

# Adsorption and desorption of phenol on activated carbon and a comparison of isotherm models

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Received 21 April 2005; received in revised form 9 August 2005; accepted 20 August 2005

Available online 28 September 2005

## Abstract

In this study, the potential of activated carbon for phenol adsorption from aqueous solution was studied. Batch kinetics and isotherm studies were carried out to evaluate the effect of contact time, initial concentration, and desorption characteristics of activated carbon. The equilibrium data in aqueous solutions was represented by the isotherm models. Desorption studies to recover the adsorbed phenol from activated carbon performed with NaOH solution. It is necessary to propose a suitable model to gain a better understanding on the mechanism of phenol desorption. For this purpose, pore diffusion and first-order kinetic models were compared. The diffusivity rate ( $D/r^2$ ) and first-order desorption rate ( $k_D$ ) constants were determined as  $6.77 \times 10^{-4}$  and  $3.924 \times 10^{-4} \text{ s}^{-1}$ , respectively. The two- and three-parameter in the adopted adsorption isotherm models were obtained using a non-linear regression with the help of MATLAB<sup>®</sup> package program. It was determined that best-fitted adsorption isotherm models were determined to be in the order: Langmiur > Toth > Redlich–Peterson > Freundlich isotherms.

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**Keywords:** Activated carbon; Adsorption; Desorption; Kinetic; Phenol

## 1. Introduction

Phenols are widely used for the commercial production of a wide variety of resins, including phenolic resins, which are used as construction materials for automobiles and appliances, epoxy resins and adhesives, and polyamide for various applications [1,2]. Phenolic pollutants occur in wastewater of a number of industries, such as high temperature coal conversion, petroleum refining, resin and plastics [3]. Such aromatic hydroxy compounds are considered as priority pollutants since they are harmful to organisms at low concentrations and can be toxic when present elevated levels and are known or suspected to be carcinogens. Therefore, it is considered necessary to remove the phenol from industrial effluents before discharging into the water stream. Different methods designed to remove phenols have been proposed. Adsorption by activated carbon (AC) is the best and most frequently used method. Other methods include aerobic or anaerobic biodegradation, oxidation by ozone, and uptake by ion exchange resins. AC possesses perfect adsorption

ability for relatively low molecular weight organic compounds, such as phenols. Recently, there has been an increasingly large amount of literature devoted to the study of adsorption for the removal of aqueous organic species, such as phenols and substituted phenols using activated carbon [4–10]. Haghseresht et al. [11] stated that the adsorption capacity of AC for aromatic compounds depends on factors, such as the physical nature of the adsorbent-pore structure, functional groups, the nature of the adsorbate, molecular weight, size and the solution conditions (pH, ionic strength and adsorbate concentration). In a review, they underlined the role of heterogeneity effects that accompany adsorption of phenol and its derivatives [12]. They described that a special emphasis is placed on the irreversible adsorption of phenols and the mechanism of this phenomenon. Adsorption of phenolic compounds on activated carbon is relatively simple, the process of regenerating the adsorbent by desorption of the organic compounds poses an important for the present studies since it has the high affinity of the compounds to the sorbent surface. Currently, techniques, such as thermal regeneration [7], chemical regeneration [13,14], bioregeneration [15] and ultrasound [4] are used for the desorption of phenols from activated carbon. This study presents desorption phenomenon and its kinetic. In order to gain a better understanding of the

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mechanism and to quantify the rates of desorption obtained in the activated carbon desorption studies, it was necessary to propose a suitable model, such as pore diffusion and first-order kinetic.

This work presents results of experimental data on the adsorption and desorption of phenol from AC. The current study was aimed kinetic of desorption phenomenon by NaOH solution of phenol onto activated carbon. In desorption kinetic studies, pore diffusion and first-order kinetic models were comparatively used to predict experimental data. Besides this, adsorption of phenol on AC was also described with the four isotherm models. The two and three unknown constants in these equations are obtained using a non-linear regression by MATLAB package program.

