 and z_2 are the parameters of extended Freundlich model for first and second component.

2.3.3. Model validation

In order to evaluate the goodness of the fit of experimental data and the prediction accuracy of the models utilised in the present work, the following statistical indices are employed for the single component system [2,29,30].

$$B_F = 10 \left(\sum \log_{10}(q_{e,cal}/q_{e,exp}) / N \right) \quad (6)$$

$$A_F = 10 \left(\sum |\log_{10}(q_{e,cal}/q_{e,exp})| / N \right) \quad (7)$$

$$RMSE = \sqrt{\frac{\sum (q_{e,exp} - q_{e,cal})^2}{N}} \quad (8)$$

$$SEP = \frac{RMSE}{\sum q_{e,exp}/N} \times 100 \quad (9)$$

$$NSD = \sqrt{\frac{\sum [(q_{e,exp} - q_{e,cal})/q_{e,exp}]^2}{N}} \times 100 \quad (10)$$

$$ND = \sum \left| \frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right| \times \frac{100}{N} \quad (11)$$

where $q_{e,exp}$ is experimental value of q_e , $q_{e,cal}$ is the predicted value of q_e by models, N indicates the number of data points in the experimental run.

To evaluate the goodness of fit of experimental data for the binary system, the statistical indice average relative error (ARE) between the experimental and calculated values is used [27] as given by Eq. (12).

$$ARE = \sqrt{\frac{\sum_{i=1}^N \left(1 - \frac{q_{e,i,cal}}{q_{e,i,exp}} \right)^2}{N}} \times \frac{100}{N} \quad (12)$$

where $q_{e,i,exp}$ is the equilibrium experimental uptake value of component 'i', $q_{e,i,cal}$ is the predicted uptake value of component 'i' by model, and N indicates the number of experimental data points.

3. Results and discussion

3.1. Effect of adsorbent dose, pH, and initial concentration

The effect of adsorbent dose on the percent removal and uptake of phenol and resorcinol on GAC are shown in Fig. 1(a) and (b) respectively. Fig. 1(a) depicts that the percent removal of phenol increases with the increase in adsorbent dose upto 4 g/l after which the removal became constant with further increase in the adsorbent dose. Similarly in Fig. 1(b), the percent removal of resorcinol increases upto 5 g/l after which the removal becomes constant. The loading capacity in both the cases decreases with the increase in the adsorbent dose as shown in Fig. 1(a) and (b). Therefore, adsorbent dose of 4 g/l for phenol and of 5 g/l for resorcinol are considered as optimum dosages for the further studies. The effect of initial pH on the adsorption of phenol and resorcinol onto GAC is shown in Fig. 2(a). The limiting pH of solution is considered on the basis of pH_{pzc} . The experimental value of pH_{pzc} for GAC is found to be 7.2 [2]. Fig. 2(a) indicates that the percentage removal of phenol increases with the increase in pH upto 5 after which the removal

