

# Adsorption of phenol and 4-nitrophenol on granular activated carbon in basal salt medium: Equilibrium and kinetics

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## Abstract

Batch studies were carried out for studying the adsorption behaviour of phenol and 4-nitrophenol on granular activated carbon from a basal salt medium (BSM) at pH  $\approx 7.1$  and temperature  $\approx 30^\circ\text{C}$ . The literature review was done in order to review the information for comparison purposes on equilibrium models of phenol and 4-nitrophenol adsorption on activated carbon. The units for measurements reported in these models were found to be diverse, thus making the comparison difficult. These units have been converted into similar units for easy reference. In all, six models of Freundlich, Langmuir, Redlich–Peterson, Radke–Prausnitz, Toth and Fritz–Schlunder as reported in the literature have been fitted to the data of phenol/activated carbon and 4-nitrophenol/activated carbon systems of the present studies using nonlinear regression technique.

Based on maximum deviations and correlation coefficients, Langmuir gave the poorest fit for both compounds; Redlich–Peterson, Radke–Prausnitz, and four parameter model of Fritz–Schlunder could represent the data with similar accuracy, i.e. with  $R^2$ -value of 0.98 and maximum deviation  $\approx 12\%$ . However, for phenol, two parameter model of Freundlich may be recommended because of ease in its parameter estimation and better accuracy. 4-Nitrophenol was found to be more adsorbed than phenol, which is consistent with the result found in literature. The kinetics of the adsorption was found to be intra-particle diffusion controlled with diffusion coefficient values of the order of  $10^{-13} \text{ m}^2/\text{s}$ . Three distinct phases of kinetics – rapid, medium, and slow – have been observed in this study.

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## 1. Introduction

Phenol and 4-nitrophenol form the part of effluents of many industries such as petrochemicals, petroleum refineries, coke-oven, steel foundry, insecticides and herbicides industries, etc., to name a few. These are toxic and carcinogenic in nature and hence found place on priority pollutant list of EPA, USA. They pose danger to the flora and fauna in the biosphere, therefore, it is mandatory to remove these compounds from the effluents before safe disposal into the surface waters [1]. Various treatment technologies with their inherent limitations and merits are available. These include catalytic wet air oxidation, biological degradation, adsorption, UV-oxidation, etc. Sometimes, they work well in synergy, hence nowadays, a combination of the technologies are also in vogue; for example, adsorption along with

biological degradation wherein both supplement each other. Biological processes are sensitive to pH and temperature, whereas in adsorption, the nature of the process is such that the adsorbent gets saturated over a period of time. Either this has to be thrown or to be regenerated, hence making the adsorption option to be energy and capital intensive. The intentional growth of bacterial film has been found to increase the adsorbent service life. This combined process is known as biological activated carbon (BAC) treatment processes.

For the design of adsorbers, the knowledge of adsorption kinetics and adsorbent's capacity is essential. These depend on many factors such as pH, temperature, chemistry of the adsorbate–adsorbent system, and composition of the solution. The capacity of an adsorbent is characterized by isotherm. Literature review related to the isotherm studies of phenol/activated carbon and 4-nitrophenol-activated carbon system was done. It was found that various isotherm models have been fitted to represent the data of above systems. Further, it was noted that these studies report isotherm parameters values using different units

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### Nomenclature

$a$	constant in Toth isotherm (mg/l) <sup>th</sup>
$1/n$	constant in Freundlich isotherm
$b$	constant in Langmuir isotherm (l/mg)
$C_e$	concentration of adsorbate in solution at equilibrium (mg/l)
$D_e$	effective diffusivity of adsorbate in solution (m <sup>2</sup> /s)
$F(t)$	fractional uptake of the adsorbate on adsorbent
$k$	constant in Radke–Prausnitz isotherm (mg/l)/(mg/l) <sup>1/p</sup>
$K_F$	constant in Freundlich isotherm (mg/g)/(mg/l) <sup>1/n</sup>
$K$	constant in Radke–Prausnitz isotherm (l/g)
$K_1$	constant in Redlich–Peterson isotherm (l/g)
$K_2$	constant in Redlich–Peterson isotherm (l/mg) <sup>m</sup>
$m$	constant in Redlich–Peterson isotherm
$n$	constant in Toth isotherm
$p$	constant in Radke–Prausnitz isotherm
$q_e$	amount of adsorbate adsorbed at equilibrium (mg/g)
$q_t$	amount of adsorbate adsorbed per gram of adsorbent at any time $t$ (mg/g)
$q_e^\infty$	monolayer adsorption capacity parameter in Toth isotherm (mg/g)
$q_{24}$	amount of adsorbate adsorbed per gram of adsorbent at 24 h (mg/g)
$Q_0$	maximum amount of adsorbate adsorbed (mg/g)
$R$	radius of activated carbon particle (m)
$t$	time (h)
th	constant in Toth isotherm
<i>Greek letters</i>	
$\alpha_1$	constant in Fritz–Schlunder isotherm (mg/g)/(mg/l) <sup><math>\beta_1</math></sup>
$\alpha_2$	constant in Fritz–Schlunder isotherm (mg/g)/(mg/l) <sup><math>\beta_2</math></sup>
$\beta_1, \beta_2$	constant in Fritz–Schlunder isotherm

and notations, thereby making the comparison (both qualitative and quantitative) difficult. Therefore, it is decided to compile above isotherm parameters [2–27] in same units and notations which are given in Tables 1–6.

Broadly, these isotherms may be categorized as two parameter models of Freundlich and Langmuir, three parameter models of Redlich–Peterson, Radke–Prausnitz, and Toth, and four parameter model of Fritz–Schlunder. Out of these models, Freundlich and Langmuir models have been mostly used for both phenol or 4-nitrophenol-activated carbon [2–22], and phenol or 4-nitrophenol—low cost adsorbent systems [28–34]. Sometimes, these models have to be used piecewise in order to represent the different concentration ranges studied. In several studies, three parameter models of Redlich–Peterson [17,23–25], Toth [25] and Radke–Prausnitz [26] were also used. Few of the studies mentioned above have used more than one

isotherm with the objective of finding that isotherm which would represent their data well. In few studies [27], four parameter model of Fritz–Schlunder was used and found to represent their adsorbate–adsorbent system well. Thus, it may be concluded that for the same system of phenol/activated carbon and 4-nitrophenol/activated carbon systems, different isotherms have been used. Besides, phenol or 4-nitrophenol-adsorbent systems have been studied for other purposes such as comparison of performance of different adsorbents, study of chemistry of the adsorbate–adsorbent system, and study of effect of porosity and its distribution on removal pattern, etc. [35–40].

