



## **Liquid Phase Adsorption of Phenol by Activated Carbon Derived From Hazelnut Bagasse<sup>#</sup>**

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**Abstract:** Wastewater containing phenolic compounds presents a serious discharge problem due to their poor biodegradability, high toxicity and ecological aspects. In this study, the adsorption of phenol from aqueous solution on activated carbon obtained from hazelnut bagasse activated with  $ZnCl_2$  was investigated. Batch adsorption experiments were carried out at constant pH value under varying experimental conditions of contact time, phenol concentration, temperature and adsorbent dose. Adsorption equilibrium was reached within 300 min. Studies showed that the removal efficiency of phenol increased with increase in adsorbent dose and phenol concentration. Temperature was not affected significantly phenol removal. Freundlich and Langmuir adsorption isotherms were applied to the experimental data. Both the Freundlich and Langmuir isotherm models adequately fit to the adsorption data for all temperatures. The adsorption capacities calculated from Langmuir equation were found to be 97.36, 91.32 and 99.27 mg/g for 25, 35 and 45 °C, respectively. The adsorption kinetics were examined at three different phenol concentrations (300, 400 and 600 mg/L). The kinetic models such as pseudo first order and pseudo second order model were fitted to identify the mechanism of adsorption process; the adsorption of phenol obeyed pseudo second order rate equation for all concentration range. The present study shows that the activated carbon derived from hazelnut bagasse can be used as low-cost adsorbent for adsorption of phenol.

**Keywords:** *Adsorption; Phenol; Activated Carbon; Hazelnut Bagasse.*

### **Introduction**

Phenol and phenolic compounds are common contaminants in the effluents from industries such as plastics, leather, paint, textile and petrochemical (Kennedy et al., 2007). The health effects following repeated exposure to low levels of phenol in water include liver damage, diarrhea, dark urine and mouth ulcer. Also, phenol is a strong eye and respiratory irritants. Phenolic compounds are harmful to organism at low concentrations and many of them have been classified as hazardous pollutants (Calace et al., 2002).

The methods used for the treatment of aqueous solutions containing phenol have been classified in two principal categories: destructive processes such as destructive oxidation with ozone, enzyme-based treatment methods and electrochemical oxidation; and recuperative processes such as adsorption, membrane separation and ion exchange (Kermani et al., 2006; Dabrowski et al., 2005; Bodalo et al., 2006; Laszlo et al., 2007). Among these, adsorption onto the activated carbon is the most widely used method for the removal of dissolved organics from waters. Activated carbon possesses perfect adsorption ability for relatively low molecular weight organic compounds such as phenols (Dabrowski et al., 2005).

Due to the high cost of activated carbons, there are number of studies regarding the preparation of economic and efficient carbons from cheaper raw materials such as agricultural wastes. For this purpose, date pits, peach cores, Tamarind nut shells, coconut shells and rice husk derived carbons which were activated physical or chemical methods have been used for the removal of phenol (Banat et al., 2004; El-Hannafi et al., 2008; Goud et al., 2005; Singh et al., 2008; Kennedy et al., 2008).

The aim of this study was to research the feasibility of activated carbon prepared from hazelnut bagasse, which is an industrial waste material, by using chemical activation method with  $ZnCl_2$  for the removal of phenol from aqueous solutions. The effects of various parameters such as contact time, phenol concentration, temperature and adsorbent dosage on the sorption capacity were also performed. The Freundlich and Langmuir isotherm models were used to analyze the adsorption equilibrium. The

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<sup>#</sup> This study has been presented at BIES'08, Giresun, Turkey.

kinetic models including pseudo first-order and pseudo second-order equation were used to discuss adsorption mechanism.