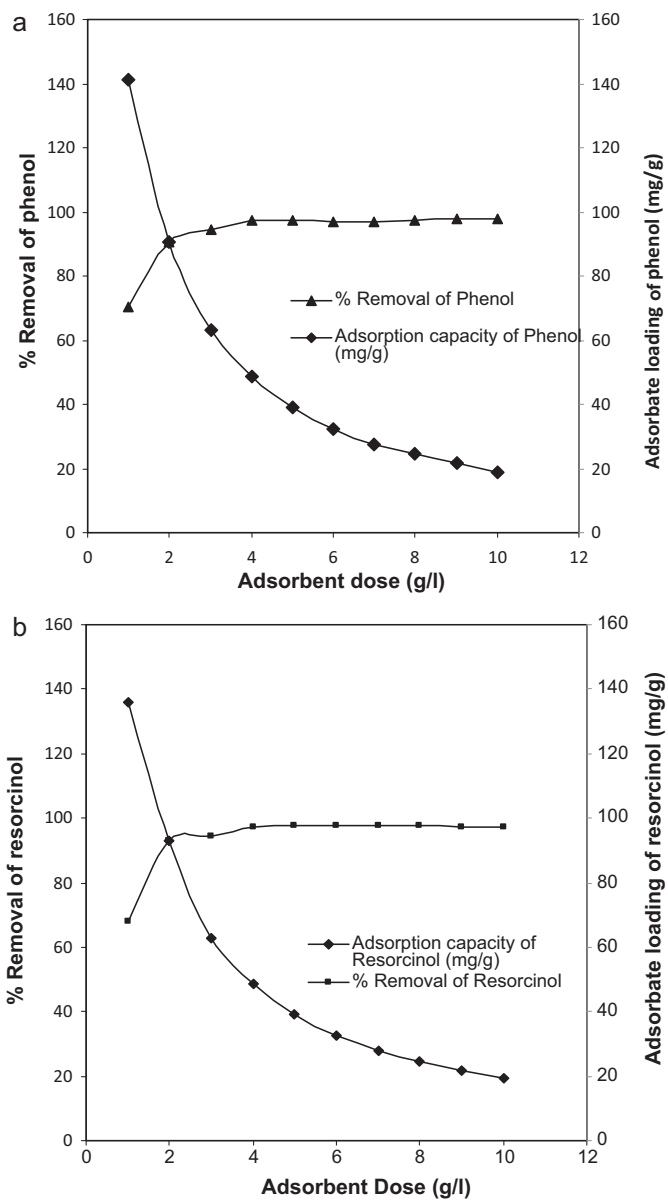


Fig. 1. Effect of adsorbent dose on the % removal and adsorbate loading of (a) phenol and (b) resorcinol.

decreases with the increase in pH. While for resorcinol, the percentage removal increases upto pH 3 after which the removal starts to decrease with the increase in pH. Hence, pH 5 and pH 3 are considered as optimum pH values for solution of phenol and resorcinol in all further adsorption experiments respectively. The effect of initial concentrations on uptake of phenol and resorcinol has been shown in Fig. 2(b). This figure shows that the % removal of phenol and resorcinol decreases with the increase in initial concentration, because high adsorbate concentration leads to saturation of the binding capacity of adsorbent, which consequently decreases the overall uptake [7].

3.2. Estimation of parameters of single component adsorption isotherm models

The adsorption equilibrium data for phenol and resorcinol onto GAC were analysed by non-linear curve fitting analysis, using MATLAB to fit the two parameter, three parameter and four parameter

Table 1
Adsorption equilibrium isotherm models parameters and statistical indices values of phenol and resorcinol onto GAC.

Adsorbate	Langmuir model			Freundlich model			Redlich–Peterson			
	Q_0	b	R^2	K_F	n	R^2	K_1	K_2	m	R^2
Phenol	216.1	0.032	0.996	25.41	2.618	0.957	7.963	0.055	0.928	0.998
Resorcinol	209	0.038	0.992	24.25	2.446	0.92	7	0.02	1.101	0.994

Adsorbate	Toth model				Radke–Prausnitz				Fritz–Schlunder				
	q_e^∞	a	n	R^2	K	k	$1/p$	R^2	α_1	α_2	β_1	β_2	R^2
Phenol	233.1	16.02	0.83	0.997	7.96	145.4	0.072	0.99	4.462	0.062	1.374	1.19	0.999
Resorcinol	189.8	90.98	1.337	0.995	8.02	207.9	0.001	0.99	4.904	0.032	1.237	1.19	0.995