The isotherms are used as constitutive relationships in the modeling and simulation of activated carbon/BAC treatment units. For correct solution of these models, one must obtain proper isotherms relationship representing entire concentration range. In the case of gas phase adsorption, the isotherms have been developed based on thermodynamic theories but in the liquid phase adsorption, the relationship is more or less empirical; nothing more than a curve fitting procedure [41]. It was therefore, decided to select the single isotherm model (out of the six) which would represent the experimental data of phenol/activated carbon, and 4-nitrophenol/activated carbon systems over the entire concentration range (~1–1000 mg/l). The adsorption kinetics data and the intra-particle diffusivity of these compounds in activated carbon in a completely mixed batch reactor are also presented for different initial concentrations for the sake of completeness. These studies have been done in basal salt medium at ~30 °C and pH value of ~7.0. These environmental conditions are suitable for the growth of *Pseudomonas putida* [42], a microorganism which was planned to be used for biofilm development on activated carbon in further studies.

## 2. Experimental details

### 2.1. Material and analytical procedure

The GAC granules were supplied by M/s s.d. fine-chem. Ltd., India in the size range of 2.00–5.00 mm, which were pulverized and sieved to obtain the particles of approximately 0.536 mm average diameter. Phenol and 4-nitrophenol with more than 99% purity were supplied by M/s s.d. fine-chem. Ltd., India and M/s SRL Pvt. Ltd., India, respectively. Stock solutions (1%) of each compound were prepared and stored in brown colour bottles to avoid photo oxidation. Basal salt medium (BSM) used in this study is a defined medium containing inorganic compounds (macro- and micronutrients) necessary for the growth of microorganisms, namely *P. putida*. The composition of the BSM is given in Kumar et al. [42–43]. The concentration of these compounds in samples was measured using a double beam UV–vis spectrophotometer [Model UV 210 A, Shimadzu, Japan]. The calibration curves were prepared and the plots between concentration and absorbance of both the compounds were found linear upto 10 mg/l. The values of maximum wavelength for phenol and 4-nitrophenol available in literature were differing, making it necessary for its determination for the system and instrument used in the present study. The values in the present study were found to be 270 and 398 nm for phenol and 4-

Table 1  
Comparison of adsorption isotherm (Freundlich) for adsorption of phenol and 4-nitrophenol on activated carbon

S. no.	Author(s)	Freundlich adsorption isotherm $q_e = K_F C_e^{1/n}$		Surface area (m <sup>2</sup> /g)	Equilibrium concentration range (mg/l)	Remarks
		$K_F$	$1/n$			
<b>Phenol</b>						
(1)	Craik et al. [2]	55.40	0.210	Not mentioned	20–500	–
(2)	Sorial et al. [3]	95.94	0.177	Not mentioned	1.4–711	Sum of squares of relative residuals = 0.039
(3)	Streat et al. [4]	36.87	0.293	1131–1151	15–517	
		32.06	0.278	1010–1114	55–504	
		9.984	0.436	1645–1753	12–517	
		29.28	0.245	841–889	1–230	
		60.81	0.103	576–616	1–435	
(4)	Abuzaid and Nakhla [5]	26.42	0.272	316–376	42–418	
		83.5	0.18	–	–	
		27.68	0.288	620	78–550	
		21.11	0.428	1010	28–371	
		19.95	0.450	1260	42–866	
(5)	Singh et al. [6]	20.79	0.454	1520	28–700	
		56.54	0.188	3000–3500	47–315	
		56.0	0.354	>1500		
		43.9	0.300	>1300		
(7)	Brasquet et al. [8]	50.3	0.289	>1200		$R^2 = 0.96$
						$R^2 = 0.99$
						$R^2 = 0.99$
(8)	Jung et al. [9]	0.851	0.396	1152	0.17–92	$R^2 = .998$
		0.863	0.441	1380	0.23–83.12	$R^2 = .965$
		1.452	0.428	798	0.1–83	$R^2 = .998$
		0.209	0.420	1955	0.56–100	$R^2 = .870$
(9)	Polart et al. [10]	55.41	0.199	847	0–4625.0	pH 3 $T = 25^\circ\text{C}$ Equilibrium Time = 1 h
(10)	Rengaraj et al. [11]	18.3	0.244	577	0.2–1.63	$T = 20 \pm 1^\circ\text{C}$
		9.94	0.286	296	0.2–8.63	$T = 20 \pm 1^\circ\text{C}$ , pH 6.2
(11)	Ayranci and Duman [12]	50.92	0.342	1464 m <sup>2</sup> /g after treatment	2.60–24.58	Neutral pH, $T = 30^\circ\text{C}$
(12)	Namane et al. [13]	1.07	0.37	640	0–14	$T = 25 \pm 2^\circ\text{C}$ , $R^2 = 0.964$
		2.41	0.12	950	0–14	$T = 25 \pm 2^\circ\text{C}$ , $R^2 = 0.980$
<b>4-Nitrophenol</b>						
(13)	Yen and Singer [14]	256.375	0.236	2800–3500	Not mentioned	$R^2 = 0.972$ for wide concentration range
(14)	Fetting and Sontheimer [15]	162.25	0.24	Not mentioned	0.19–3.4	Fitted piece-wise
		172.59	0.16		3.4–96.53	
(15)	Traegner and Suidan [16]	165.86	0.144	1050–1200	0.69–2.9	–
(16)	Brasquet et al. [8]	187.5	0.110	>1500		$R^2 = 0.97$
		196.2	0.153	>1300		$R^2 = 0.97$
		174.7		>1200		$R^2 = 0.99$ , $T = 20 \pm 1^\circ\text{C}$
(17)	Chern and Chien [17]	224.86	0.167	–	0–925	$25^\circ\text{C}$ neutral pH buffer solution used to maintain pH, Freundlich's reported to fit the data well
(18)	Wu et al. [18]	51.88	0.34	Not given	1.59–220.38	$T = 25^\circ\text{C}$ , pH 3.0 used in combination with electro-catalysis
(19)	Ayranci and Duman [12]	205.63	0.353	–	0–2.63	