## Materials and Methods

### Adsorbents and reagents

The activated carbon (AC) used in this study was prepared from hazelnut bagasse by chemical activation with  $\text{ZnCl}_2$ . The preparation of adsorbent was explained in detailed in our previous study (Demiral et al., 2008). The surface area of activated carbon which was determined by  $\text{N}_2$  adsorption at 77 K is  $1489 \text{ m}^2/\text{g}$  and micropore volume is  $0.454 \text{ cm}^3/\text{g}$ .

Phenol solutions were prepared by diluted of stock solutions ( $1000 \text{ mg/L}$ ) to the desired concentrations. The concentration of phenol in solutions was determined by spectrophotometrically at 270 nm (Thermoelectron Aquamate UV-vis.). In all experiments, it was studied at original pH value of phenol solutions without pH adjustment in view of practical considerations.

### Adsorption experiments

Adsorption studies were performed by using batch technique in a shaker bath (Memmert) at constant temperature. The adsorption kinetics were determined at three different initial phenol concentrations ( $300, 400$  and  $600 \text{ mg/L}$ ) at a constant temperature of  $25^\circ\text{C}$ .  $0.5 \text{ g}$  of adsorbent was added to  $250 \text{ mL}$  phenol solutions and the concentration of phenol was measured at specific time interval.

Adsorption isotherms were obtained by introducing  $0.1 \text{ g}$  of AC in erlenmayer flask containing  $50 \text{ mL}$  of phenol solutions ranging from  $50$  to  $500 \text{ mg/L}$  at  $25, 35$  and  $45^\circ\text{C}$ . The effect of adsorbent dosage were studied by introducing different quantities of AC (between  $0.05$  and  $0.4 \text{ mg}$ ) in  $50 \text{ mL}$  of phenol solutions of  $500 \text{ mg/L}$ .

The amount of phenol adsorbed on the AC samples at experiments was calculated as follows:

$$q_e = (C_0 - C_e)V / m \quad (1)$$

were  $C_0$  is the initial concentration ( $\text{mg/L}$ ),  $C_e$  the equilibrium concentration ( $\text{mg/L}$ ),  $V$  the volume of the solution ( $\text{L}$ ) and  $m$  is the mass of the adsorbent ( $\text{g}$ ).

## Results and Discussion

All the experiments were carried out original pH of phenol solutions ( $\text{pH}=5.5-6$ ). The  $\text{pK}_a$  value of phenol is  $9.89$ . For this reason the solution pH should be less than this value so phenol exists mostly as the undissociated forms. The pH of the aqueous solution of phenol affects its uptake an adsorbent and in general the uptake decreases at lower as well as higher pH values (Dabrowski et al., 2005). According to phenol adsorption studies in literature, in general, the removal efficiency decreases in the pH value greater than  $9$  and smaller than  $3$ . The maximum phenol adsorption has been observed at pH values of between  $5$  and  $7$ . (Dabrowski et al., 2005; Vasu, 2007, El-Hannafi et al., 2008)

### Effect of time

The effect of time for adsorption process was carried out to determine the equilibrium point. Figure 1 shows a plot of the amount of phenol adsorbed ( $\text{mg/g}$ ) versus contact time for different phenol concentrations at  $25^\circ\text{C}$ . It was found for all the set of experiments, the adsorption was rapid up to  $120 \text{ min}$  and latter on became slow, and finally the systems reached equilibrium around  $300 \text{ min}$  (Figure 1). Therefore the maximum time of adsorption was restricted up to  $300 \text{ min}$ . It is evident that most of the adsorption sites are filled up in the period of  $110 \text{ min}$ . Initially, the number of sites available is higher; therefore adsorbate reaches the adsorption site with ease. With time, number of active sites becomes less and the movement of the adsorbate decreases (Kennedy et al., 2007).