Sl. no.	Models	Phenol						Resorcinol					
		ND	NSD	RMSE	SEP	B_F	A_F	ND	NSD	RMSE	SEP	B_F	A_F
1	Langmuir	2.4	2.61	3.52	3.13	0.99	1.02	11.45	20.80	5.13	5.33	1.06	1.10
2	Freundlich	21.9	33.7	12.8	11.3	1.09	1.20	31.30	53.40	15.9	16.5	1.15	1.26
3	Redlich–Peterson	3.32	4.11	2.6	2.31	1.01	1.03	10.36	16.86	4.60	4.78	1.05	1.09
4	Toth	3.49	4.13	2.98	2.65	1.01	1.03	9.81	15.35	4.42	4.59	1.03	1.00
5	Radke–Prausnitz	3.33	4.12	2.64	2.34	1.01	1.03	11.50	20.90	5.27	5.48	1.07	1.11
6	Fritz–Schlunder	2.69	3.9	1.6	1.42	0.99	1.02	9.18	13.28	4.42	4.59	1.02	1.09

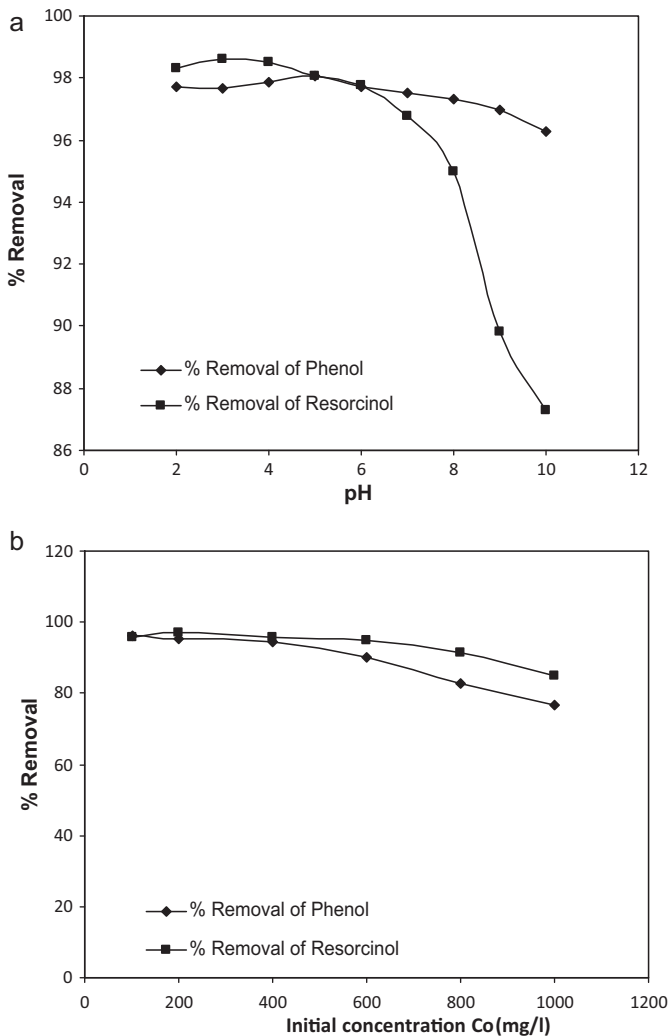


Fig. 2. Effect of (a) pH on % removal of phenol and resorcinol and (b) initial concentration on % removal of phenol and resorcinol.