This study objectives are:

- (1) to solve two (Freundlich, Langmuir and first-order models) and three (Toth, Redlich–Peterson and pore diffusion models) unknown models by the help of MATLAB computer program;
- (2) to choose most suitable isotherm models among the four different model for the activated carbon adsorption of phenol;
- (3) to determine the desorption mechanism by using different models.

## 2. Experimental

The commercial activated carbon was used in the batch experiments without any pretreatment. The physical properties of granular activated carbon are apparent density of  $0.4 \text{ g/cm}^3$ , particle size of 1.4 mm and average pore diameter of  $18 \text{ \AA}$ . Phenol analyses are performed according to standard methods of APHA [16]. A 100 ml each of phenol solution (100 mg/l) were placed in 250 ml reaction bottles and a known amount of AC was added to each bottle. The solution was equilibrated for 2 h in a mechanical shaker. After the equilibration period, the carbons were filtered and analyzed for phenol following the direct photometric method. In this method, phenol reacts with 4-aminoantipyrine in the presence of potassium ferricyanide to form a colored antipyrine dye. Adsorbance of colored samples was measured at 500 nm. Calibration curves used to determine the concentration of phenol at concentration range of 0–5 mg/l. Desorption studies were conducted using NaOH solution at various strengths by providing and equilibration time of 2 h. Because desorbed phenol reached to equilibrium concentration after 1 h. Phenol was desorbed by NaOH solution after adsorption experiments ( $C_i = 100 \text{ mg/l}$ ,  $t = 2 \text{ h}$ ). Kinetic experiments were conducted using a known weight of carbon dosage and employing phenol concentration in the range of 10–200 mg/l.

The activated carbon–phenol solution was taken in a sealed flask and placed in a shaker maintained at  $20^\circ\text{C}$  for 2 h to determine the amount of phenol desorbed. The phenol solution in the flask was analyzed for phenol concentration both before and after adsorption. Amount of adsorbed phenol is minus between, after and before concentration. The AC was then filtered from the phenol solution using vacuum filtration. Eight samples of 0.5 g each of AC saturated with phenol at initial concentration of 100 mg/l were prepared. Seven AC samples were taken to be

used at desorption experiment by various strengths (0.01–0.30N) NaOH solution, while the eighth sample was taken in a flask, including only distilled water to determine amount of desorbed phenol by shaker. Amount of desorbed phenol by NaOH was calculated from minus between last concentration in eighth flask and last concentration of seventh flask.

## 3. Results and discussions

### 3.1. Phenol adsorption on AC

Activated carbon dosage was varied from 0.05 to 0.9 g/100 ml and equilibrated for 2 h. Fig. 1 shows the amount of phenol removed as a function of carbon dosage. While the phenol removal efficiency of AC was 94% at the adsorbent concentration of 5 g/l, it was between 94 and 96% at the adsorbent concentration of 6–10 g/l. This means that phenol removal was same for  $>5 \text{ g/l}$  adsorbent concentration. Hence, optimum AC dosage for 94% removal of phenol was obtained as 0.5 g of AC. Fig. 2 shows the effect of contact time on the removal of phenol by AC. From this, it is seen that AC saturates nearly after 1 h.

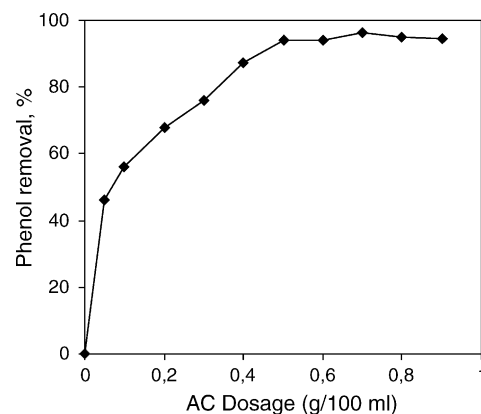


Fig. 1. The relationship between carbon dosage and removal of phenol by AC ( $C_i = 100 \text{ mg/l}$ , contact time ( $t$ ) = 2 h).