### Kinetic Modeling

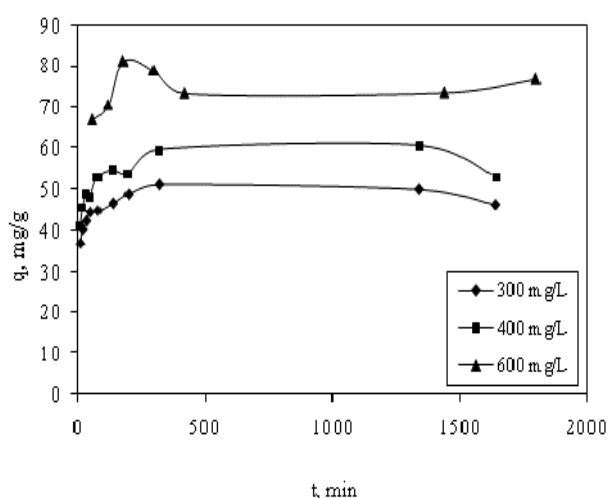
The mechanism of adsorption depends on the physical and/or chemical characteristics of the adsorbent as well as on the mass transport process. In order to investigate the adsorption process of phenol onto activated carbon, the adsorption rate data were analyzed using pseudo

first-order and pseudo second-order kinetic models. The linearized forms of these equations are represented as (Ho and McKay, 1998; Kennedy et al., 2007):

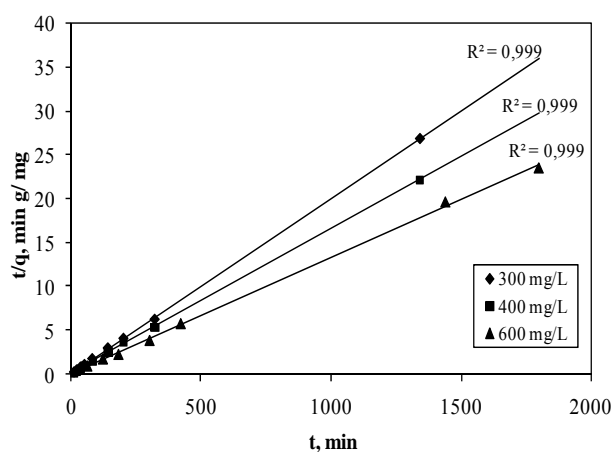
$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where  $q_e$  and  $q_t$  are the amount of phenol adsorbed (mmol/g) at equilibrium and at time  $t$  (min),  $k_1$  is the first order equilibrium rate constant (1/min),  $k_2$  the pseudo second order rate constant (g/mg min).



**Figure 1:** Adsorbed amounts of phenol at 25 °C as a function of time for the different initial concentration (V=250 mL; m=0.5 g).



**Figure 2:** Kinetics of phenol adsorption according to the pseudo second order model at different concentration (V=250 mL; m=0.5 g; temp.=25 °C, ).

The pseudo first order and second order rate constants were evaluated from the linear plots of  $\log(q_e - q_t)$  versus  $t$ , and  $t/q_t$  versus  $t$ , respectively. The plots of pseudo second order kinetic model at different concentrations are shown in Fig. 2.

**Table 1:** First order and second order parameters for different initial concentrations

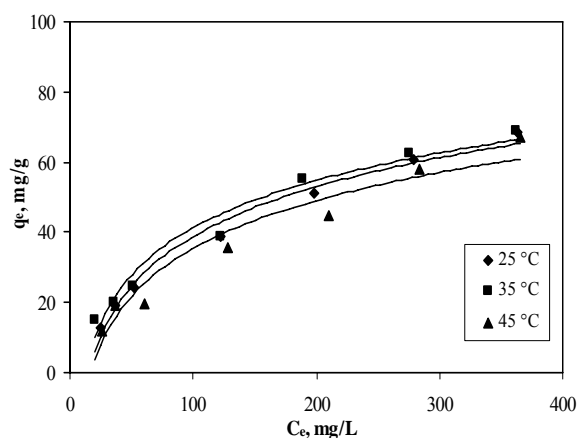
$C_0$ (mg/L)	$q_e$ (exp.) (mg/g)	Pseudo first order			Pseudo second order		
		$k_1 \cdot 10^3$ (1/min)	$q_e$ (cal.) (mg/g)	$R^2$	$k_2 \cdot 10^3$ (minmg/g)	$q_e$ (cal.) (mg/g)	$R^2$
300	50.99	1.58	12.74	0.946	3.58	50.11	0.999
400	60.44	1.55	18.34	0.900	1.39	60.89	0.999
600	81.18	0.09	12.08	0.773	4.97	76.92	0.999