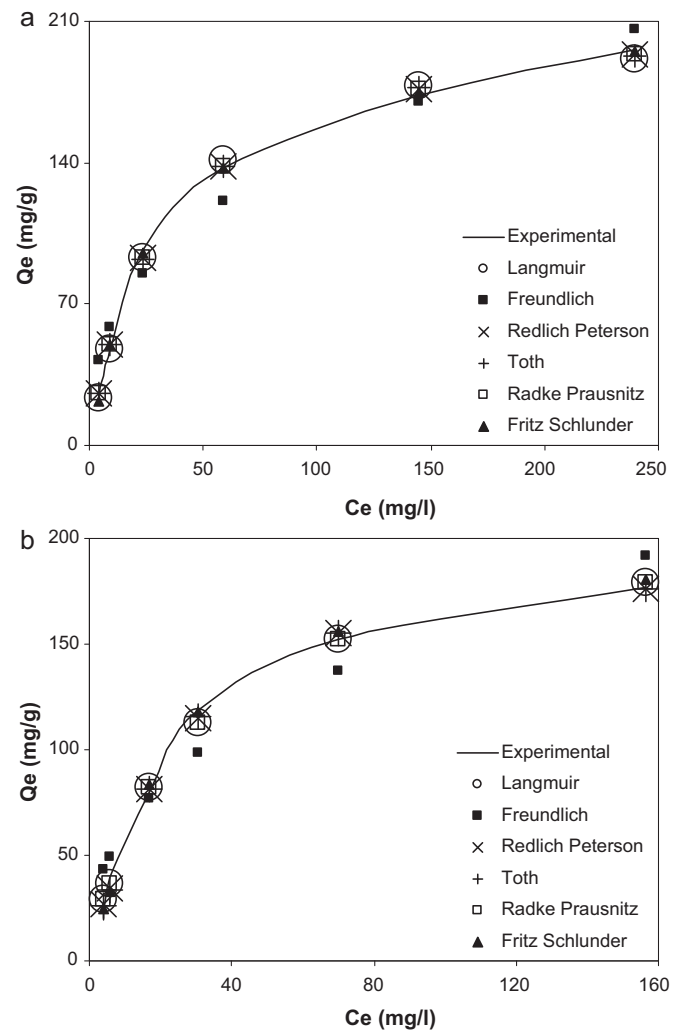


Fig. 3. Comparison of different isotherm models for adsorption of (a) phenol and (b) resorcinol on GAC.

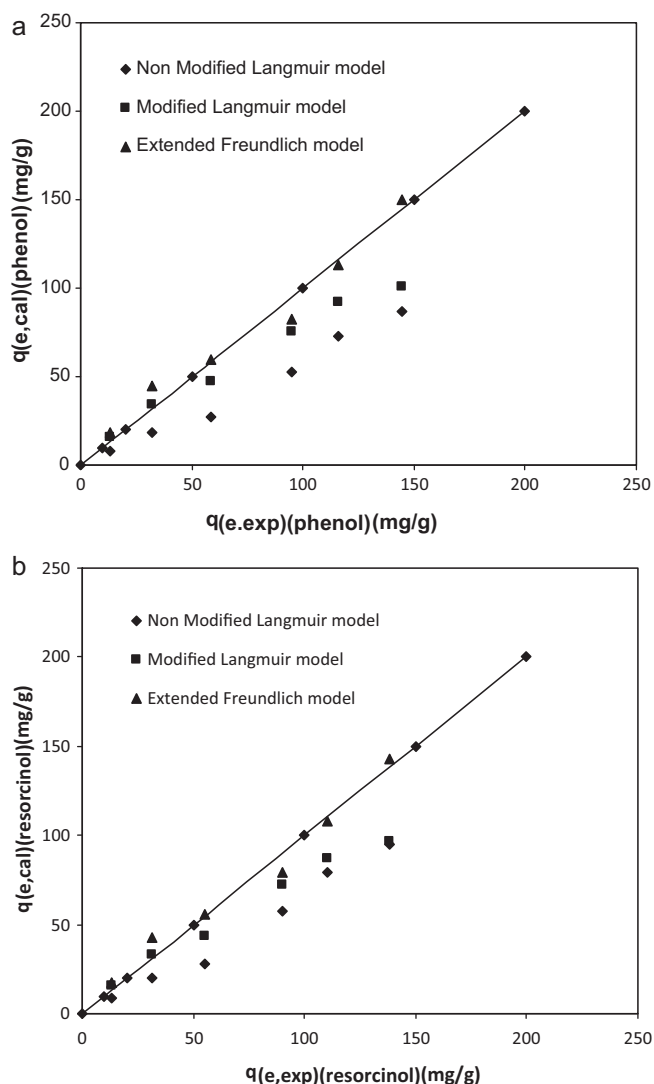


Fig. 4. Comparison of the experimental and calculated q_e values of (a) phenol in a binary mixture of phenol and resorcinol and (b) resorcinol in a binary mixture of phenol and resorcinol.

isotherm models. All the parameters of the six different isotherms and, the values of their corresponding correlation coefficients (R^2) and statistical indices of phenol and resorcinol for the isotherm models are tabulated in Table 1, while Fig. 3 provides the comparison between the six different isotherm models for phenol and resorcinol.