Table 2  
Comparison of adsorption isotherm (Langmuir) for adsorption of phenol and 4-nitrophenol on activated carbon

S. no.	Author(s)	Langmuir adsorption isotherm $q_e = \frac{Q_0 b C_e}{1 + b C_e}$		Surface area (m <sup>2</sup> /g)	Equilibrium concentration range (mg/l)	Remarks
		$Q_0$ (mg/g)	$b$ (l/mg)			
<b>Phenol</b>						
(1)	Huang and Steffens [19]	124.08 244.40	0.404 0.0278	970 970	2.97–23.5 23.5–129.25	Langmuir's isotherm was fitted piece-wise
(2)	Yen and Singer [14]	202.48	0.189	2800–3500	0.75–846	For Langmuir $R^2 = 0.936$
(3)	Mckay et al. [20]	213	0.1	1050–1200	8–250	–
(4)	Singh et al. [6]	200 327.27 542.86 571.42	0.014 0.00873 0.00335 0.00390	620 1010 1260 1520	78–550 28–371 42–866 28–700	Data analysis using Freundlich isotherm also performed
(5)	Khan et al. [7]	180.376	0.0366	3000–3500	47–315	–
(6)	Hu and Srinivasan [21]	206 396	0.0527 0.0335	937 2450	0–140 0–140	– –
(7)	Alvarez et al. [22]	160.65 ± 12.32 189.35 ± 11.01 176.36 ± 3.67 207.04 ± 23.06 201.40 ± 11.76 221.35 ± 9.60	0.0349 ± 0.0085 0.0491 ± 0.0114 0.0092 ± 0.0005 0.0378 ± 0.0135 0.0113 ± 0.002 0.0240 ± 0.003	866.4 863.7 817.1 800.7 833.9 836.4	6.4–293.3 6.0–308.29 7.41–355.69 7.0–303.82 3.70–307.52 7.0–329.76	$T = 25^\circ\text{C}$ , initial pH 6.1, phenol, pH 4.8, PNP, 95% confidence interval basis for parameter estimation
(8)	Ayranci and Duman [12]	173.16	0.22	14.64 after treatment	2.60–24.58	Neutral pH, H <sub>2</sub> O medium, normalized percent deviation, isotherm recommended
(20)	Namane et al. [13]	3.22 3.70	0.33 1.08	640 950	0–14 0–14	$T = 25 \pm 2^\circ\text{C}$ , $R^2 = 0.998$ $T = 25 \pm 2^\circ\text{C}$ , $R^2 = 0.987$
<b>4-Nitrophenol</b>						
(9)	Yen and Singer [14]	619.17	0.702	2800–3500	Not mentioned	$R^2 = 0.905$
(10)	Hu and Srinivasan [21]	251.00 573.00	0.444 0.343	937 2450	1.4–75 0–34	–
(11)	Chern and Chien [17]	613.33	0.234	0–925		25 °C neutral pH buffer solution used to maintain pH Freundlich, R–P reported to fit the data well
(12)	Alvarez et al. [22]	244.69 ± 13.91 329.83 ± 12.66 215.62 ± 13.08 328.02 ± 14.74 218.26 ± 24.90 330.94 ± 31.44	0.0674 ± 0.0189 0.0922 ± 0.0322 0.0386 ± 0.0074 0.0409 ± 0.0054 0.0833 ± 0.0229 0.0836 ± 0.0238	866.4 863.7 817.1 800.7 833.9 836.4	9.6–345.37 9.6–95.94 13–319.51 9.7–208.67 3.3–71.73 9.7–172.80	$T = 25^\circ\text{C}$ , initial pH 6.1, phenol, pH 4.8, PNP, 95% confidence interval basis for parameter estimation
(13)	Ayranci and Duman [12]	292.13	3.80	–	2.60–24.58	Neutral pH, H <sub>2</sub> O medium normalized percent deviation, isotherm recommended

Table 3  
Comparison of adsorption isotherm (Redlich–Peterson) for adsorption of phenol and 4-nitrophenol on activated carbon

S. no.	Author(s)	Redlich–Peterson adsorption isotherm $q_e = \frac{K_1 C_e}{1 + K_2 C_e^m}$			Surface area (m <sup>2</sup> /g)	Equilibrium concentration range (mg/l)	Remarks
		$K_1$ (l/g)	$K_2$ (l/mg) <sup>m</sup>	$m$			
Phenol							
(1)	Mathews and Su [23]	97.5	1.34	0.81	1050–1200	0–80	
(2)	Seidel et al. [24]	524	9.51	0.78	Not mentioned	Not mentioned	
		1498	28.69	0.75	Not mentioned	Not mentioned	
		7064	80.53	0.80	1050–1200	0.06–442	
		4598	101.30	0.75	Not mentioned	Not mentioned	
4-Nitrophenol							
(3)	Jossens et al. [25]	–	–	–	1400–1500	0.01–1715	Parameter values not given—Abs. relative dev. = 2%
(4)	Chern and Chien [17]	193.5	700	0.868	0–925		25 °C, neutral pH buffer solution used to maintain pH, Freundlich R–P reported to fit the data well

Table 4  
Comparison of Toth isotherm for adsorption of phenol and 4-nitrophenol on activated carbon

S. no.	Author(s)	Toth adsorption isotherm $q_e = \frac{q_e^\infty C_e}{[a + C_e^{\text{th}}]^{1/\text{th}}}$			Surface area (m <sup>2</sup> /g)	Equilibrium concentration range (mg/l)	Remarks
		$q_e^\infty$ (mg/g)	$a$	th			
Phenol							
1	Jossens et al. [25]	1330.10	0.628	0.148	1400–1500	0.06–813.1	–
4-Nitrophenol							
2	Jossens et al. [25]	1656.80	0.254	0.107	1400–1500	0.013–1175	–

Table 5  
Comparison of Radke–Prausnitz isotherm for adsorption of phenol and 4-nitrophenol on activated carbon

S. no.	Author(s)	Radke–Prausnitz Isotherm $\frac{1}{q_e} = \frac{1}{K C_e} + \frac{1}{k C_e^{1/p}}$			Surface area (m <sup>2</sup> /g)	Equilibrium concentration range (mg/l)	Remarks
		$K$	$k$	$1/p$			
Phenol							
(1)	Costa et al. [26]	37.33	68.39	0.203	1232	0.188–13.44	–
4-Nitrophenol							
(2)	Costa et al. [26]	608.16	124.80	0.188	1232	Not mentioned	–

nitrophenol, respectively. Same instrument and conditions were used throughout this study.