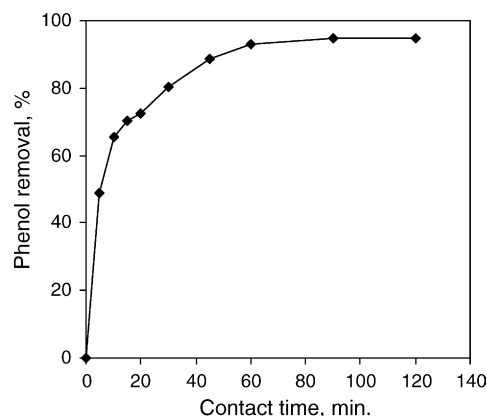


Fig. 2. The relationship between contact time and removal of phenol by AC (AC dosage = 0.5 g/100 ml,  $C_i = 100 \text{ mg/l}$ ,  $t = 2 \text{ h}$ ).

### 3.1.1. Evaluation of adsorption isotherms

Several models have been published in the literature to describe experimental data of adsorption isotherm. For the sake of convenience, explicit and simple models are preferred and commonly used; these include several two- and three-parameter isotherm models. The Langmuir and Freundlich models are the most frequently employed models. The Langmuir model is obtained under the ideal assumption of a totally homogenous adsorption surface, whereas the Freundlich isotherm is suitable for a highly heterogenous surface. The Redlich–Peterson equation is a combination of the Langmuir and Freundlich model. It approaches the Freundlich model at high concentration and is in accord with the low concentration limit of the Langmuir equation. The Toth isotherm model, similar to the Redlich–Peterson model, combines the characteristics of both the Langmuir and Freundlich isotherm [17].

In this work, adsorption of phenol is evaluated and compared with popular two- and three-parameter single-solute isotherm models. Four popular isotherms adopted in this work are given in Table 1 [17].

The two parameters in the Langmuir and Freundlich equations can be graphically determined. Since there are three unknowns of Redlich–Peterson and Toth isotherm models, the unknown constants in these equations are need to obtain using a non-linear regression. It is necessary to propose a suitable model to gain a better understanding of the mechanism and to quantify the isotherm models obtained in the activated carbon adsorption experiments. For this purpose, Langmuir, Freundlich, Redlich–Peterson and Toth isotherm models were considered and compared against experimental data for the goodness of fit. So as to evaluate the goodness obtained fits, the sum of squares

Table 1

Four isotherm model adopted in this work and their parameters

Isotherm	Model
Freundlich	$q_e = k_f \cdot C_e^{1/n}$
Langmuir	$q_e = \frac{Q_0 \cdot k_L \cdot C_e}{1 + k_L \cdot C_e}$
Redlich–Peterson	$q_e = \frac{r_e \cdot C_e}{1 + p_e \cdot C_e^g}$
Toth	$q_e = \frac{A \cdot C_e}{(B + C_e^D)^{1/D}}$

$q_e$ : Adsorption capacity (mg/g AC);  $C_e$ : concentration in liquid phase (mg/l);  $1/n$ : Freundlich constant;  $k_f$ : Freundlich constant;  $Q_0$ : maximum saturation capacity at the isotherm temperature (mg/g);  $k_L$ : Langmuir constant;  $r_e, p_e, g$ : parameters of Redlich–Peterson model;  $A, B$  and  $D$ : parameters of Toth model.

due to the errors (SSE),  $R^2$ , the residual degrees of freedom and root mean square errors (RMSE) associated with the output model results were calculated with the help of MATLAB. The fitted parameter values are listed in Table 2 and the model curves are plotted in Fig. 3. As can be seen from this figure, Freundlich isotherm did not represent activated carbon data. Three-parameter isotherm models predicted the data better for activated carbon, but Langmuir isotherm gave a better fit for the phenol adsorption by activated carbon. The adsorption capacity ( $k$ ) is found to be 6.193 mg/g and adsorption intensity ( $n$ ) is found to be 0.616. The value of  $n$  indicates favorable adsorption [8]. The values of adsorption capacity ( $k$ ) and intensity of adsorption ( $n$ ) indicates the greater affinity for phenol by this adsorbent.