Based on the results listed in Table 1, best isotherm models fitted for phenol are determined in the order: (Langmuir > Fritz–Schlunder > Redlich–Peterson > Radke–Prausnitz > Toth > Freundlich) and for resorcinol in the order: (Fritz–Schlunder > Toth > Redlich–Peterson > Langmuir > Radke–Prausnitz > Freundlich). Between the two parameter models, the Langmuir model gives a better fit than the Freundlich model. The constant 'b' in the Langmuir isotherm model is an indicator of the favourability of adsorption through the determination of the dimensionless separation factor or equilibrium parameter R_L , given by $R_L = 1/(1 + bC_0)$ [2,31,32]. Here C_0 is the initial concentration of adsorbate (mg/l), and 'b' is Langmuir constant (l/g). This indicates the nature of adsorption as $R_L > 1$ (unfavourable), $0 < R_L < 1$ (favourable), $R_L = 0$ (irreversible), and $R_L = 1$ (linear). The values of R_L for all studies mentioned in the literature regarding adsorption of phenol and resorcinol on GAC at different operating conditions are in favourable range (Table 2). In the present investigation, the values of R_L have been found to

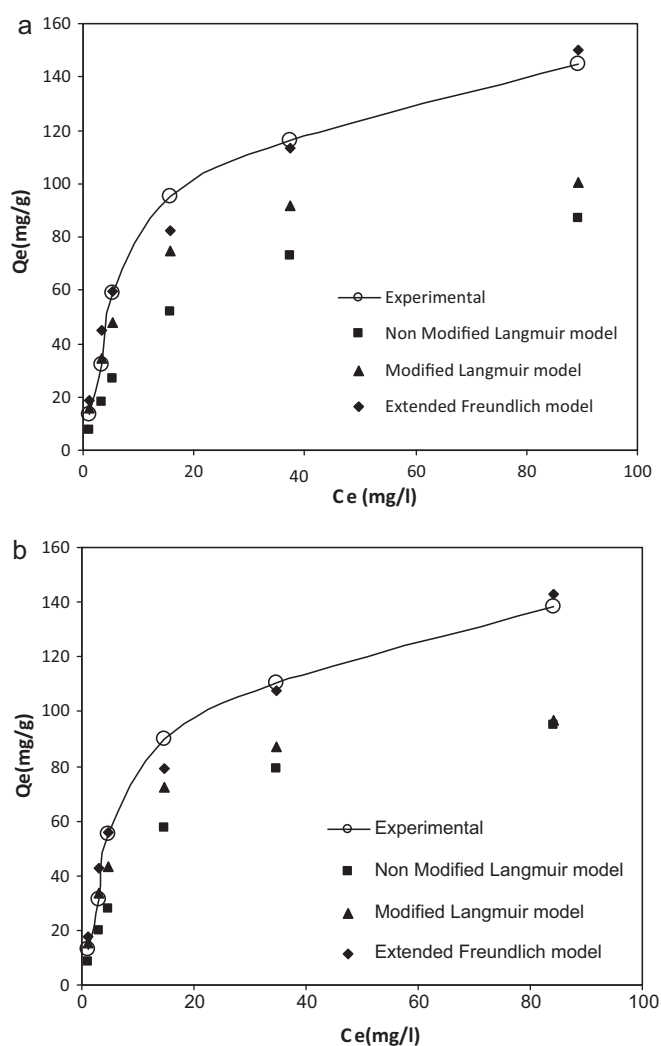


Fig. 5. Comparison of multicomponent isotherms for (a) phenol and (b) resorcinol.

be below 1.0 for both phenol and resorcinol on to GAC, showing that the adsorption of phenol and resorcinol on GAC is very much favourable under prevailing operating conditions.