## 2.2. Sorption kinetics

Sorption kinetics studies were carried out in batch mode. The working solution (200 ml in each flask) was prepared by adding appropriate amounts of BSM and the stock solution of phenol

or 4-nitrophenol in 250 ml Stoppered conical flasks. Incubator-shaker (INCON, India Make) was used for shaking and maintaining temperature at  $29.9 \pm 0.3$  °C. As the temperature of the solutions reached at 30 °C, the activated carbon at 5 g/l was added to each flask, and this time was taken as the starting time. The flasks at pre-specified time interval were taken out one at a time and filtered. The filtrate was kept in refrigerator for analysis. The kinetics data were taken for 24 h.

Table 6  
Comparison of Fritz–Schlunder isotherm for phenol adsorption on activated carbon

S. no.	Author(s)	Fritz–Schlunder isotherm $q_e = \frac{\alpha_1 C_e^{\beta_1}}{1 + \alpha_2 C_e^{\beta_2}}$				Surface area (m <sup>2</sup> /g)	Equilibrium concentration range (mg/l)	Remarks
		$\alpha_1$	$\alpha_2$	$\beta_1$	$\beta_2$			
1	Hutchinson and Robinson [27]	29.04	0.037	0.456	0.626	970	Not mentioned	–

2.3. Adsorption equilibrium studies

The equilibrium studies were conducted at  $29.9 \pm 0.3^\circ\text{C}$  using the “bottle point” procedure. The working solutions (200 ml in each flask) at 1000 mg/l concentration of phenol or 4-nitrophenol were prepared in 250 ml stoppered conical flasks by adding required amount of stock solutions to the BSM. After addition of pre-weighed quantities of activated carbons, these flasks were kept in an incubator-cum-shaker at  $29.9 \pm 0.3^\circ\text{C}$  for 48 h as the system attains equilibrium within this time period. To prevent bacterial growth, mercuric chloride ( $\text{HgCl}_2$ ) was found appropriate and added at 6 mg/l to each solution. After 48 h, the flasks were taken out and filtered through Whatman filter. The filtrate was kept in refrigerator for analysis.

3. Results and discussion

3.1. Adsorbent properties

The BET-surface area of the GAC was found to be  $579.23 \pm 17.02 \text{ m}^2/\text{g}$ . The pore structure was determined to be trimodal with most of pores (68%) having diameter less than 5 nm, 32% pores having diameter greater than 5 nm and some of the pores (12%) having less than 1 nm diameter. Other physical properties of the GAC used have been given in previous work [43].

3.2. Isotherm studies

Various adsorption isotherm models given in Tables 1–6 were fitted to adsorption equilibrium data of this study. A Window based statistical software, SPSS Version 6.0 was used for determining the isotherm parameters. This software utilizes a nonlinear regression technique based on Marquardt–Levenberg optimization procedure.

This procedure uses two criteria, namely sum of squares and parameter convergence to obtain parameter values. The correlation coefficient ( $R^2$ ) is also reported along with the values. However, to obtain reasonable results and faster convergence, a correct estimation of initial values is essential. In the present study, this objective was achieved by linearly fitting the two parameter models of Freundlich and Langmuir in Excel spreadsheet. The parameter values of these two isotherms help in rough estimation of the initial values. With this insight, Marquardt–Levenberg procedure was used to obtain parameter values.

The adsorption isotherm models for aqueous systems are empirical as compared to gas systems and depend on many factors such as functional groups present on the surface, type of activated carbon, pH and temperature of the solution, time allowed to reach equilibrium, etc., apart from surface area and pore structure. However, to validate the methodology and results of this study, the data of this study were compared with the study by Singh et al. [6] on the premise that surface area is a major contributor in adsorption equilibrium process. The surface area of carbon used in this study was comparable with the study by Singh et al. [6]. Freundlich isotherm was fitted to the

Table 7  
Equilibrium isotherm constants of phenol and 4-nitrophenol on activated carbon from basal salt medium at  $29.9 \pm 0.3^\circ\text{C}$

Phenolic compound	Freundlich, $q_e = K_F C_e^{1/n}$			Langmuir, $q_e = \frac{Q_0 b C_e}{1 + b C_e}$			Redlich–Peterson, $q_e = \frac{K_1 C_e}{1 + K_2 C_e^m}$									
	$K_F$	$1/n$	$R^2$	Max. dev.%	$Q_0$	$b$	$R^2$	Max. dev.%	$K_1$	$K_2$	$m$	$R^2$	Max. dev.%			
Phenol	36.51	0.245	0.98	10.59	165.80	0.04	0.86	117.24	82.47	2.038	0.77	0.98	10.27			
4-Nitrophenol	83.12	0.170	0.98	14.88	206.30	0.49	0.80	93.39	735.04	8.047	0.85	0.98	12.39			
Phenolic compound	Toth, $q_e = \frac{q_e^\infty C_e}{[a + C_e^h]^{1/h}}$			Redke–Prausnitz, $\frac{1}{q_e} = \frac{1}{K C_e} + \frac{1}{k C_e^{1/p}}$			Fritz–Schlunder, $q_e = \frac{\alpha_1 C_e^{\beta_1}}{1 + \alpha_2 C_e^{\beta_2}}$									
	$q_e^\infty$	$a$	$th$	$R^2$	Max. Dev.%	$K$	$k$	$1/p$	$R^2$	Max. Dev.%	$\alpha_1$	$\alpha_2$	$\beta_1$	$\beta_2$	$R^2$	Max. Dev.
Phenol	454.34	0.83	0.21	0.98	14.14	82.47	40.47	0.23	0.98	10.35	40.56	1.05	1.59	1.35	0.98	10.10
4-Nitrophenol	583.50	0.32	0.14	0.98	15.65	735.04	91.34	0.15	0.98	12.39	1010.01	11.32	1.51	1.35	0.98	12.50