When visually checked, Langmuir, Freundlich, Redlich–Peterson and Toth isotherm models gave reasonably better fits

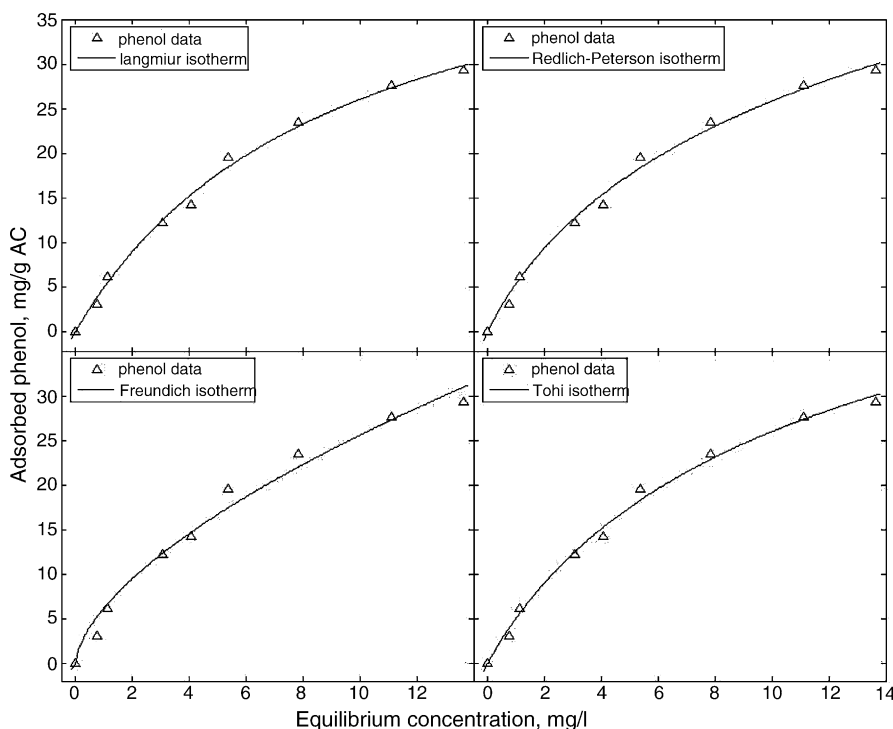


Fig. 3. Equilibrium adsorption isotherm comparisons for different models.

Table 2  
Fitted parameter values using different adsorption isotherm model

Isotherm model	Number of parameters	Parameter values
Freundlich	2	$k_f = 6.193$ ; $n = 0.616$ $R^2 = 0.9839$ SSE = 14.63; RMSE = 1.446
Langmiur	2	$Q_o = 49.72$ ; $k_L = 0.1099$ $R^2 = 0.9947$ SSE = 4.214; RMSE = 0.7759
Redlich–Peterson	3	$r_c = 6.70$ ; $p_c = 0.2445$ ; $g = 0.8138$ $R^2 = 0.9937$ SSE = 5.747; RMSE = 0.9061
Toth	3	$A = 60.05$ ; $B = 6.817$ ; $D = 0.8314$ $R^2 = 0.9947$ SSE = 4.849; RMSE = 0.8323

which can explain the characteristic of the data. Although all the evaluated equilibrium models gave good fit to the experimental data, it can be concluded that the Langmiur is the best model describing adsorption of phenol on the activated carbon, as it gave the maximum  $R^2$  value among the considered models. Based on the results of the study, best isotherm models fitted for phenol adsorption were determined in the order: Langmiur > Toth > Redlich–Peterson > Freundlich isotherms.

### 3.2. Desorption studies and its kinetic rate constants

Desorption studies help elucidate the mechanism of adsorption and recover the precious phenols, water and adsorbent. Attempts were made to desorb phenol from the spent carbons using sodium hydroxide of various strengths [3]. NaOH reagent may be attributed to the formation of sodium salt of phenol which may facilitate desorption of phenol from the carbon surfaces [3,14]. Rengaraj et al. [3] were found that approximately 0.14N NaOH is required for quantitative desorption of phenol from AC. In this study, NaOH was used as a reagent for desorption. Phenol adsorbed on AC was desorbed using NaOH solution at various strengths after saturation of AC with phenol under conditions:  $C_i = 100$  mg/l,  $t = 2$  h, AC = 0.5 g/100 ml. Fig. 4 shows the amount of phenol desorbed as a function of its various strengths NaOH solution. It was found that 0.15N NaOH is required for quantitative desorption of phenol from AC. The desorbed phenol fraction was 61% for 0.15N NaOH elution solution.