It is obvious from Table 1 and Fig. 3 that the phenol has higher adsorbability than resorcinol onto GAC. This difference in adsorbability can be explained in terms of solubility of compounds, pH and density. The solubility of phenol is lesser than that of resorcinol in water, thus it is hydrophobic. In aqueous solutions, the adsorbate with higher hydrophobicity has higher tendency to be adsorbed onto carbon surface [31].

3.3. Multicomponent equilibrium studies

The binary component adsorption data of phenol and resorcinol onto GAC have been analysed by non-modified Langmuir model, modified Langmuir model and extended Freundlich model. The values of parameters of all these adsorption models are given in Table 3. The average relative error (ARE) between the experimental and calculated q_e values for phenol and resorcinol in the binary system are also tabulated in Table 3. The experimental and calculated ' q_e ' values of phenol and resorcinol in the aqueous solution are compared in Fig. 4(a) and (b). Fig. 4(a) and (b) indicates that since most of the data points fall around the 45° line, the multicomponent isotherm models could represent the experimental binary adsorption data with varying degree of fit. The multicomponent adsorption isotherm models used in our present

Table 2
Comparison of Langmuir adsorption isotherm parameters for adsorption of phenol and resorcinol on different activated carbons.

Sl. no.	Surface area	Temperature	Medium	Adsorbate concentration	Langmuir model		References
					Q_0	b	
Phenol							
1	3000–3500 m ² /g	30 °C	Aqueous	500 ppm	1.9189	3.444	[16]
2	800 m ² /g	20 °C	Aqueous	200 ppm	142.4	0.103	[19]
		40 °C		200 ppm	163.0	0.055	
3	929 m ² /g	21 °C	Aqueous	100 ppm	238.09	0.083	[7]
4	579 ± 17.02 m ² /g	29.9 ± 0.3 °C	Basic salt	1000 ppm	165.8	0.04	[9]
5	–	20 °C	Aqueous	100 ppm	49.72	0.12	[3]
6	686 m ² /g	30 °C	Aqueous	100–1000 ppm	216.1	0.032	Present study
Resorcinol							
1	579 ± 17.02 m ² /g	30 °C	Basic salt	1000 ppm	142.82	0.047	[5]
2	686 m ² /g	30 °C	Aqueous	100–1000 ppm	209.0	0.038	Present study

Table 3
Binary adsorption isotherm model parameters estimated in present study and in study of Leitao and Serrao [20].

Parameters and ARE	Present study Non-modified Langmuir model		Leitao and Serrao study [20] Non-modified Langmuir model	
	Phenol ($i = 1$)	Resorcinol ($i = 2$)	Phenol ($i = 1$)	m-Cresol ($i = 2$)
$Q_{0,i}$	216.1	0.032	142.4	142.4
b_i	209	0.038	0.103	0.207
ARE	18.033	15.012	14.6	15.9
Parameters and ARE	Modified Langmuir model		Modified Langmuir model	
	Phenol ($i = 1$)	Resorcinol ($i = 2$)	Phenol ($i = 1$)	m-Cresol ($i = 2$)
$Q_{0,i}$	216.1	0.032	142.4	142.4
b_i	209	0.038	0.103	0.207
η_i	0.44	0.5	0.999	0.365
ARE	8.34	8.31	6.2	6.6
Parameters and ARE	Extended Freundlich model		Extended Freundlich model	
	Phenol ($i = 1$)	Resorcinol ($i = 2$)	Phenol ($i = 1$)	m-Cresol ($i = 2$)
$K_{F,i}$	25.41	24.25	52.1	66.49
n_i	2.618	2.456	5.155	6.452
x_i	–1.08	–1.29	–4.09	–6.2
y_i	0.834	0.79	8.565	1.8
z_i	1.19	0.81	0.79	0.11
ARE	7.0	6.46	4.4	7.9