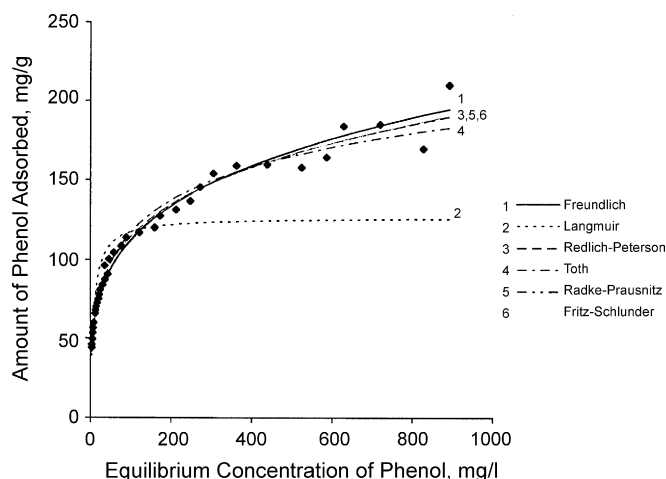


Fig. 1. Comparison of different isotherm models for phenol adsorption on activated carbon with experimental results.

equilibrium concentration data of the present study in the range (78–550 mg/l) and the values of  $K_F$  and  $1/n$  were found to be 37.40 and 0.240, respectively, with correlation coefficient value of 0.98. Freundlich isotherm values fitted for similar concentration range were found to be 27.68 and 0.288, respectively, in the study by Singh et al. [6]. Despite the slightly high surface area in Singh et al. [6], the low  $K_F$  value may be due to less time (only 4 h) given to reach equilibrium. Beside other factors as discussed above, pseudo-equilibrium might have reached as suggested by Streat et al. [4].

Six isotherm models were fitted to equilibrium data of each compound over whole concentration range and parameter values were estimated. With these parameter values, the percentage deviation based on predicted values were calculated. Table 7 shows the parameter values along with the correlation coefficients and maximum deviations for each isotherm models for both phenol and 4-nitrophenol. Figs. 1 and 2 show the comparisons of different models (all the six isotherms studied) for the adsorption of phenol and 4-nitrophenol, respectively. The best

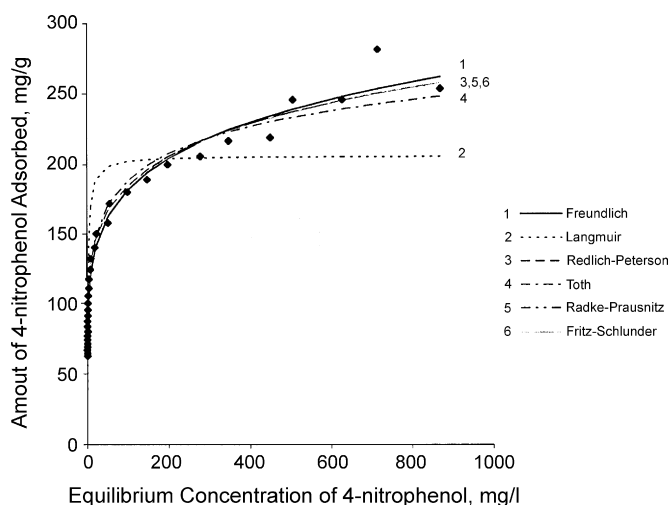


Fig. 2. Comparison of different isotherm models for 4-nitrophenol adsorption on activated carbon with experimental results.

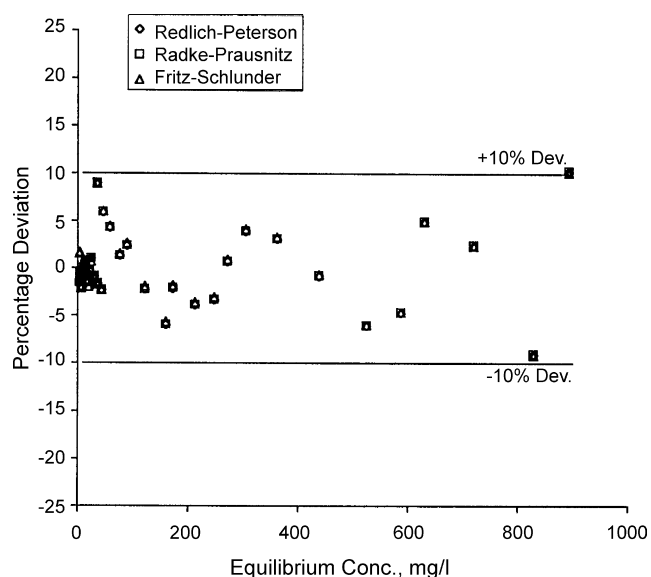


Fig. 3. Comparison of experimental and predicted amount of phenol adsorbed on activated carbon.

model could be selected on the basis of the values of correlation coefficient and maximum deviation. Figs. 3 and 4 depict the comparison of experimental and predicted amounts of phenol and 4-nitrophenol adsorbed on activated carbon only for those models found to represent the data well. As is evident from the Table 7 and Figs. 1 and 2, Langmuir model could not represent the data reasonably well with correlation coefficient 0.86 and 0.80 and maximum deviation 117.24 and 93.39 for phenol and 4-nitrophenol, respectively. For other models, the correlation coefficient values were 0.98. The two parameter model of Freundlich could represent the data of phenol better than those of 4-nitrophenol with maximum deviation value

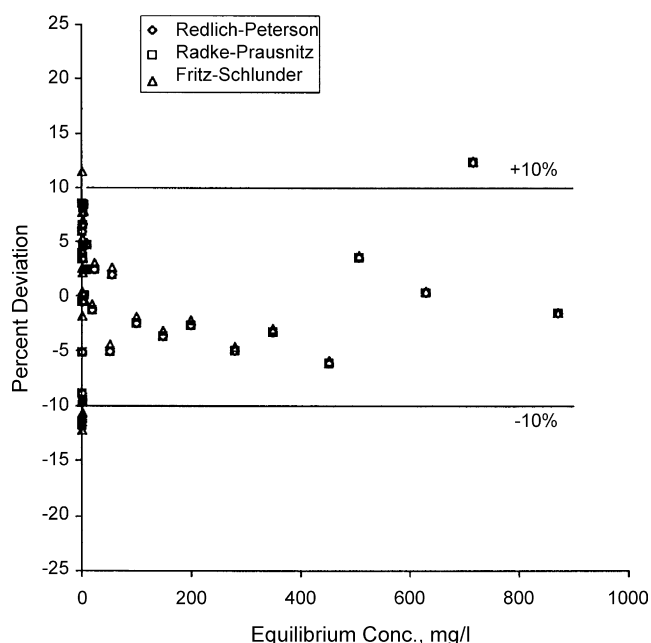


Fig. 4. Comparison of experimental and predicted amount of 4-nitrophenol adsorbed on activated carbon.

of 10.59% whereas, in case of 4-nitrophenol, the maximum deviation was 14.88%. Among the three parameters models, the Toth's model gave the poorest fit. Remarkable similarity in accuracy and fitness was observed in case of Redlich–Peterson and Radke–Prausnitz. It was but expected as the two are same except the forms of equations. The four parameter model gave the highest accuracy for both the compounds.