The plots of pseudo first-order kinetic model are not given, but only calculated parameters are presented. Table 1 gathers the parameters derived from the pseudo first-order equation ( $q_e$  and  $k_1$ ) and pseudo second-order kinetic model ( $q_e$  and  $k_2$ ). For each case, the corresponding correlation coefficients,  $R^2$ , are given.

The analysis of the  $R^2$  values shown in Table 1 suggest that the experimental data fit the pseudo second-order model with  $R^2$  value equal to 0.999 than that of the pseudo first-order with  $R^2$  values ranging between 0.773 and 0.946 for all concentrations. The  $q_e$  values calculated from pseudo second-order kinetics is very close to experimental values of  $q_e$ . For this reason pseudo second order model better predicts the sorption kinetics than the pseudo first-order model. Such a finding is also good agreement with previous studies (Fierro et al., 2008; Kennedy et al., 2008).

### Adsorption Isotherms

Figure 3 shows the adsorption isotherms of phenol. As seen from Figure 3, when the initial phenol concentration increased from 50 to 500 mg/L, the phenol uptake increased from 12.68 to 68.58 mg/g at 25 °C. Increasing the initial phenol concentration would increase the concentration difference between bulk solution and adsorbent surface. The net result of this phenomenon is increased in mass transfer rate (Banat et al., 2004). Hence, higher concentration of phenol enhances the adsorption process. The phenol uptake was not affected significantly from temperature as seen in Figure 3. For this reason, phenol adsorption may be carried out at ambient temperature.



**Figure 3:** Adsorption isotherms of phenol onto activated carbon at different temperatures ( $V=50$  mL;  $m=0.1$  g;  $C_0=50-500$  mg/L).

Since the isotherms presented in Figure 3 are of L type according to Giles classification. The Langmuir class (L) is the widespread in the case of adsorption of phenolic compounds from water, and it is characterized by an initial region, which is concave to the concentration axis. Type L suggests that the aromatic ring adsorbs parallel to the surface and no strong competition exist between the adsorbate and the solvent to occupy the adsorption sites (Dabrowski et al., 2005). Langmuir and Freundlich

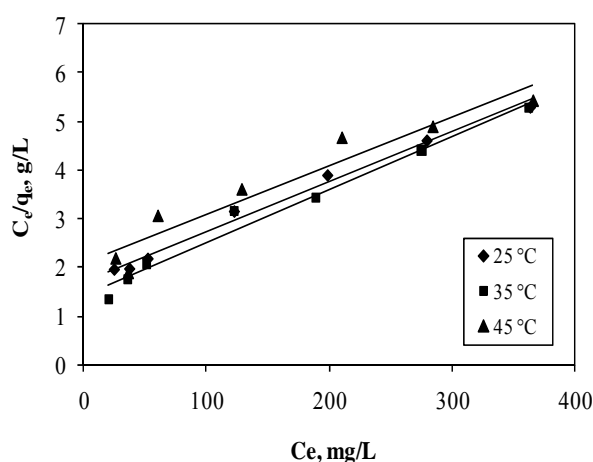
equations which are the most frequently employed isotherm models could be applied. The main difference these models concerns the way of heat of adsorption decreases with the surface coverage: Langmuir assumes no decrease at all while Freundlich assumes a logarithmic decrease (Fierro et al., 2008).