study are plotted in Fig. 5(a) and (b) for phenol and resorcinol respectively. From Fig. 5(a) and (b), it is clear that the extended Freundlich model represents the best fit for higher equilibrium concentrations and the modified Langmuir model represents the best fit for low equilibrium concentrations of phenol and resorcinol. The multicomponent non-modified Langmuir model shows a very poor fit to the experimental data with a very high average relative error for both phenol and resorcinol (ARE = 18.033 and ARE = 15.012 respectively). The values of the correction factors for modified Langmuir model are less than 1.0 (Table 3) indicating that the modified Langmuir model could predict the binary adsorption equilibrium data very well [20]. The use of the correction factors (η_1 and η_2) slightly improves the fit of the modified Langmuir model with an average relative error (ARE = 8.34 and ARE = 8.31 for phenol and resorcinol respectively). The extended Freundlich model fitted the binary adsorption data well with a low average relative error (ARE = 7.0 and ARE = 6.46 for phenol and resorcinol respectively). This indicates its ability to fit the binary adsorption data better than the other models. The similar conclusions have been made by Leitao and Serrao [20] as illustrated in Table 3.

3.4. Comparison and validation of multicomponent equilibrium isotherm models

The model results obtained in the present study on binary adsorption of phenol and resorcinol onto GAC, have been compared

with the results of experimental studies reported in the literature. For this purpose, the experimental studies of Leitao and Serrao [20] on adsorption of phenol and m-cresol on activated carbon have been considered. Leitao and Serrao [20] carried out batch-type experiments to obtain adsorption equilibrium data for single and binary component systems. The solution was fed to 250 cm³ jacketed narrow neck bottles closed with stoppers which were placed in a shaker at constant temperature of 20 °C and 40 °C. The single component adsorption isotherm data were correlated in the range of concentration upto 200 mg/l at 20 °C and 40 °C. In the binary component adsorption, the adsorption isotherm data were measured at 20 °C with two different initial concentrations of phenol and m-cresol; one at 200 mg/l each in solution and other at 100 mg/l each in solution. The adsorption isotherms for binary component systems were predicted solely on the basis of single component equilibrium isotherm parameters. The experimental data of Leitao and Serrao [20] are fitted to three multicomponent adsorption isotherm models considered in the present study viz., non-modified Langmuir model, modified Langmuir model, and extended Freundlich model. The values of the isotherm model parameters and corresponding average relative error (ARE) estimated for Leitao and Serrao [20] studies are mentioned in Table 3. It can be seen that for phenol and resorcinol, the parameters and ARE values are of same order of magnitude as estimated for phenol and m-cresol using experimental data of Leitao and Serrao [20]. The extended Freundlich model has wide applicability as reported in literature. For instance,

adsorption isotherm in the studies of Leitao and Serrao [20] on simultaneous adsorption of phenol and *m*-cresol are described by extended Freundlich model. In the present study, the simultaneous adsorption of phenol and resorcinol on GAC also follows extended Freundlich model. However, in the studies of Liu and Sorial [33], the ideal adsorption solution theory (IAST) predicts the multicomponent adsorption of phenolic compounds on GAC very well.

4. Conclusion

The adsorption of phenol and resorcinol onto GAC has been studied using single and binary component systems in aqueous solutions at 303 K. The simultaneous adsorption of phenol and resorcinol on GAC shows that extended Freundlich model gives a best fit with experimental observations. It has been observed that for low initial concentrations of the adsorbates i.e. 100–200 mg/l, modified Langmuir model represents the data very well and at high initial concentrations of adsorbates i.e. 400–1000 mg/l, extended Freundlich model gives better result. It is our view that these models would be useful for the design of continuous adsorption column for simultaneous adsorption of phenol and resorcinol.

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