It is clear from Table 7 and Figs. 1 and 2 that 4-nitrophenol has higher adsorbability than that of phenol. This behaviour might be attributed to the difference in their chemical structure, i.e. presence of -nitro functional group in case of 4-nitrophenol, higher solubility of phenol than 4-nitrophenol. Also they might interact with the functional group present on carbon surface differently. Mattson and Mark [44] concluded that the carbonyl, and oxygen groups on the carbon acts as electron donor and interacted with the aromatic ring of phenols as electron acceptor in a complex donor–acceptor mechanism. Whereas Coughlin et al. [45] reported that dispersive forces between  $\pi$ -electrons in the phenol and  $\pi$ -electrons in the carbon contributes to such interaction. The electron density in the  $\pi$ -system of the aromatic ring is decreased because of the -nitro group in 4-nitrophenol in comparison to phenol itself. This gives rise to the enhanced possibility of donor–acceptor mechanism. Also the position of functional group affects the adsorbability. In 4-nitrophenol, the functional group is at para position, making it more susceptible to adsorption. All the above factors enhance the adsorbability of the 4-nitrophenol as much as almost double the value of phenol.

### 3.3. Adsorption rate controlling mechanism

Adsorption on porous solid adsorbent from aqueous phase generally involves the transport of adsorbate in bulk phase, solid phase (by either pore diffusion and/or surface diffusion), and actual adsorption step. The last step is considered to be fast enough [46], thus the slowest of the transport steps would determine the overall rate of adsorption. The rate of uptake is limited by several characteristics of the adsorbate, adsorbent, and the solution phase. In general, the rate of uptakes in systems with poor mixing, having adsorbate at low enough concentration, high affinity towards adsorbent and small particles are governed by external transport. In contrast, transport in systems with different characteristics than those mentioned above are limited by intra-particle diffusion step. The present studies were done in well mixed conical flasks in batch mode, it is expected that the rate of uptakes would be governed by intra-particle diffusive transport.

Mathematical formulations representing the diffusion and adsorption are not generally solvable analytically, except for some simple cases. Weber and Morris [47] noted that these solution invariably show the fractional uptake of the adsorbate to be a function of square root of time  $t^{0.5}$  rather than time  $t$ . As a corollary, this dependence may be used for determining qualitatively the rate controlling step. Figs. 5 and 6 show the typical plots of fractional uptake of phenol and 4-nitrophenol versus square root of time, respectively. As is evident from the Figs. 5 and 6 that there are three regions of rates of uptakes; each being a straight line. The uptake rate is initially very fast, then medium and

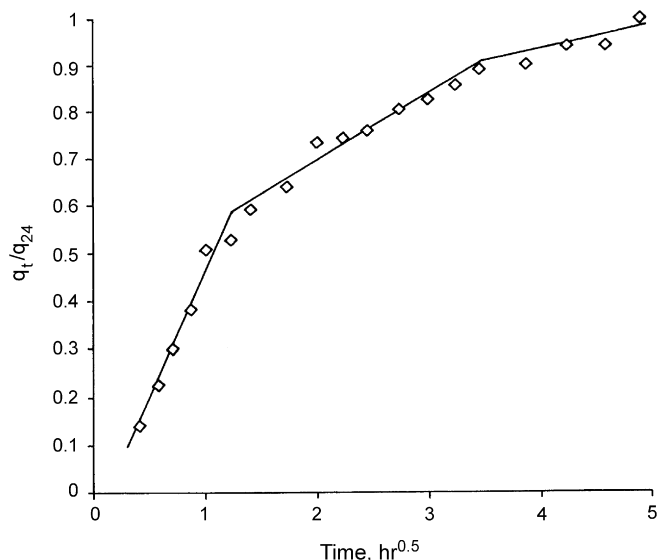


Fig. 5. Typical fractional uptake curve for phenol adsorption on activated carbon [initial conc. = 1000 mg/l, temperature =  $29.9 \pm 0.3$  °C, pH 7.1].

finally giving way to slow uptake. It is likely that the adsorbate is initially transported to macro-, then meso-, and finally slowly diffused into micropores. The linear relationship between  $q_t$  and  $t^{0.5}$  indicates that the adsorption in the present studies was governed by diffusive transport of adsorbates. Similar trends (not shown here for the sake of brevity) were observed for both phenol and 4-nitrophenol at all concentrations (concentrations being varied from 1000 mg/l to approximately 600 mg/l). Allen et al. [48] noted the similar trend for dye adsorption on peat at various initial concentrations and linked this behaviour to pore structure of the peat used.

### 3.4. Sorption kinetics

As has been discussed in previous section, the simple mathematical relationships have been obtained to represent the

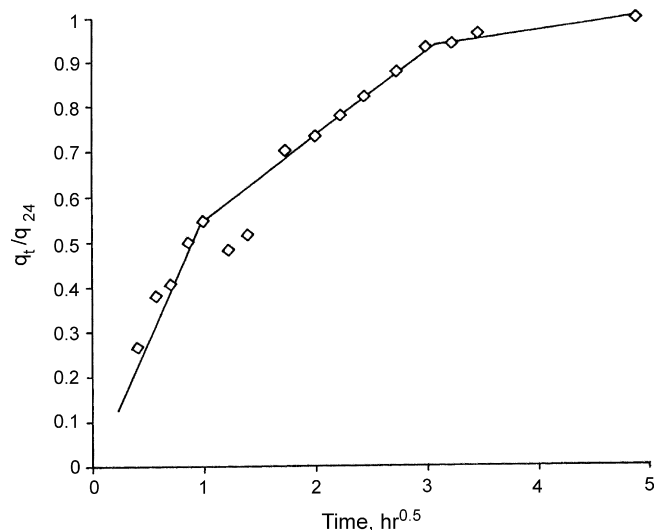


Fig. 6. Typical fractional uptake curve for 4-nitrophenol adsorption on activated carbon [initial conc. = 1054 mg/l, temperature =  $29.9 \pm 0.3$  °C, pH 7.1].