### Langmuir Isotherm

Langmuir equation is applicable to homogeneous sorption where the sorption of each sorbate molecule onto the surface has equal activation energy and its linearized form is given as (Kennedy et al., 2008):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (5)$$

where  $q_e$  is the amount adsorbed per unit weight of adsorbent (mg/g),  $C_e$  is the equilibrium concentration of the adsorbate (mg/L),  $Q_0$  (mg/g) and  $b$  (L/mg) are the Langmuir constants related to the maximum adsorption capacity and the adsorption energy, respectively. These constants can be evaluated from the intercept and the slope of the linear plot of experimental data of  $C_e/q_e$  versus  $C_e$ .



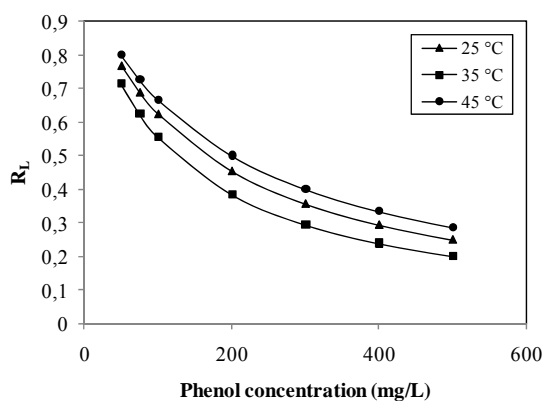
**Figure 4:** Langmuir adsorption isotherms of phenol at different temperatures ( $V=50$  mL;  $m=0.1$  g;  $C_0=50$ -500 mg/L).

The Langmuir  $b$  values determined are further used to calculate the dimensionless separation factor,  $R_L$ ; defined as (Fierro et al., 2008):

$$R_L = 1 / (1 + bC_0) \quad (6)$$

The magnitude of  $R_L$  value gives an idea about nature of adsorption equilibrium; when  $R_L$  is greater than 1 the process is non spontaneous; favorable when  $R_L$  lies between 0 and 1; irreversible when  $R_L$  is zero (Vadivelan, 2005; Vasu, 2007). The calculated  $R_L$  values according to different initial phenol concentration are shown in Figure 6.

In all the temperatures studied  $R_L$  values were comprised between 0 and 1 indicating favorable on the activated carbon. Similar observations have been reported of the adsorption of phenol on rice husk (Kermani et al., 2006). Also the higher  $R_L$  values at lower phenol concentrations show that the adsorption of phenol onto the activated carbon prepared from hazelnut bagasse is more favorable at lower concentrations.



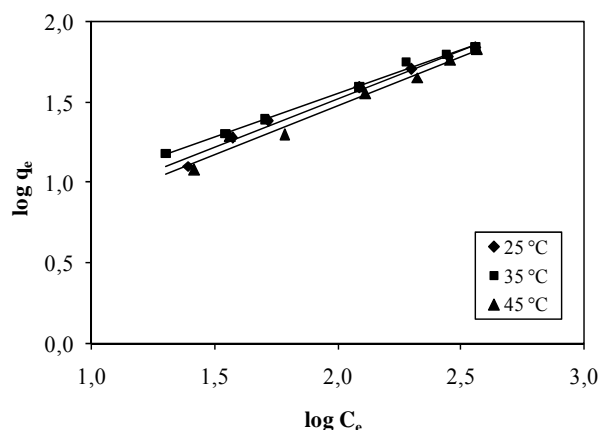
**Figure 5:** Separation factor for phenol onto activated carbon at different temperatures (V=50 mL; m=0.1 g; C<sub>0</sub>=50-500 mg/L).

#### Freundlich isotherm

Freundlich adsorption isotherm is the most important multisite adsorption isotherm for heterogenous surfaces and the linearized form of Freundlich equation is represented by the expression (Kennedy et al., 2008):

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (7)$$

where  $k_F$  (mg/g)(L/mg) and  $1/n$  are Freundlich constants of the adsorbent related to adsorption capacity and adsorption intensity, respectively. The values of  $k_F$  and  $1/n$  can be obtained from the intercept and slope, respectively, of the linear plot of experimental data of  $\ln q_e$  versus  $\ln C_e$ .