In order to gain a better understanding of the mechanism and to quantify the rates of desorption obtained in the AC desorption experiments, it was necessary to propose a suitable model for desorption of phenol. For this purpose, pore diffusion and first-order kinetics, were used to model experimental data.

The average pore diameter of the AC as given in Section 3.1 is 18 Å. Puri [18] gives for the cross section area of phenol in flat orientation  $\sigma = 52.4$  Å<sup>2</sup>. Hence, the average diameter of the phenol molecule is equal to 25 Å. It is for that it is kinetics could possibly be first-order kinetic, which governs the mechanism of diffusion. In a study examined the role of carbon surface

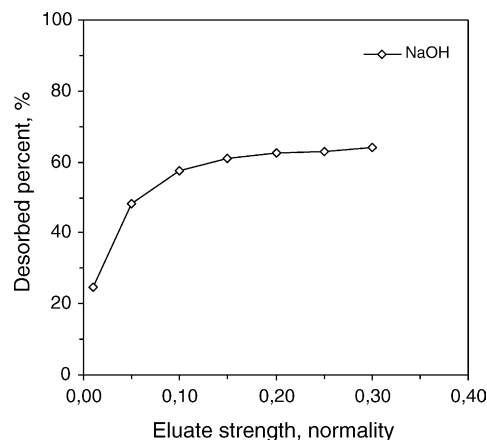


Fig. 4. Fraction of desorbed phenol from AC by NaOH solution after saturated by 100 mg/l initial phenol solution for 2 h contact time (desorption contact time = 2 h).

functionalities in the mechanism of phenol adsorption, Terzyk [19] stated that Puri [18] emphasized the important role of surface carbonyls positive charge of the carbonyl carbon atom in adsorption of phenol.

For isothermal diffusion in a spherical adsorbent particle of radius,  $r$ , the sorption curve has been shown to follow the following equation [4]:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=3}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D}{r^2} n^2 \pi^2 t\right) \quad (1)$$

One of the assumptions of this equation is that the surface concentration of the spherical particle is constant. Hence, this equation was fit using the initial data obtained immediately after the start of desorption experiment, i.e., when the concentration of the regenerating solution remained essentially unchanged. In the short time region, Eq. (1) approaches the limiting parabolic form [4]:

$$\frac{M_t}{M_\infty} = 6\sqrt{\frac{D \cdot t}{r^2 \cdot \pi}} \quad (2)$$

where  $D$  is diffusivity of sorbate within the sorbent-pores ( $\text{m}^2 \text{s}^{-1}$ ),  $r$  the radius of adsorbent particle,  $M_t$  the amount of sorbate desorbed from the sorbent surface at time  $t$  (mg/g wet AC) and  $M_\infty$  is total amount of sorbate adsorbed on the sorbent surface (mg/g wet AC).

Habitually for determining diffusivity rate ( $D/r^2$ ), firstly a straight line is plotted the fractional uptake versus ( $\sqrt{t}$ ), then the ( $D/r^2$ ) value calculates by the help of straight line passing through the origin with a slope ( $6/r\sqrt{D/\pi}$ ) [20]. But, in this study (Eq. (2)) (pore diffusion model) were fitted to growth data by non-linear regression with a Trust-Region Reflective Newton algorithm using MATLAB<sup>®</sup> 7 (R14). This is a search method to minimize the sum of the squares of the differences between the predicted and measured values. Outliers have a large influence on the fit because squaring the residuals magnifies the effects of these extreme data points. To minimize the influence of outliers, robust least squares regression was used. Least absolute residuals (LAR) scheme finds a curve that minimizes the absolute