Table 8

Effective particle phase diffusivity of phenol and 4-nitrophenol on activated carbon from BSM at  $29.9 \pm 0.3^\circ\text{C}$  [adsorbent dose = 5 g/l]

Phenol			4-Nitrophenol		
Initial conc. (mg/l)	$D_e \times 10^{13}$ (m <sup>2</sup> /s)	$R^2$	Initial conc. (mg/l)	$D_e \times 10^{13}$ (m <sup>2</sup> /s)	$R^2$
1000	2.42	0.95	1054	3.32	0.92
900	3.15	0.93	949	3.73	0.99
800	1.46	0.99	821	2.69	0.97
700	2.79	0.91	738	4.89	0.91
600	2.72	0.98	633	5.63	0.85

complicated phenomena of diffusion and adsorption on porous adsorbents. One such relationship is due to Vermeulen [49] for adsorption in a finite bath. According to the above study, the fractional approach to the equilibrium is related to dimensionless  $D_e t/R^2$  as follows:

$$F(t) = \left[ 1 - \exp\left(-\frac{D_e t \pi^2}{R^2}\right) \right]^{0.5} \quad (1)$$

In a study by Streat et al. [4], the above relationship has been solved for half time  $t^{0.5}$  (being time taken to reach half the capacity) to calculate the effective particle diffusivity of phenol and chlorophenol into different types of activated carbons in batch mode. These values of the effective particle diffusivities were used to compare the adsorption kinetics of these compounds on different carbons. In the present study, a different approach has been adopted whereas most of the data points have been considered for calculating the effective particle diffusivity. The above equation can be written as

$$\ln \left[ \frac{1}{(1 - F^2(t))} \right] = \frac{D_e t \pi^2}{R^2} \quad (2)$$

Thus the slope of the plot of  $\ln[1/(1 - F^2(t))]$  versus  $t$  should give  $D_e$ . The diffusivities of the phenol and 4-nitrophenol based on this approach have been found comparable to those found in literature for the similar systems [4,11,15]. The correlation coefficient was more than 0.9 in all cases of different initial concentrations. Table 8 shows the diffusivities of phenol and 4-nitrophenol from BSM into activated carbon. However, no conclusive trend for effect of concentration on diffusivity can be discerned suggesting the need for further studies.

### 3.5. Concentration decay and contact time

Figs. 7 and 8 show the concentration decay curves for phenol and 4-nitrophenol, respectively. The initial concentration of phenol and 4-nitrophenol were varied from 1000 to 600 mg/l in the decremental step of 100 mg/l. The initial concentrations experiments were stopped when initially present phenol or 4-nitrophenol could be fully adsorbed. Initially, the rate of removal of each compound was faster. However, 4-nitrophenol is more readily adsorbed than phenol, showing higher affinity of 4-nitrophenol towards activated carbon. In each case, the more dilute the concentration of compound in solution, the more fraction of it is removed. But, the total amount adsorbed per unit

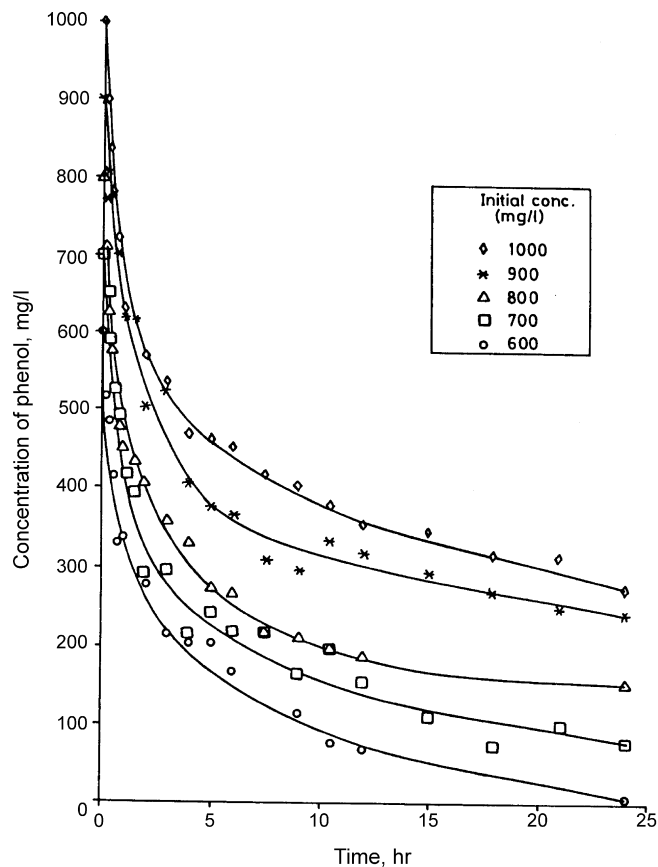


Fig. 7. Concentration decay curves for phenol adsorption on activated carbon [dose of activated carbon = 5 g/l, temperature =  $29.9 \pm 0.3^\circ\text{C}$ , pH 7.1].

gram of activated carbon is less. This indicates that at dilute concentrations, the capacity of the adsorbent is not fully realized.