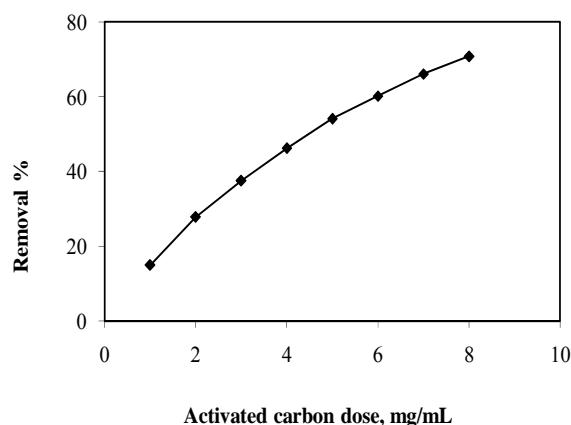
**Figure 6:** Freundlich adsorption isotherms of phenol at different temperatures (V=50 mL; m=0.1 g; C<sub>0</sub>=50-500 mg/L).

The constant parameters of Langmuir and Freundlich isotherm equations at various temperatures are given in Table 2. The high correlation coefficient values which were found greater than 0.9 show the applicability of both these isotherm models.  $k_F$  values should be occur in the range of 1-10. High values of  $k_F$ , the Freundlich constant, showed easy uptake of phenol by activated carbon.  $1/n$  is an empirical constant related to the adsorption driving force. As seen in Table 2, the values of  $1/n$  which are less than 1 (between 0 and 1) indicates the phenol molecules are favorably adsorbed by the activated carbon derived from hazelnut bagasse (Singh et al., 2008).

#### The Effect of Adsorbent Dosage

The effect of adsorbent dosage on the removal of phenol by activated carbon is shown in Figure 7. The removal efficiency of phenol was calculated by the difference between the initial and the final phenol concentrations. From the Figure, it was observed that the percentage removal of phenol increased from 14.97 to 70.80% with an increase in the adsorbent mass from 1 to 8 mg per 50 mL of

solution. The phenol removal increased rapidly up to adsorbent dose of 5 mg/mL and then it increased slightly but not reached constant value.



**Figure 7:** Effect of adsorbent dosage on the percent removal of phenol ( $V=50$  mL;  $m=0.05-0.4$  g;  $C_0=500$  mg/L).

This trend is expected because as the adsorbent amount increases, the number of adsorbent particles increases and the more adsorption sites is available, so more phenol is attached to their sites. At higher adsorbent to solution volume ratios, there is very fast superficial sorption onto the adsorbent surface (Vadivelan *et al.*, 2005)

**Table 2:** The Langmuir and Freundlich isotherm constants at different temperatures.

T (°C)	Langmuir			Freundlich		
	$Q_0$ (mg/g)	$b$ (L/mg)	$R^2$	$k_F$	$1/n$	$R^2$
25	97.36	0.006	0.991	2.033	0.606	0.989
35	91.92	0.008	0.978	2.905	0.546	0.994
45	99.28	0.005	0.923	1.771	0.614	0.977

## Conclusion

The maximum adsorption capacity of phenol onto activated carbon calculated from Langmuir equation was found to be 99.27 mg/g at 45 °C. The amount of phenol uptake was found to increase with increase in solution concentration and contact time. In all the cases, the kinetics of phenol adsorption well followed the pseudo second-order rate equation. The Langmuir and Freundlich isotherm models could adequately describe the adsorption data of phenol. The activated carbon prepared from hazelnut bagasse is industrially viable, cost effective and environmentally compatible adsorbent for the removal of phenol from aqueous solutions.

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