Table 3  
Curve fittings results and the desorption rate constants

Parameter	Pore diffusion model	First-order kinetic
$D/r^2$ ( $s^{-1}$ )	$6.77 \times 10^{-4}$	–
$k_D$ ( $s^{-1}$ )	–	$3.924 \times 10^{-4}$
$R^2$	0.9699	0.9868
SSE	0.008118	0.003548
RMSE	0.04029	0.02432

SSE: sum of squares due to error; RMSE: square and root mean square errors.

difference of the residuals, rather than the squared differences. Therefore, extreme values have a lesser influence on the fit. Then, the model coefficients (with 95% confidence bounds) were calculated plotting  $M/M_\infty$  versus  $t$  values and the results are given in Table 3.

It was also possible that desorption rate was limited by the breaking of the surface bonds that bound the adsorbate molecule with the sorbent surface. Hence, the rate of desorption was also tried to define with first-order reaction process;

$$-\frac{dC}{dt} = k_D C \quad (3)$$

where  $C$  is concentration of phenol on the AC at time  $t$ , and  $k_D$  is desorption rate constant ( $s^{-1}$ ).

Integrating Eq. (3) gives:

$$\ln\left(\frac{C}{C_0}\right) = -k_D \cdot t \quad \text{or} \quad \frac{C}{C_0} = \exp(-k_D \cdot t) \quad (4)$$

In order to discriminate between the pore diffusion and first-order surface kinetic models, the predictions of both were compared against the experimental fractional desorption data. Fig. 5 shows the comparison of model and experimental results at 20 °C. It can be seen from the figure that first-order kinetic model showed excellent agreement with the phenol desorption data ( $R^2 = 0.9868$ ), besides pore diffusion model prediction ( $R^2 = 0.9699$ ) of desorption was not as good as that predicted by first-order model. In this case, the first-order kinetic model represented the data for NaOH desorption more suitable fitting

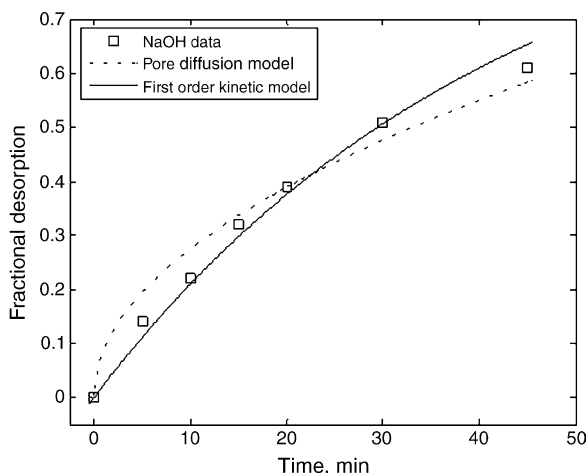


Fig. 5. Fractional desorption of phenol from activated carbon vs. time ( $T = 20$  °C).

than the pore diffusion model. The value of  $k$  for desorption process indicates that the adsorbed phenol remains almost stable on the on the adsorbent and can be recovered from the adsorbent by desorption with NaOH. The regenerated adsorbent can be reactivated and reused.

The values of the first-order and pore diffusion desorption kinetic rate constants are summarized in Table 3. From this, it is seen that the diffusivity rate ( $D/r^2$ ) and first-order desorption rate ( $k_D$ ) constants are  $6.77 \times 10^{-4}$  and  $3.924 \times 10^{-4} s^{-1}$ , respectively.

#### 4. Conclusion

Adsorption of phenol from aqueous solutions presents the most widespread uses of activated carbons in water treatment. The three-parameter isotherm models as well as two-parameter models were found to be applicable for the adsorption equilibrium data by non-linear regression. The low value of desorption kinetic constant indicates that the adsorbed phenol remains almost stable on the adsorbent and can be recovered from the adsorbent by desorption with sodium hydroxide. The results showed that the first-order kinetic model represented the data for NaOH desorption more suitable fitting than the pore diffusion model. The results also demonstrated that the Langmuir model fitted the experimental data a little better than the three-parameter models, Redlich–Peterson and Toth. It is determined that the standard errors were minimum level in fitted three models.

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