### 3.6. Effect of adsorbent mass

Varying amounts of activated carbon were contacted with the BSM containing  $\sim 1000$  mg/l of phenol or 4-nitrophenol to optimize the dose of adsorbent. Figs. 9 and 10 show the percent of phenol and 4-nitrophenol removed, respectively, with the change in activated carbon dose. For the initial step change in activated carbon dose, the percent removal is higher, but afterwards the incremental change in percent removal with change in activated carbon is very low. However, 4-nitrophenol showed more adsorbability than phenol. Only 6 g/l of activated carbon

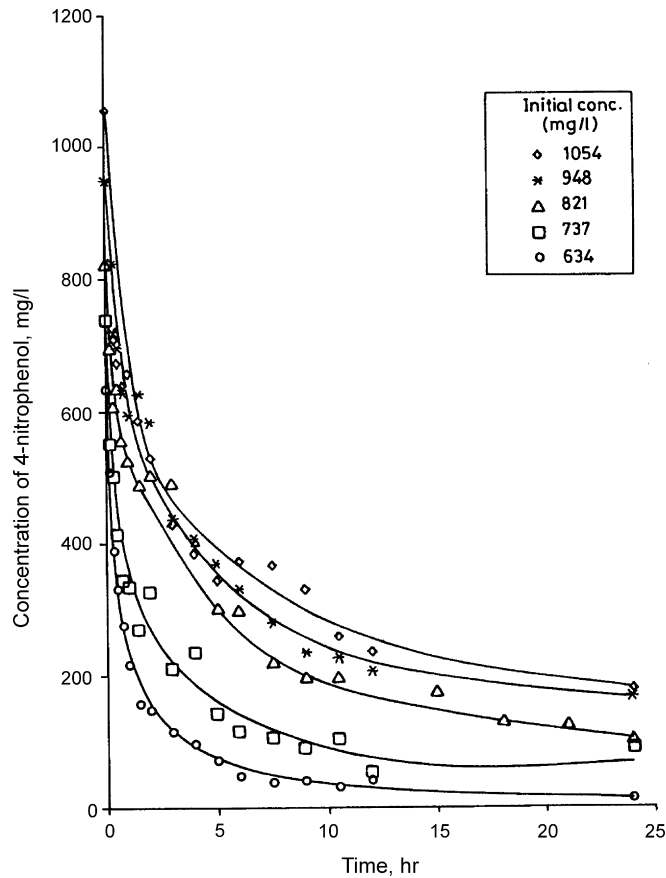


Fig. 8. Concentration decay curves for 4-nitrophenol adsorption on activated carbon [dose of activated carbon = 5 g/l, temperature =  $29.9 \pm 0.3$  °C, pH 7.1].

dose was required in case of 4-nitrophenol as against the 10 g/l of activated carbon dose to effect the same amount of phenol, i.e. 95%, showing a good interaction between -nitro group of 4-nitrophenol and functional groups present on activated carbon

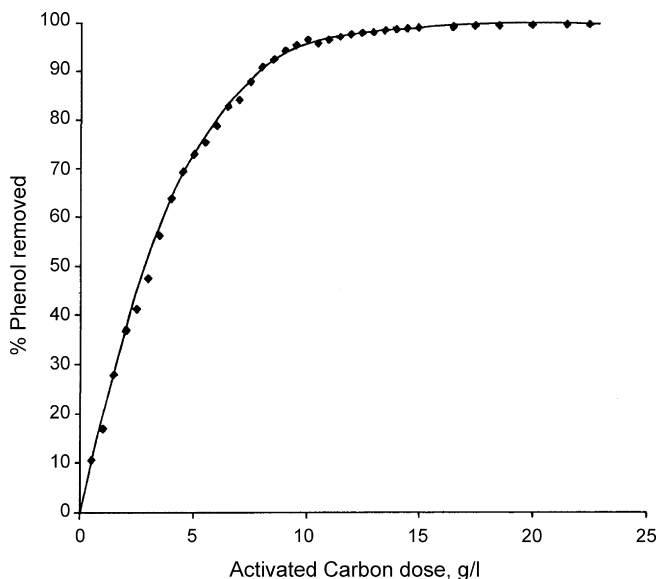


Fig. 9. Effect of activated carbon dose on removal of phenol [initial phenol conc. = 1000 mg/l, temperature =  $29.9 \pm 0.3$  °C, pH 7.1].

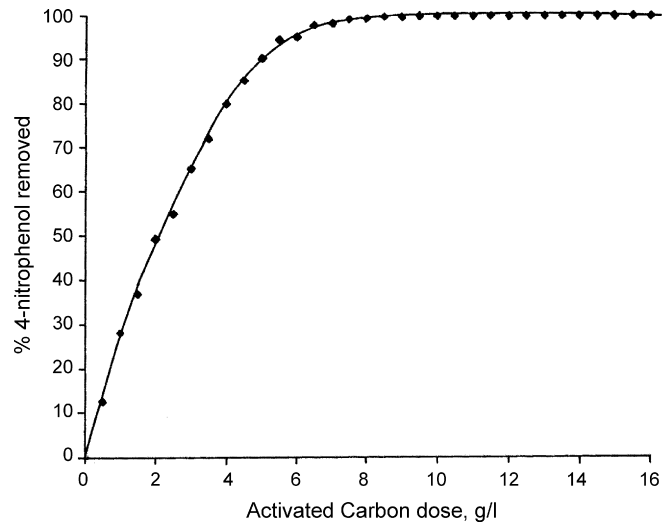


Fig. 10. Effect of activated carbon dose on removal of 4-nitrophenol [initial 4-nitrophenol conc. = 1000 mg/l, temperature =  $29.9 \pm 0.3$  °C, pH 7.1].

surface. After 95% removal, the activated carbon dose is not much effective suggesting that the whole of the phenol and 4-nitrophenol concentration cannot be reduced efficiently to zero in single stage batch reactor.

#### 4. Conclusions

The following conclusions are made from the present study.

- Various adsorption isotherm models have been reported in literature for the same phenol or 4-nitrophenol/activated carbon systems reflecting an empirical nature of modeling of such systems. Moreover, the parameter values reported in literature have been given in different measurement units making comparison difficult. An effort has been made to compile above information in same units as well as notations for ready reference and comparison.
- Owing to empiricism involved, a statistical analysis is desirable. As such, the fitted models were tested for accuracy based on correlation coefficient and maximum derivation. In case of phenol, the easy-to-use two parameter model of Freundlich may be recommended. However, for 4-nitrophenol the four parameter model of Fritz–Schlunder gave the highest accuracy. In both the cases, Langmuir gave the poorest fit.
- Vermeulen [49] approximation were adopted for calculation of intra-particle diffusion coefficients and the value were found to be in conformity with the values given in literature, and were of the order of  $10^{-13}$  m<sup>2</sup>/s.
- Three distinct phases of adsorption kinetics were observed – rapid, medium and slow – showing the trimodel structure of the activated carbon used in the present studies.

It is our view that the information contained herein shall be useful for designing activated carbon adsorption units.

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