

Adsorption of phenol from aqueous solution by using carbonised beet pulp

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Received 27 February 2005; received in revised form 17 May 2005; accepted 24 May 2005

Available online 28 June 2005

Abstract

The beet pulp, a major low value by-product in sugar industry was used to prepare carbon for phenol adsorption. It was produced by carbonisation in N₂ atmosphere at 600 °C for 1.5 h. The surface area of beet pulp carbon was measured as 47.5 m² g⁻¹ by using BET method.

The adsorption studies of phenol from aqueous solution on beet pulp carbon (BPC) have been studied in the range of 25–500 mg dm⁻³ initial phenol concentrations and at the temperatures of 25, 40 and 60 °C. The maximum phenol adsorption capacity was obtained as 89.5 mg g⁻¹ at the temperature of 60 °C at pH = 6.0. The Freundlich and Langmuir adsorption models were used for the mathematical description of the adsorption equilibrium and it was reported that experimental data fitted very well to Freundlich model, although they could be modelled by the Langmuir equation. Batch adsorption models, based on the assumption of the pseudo-first order and pseudo-second order mechanism, were applied to examine the kinetics of the adsorption. The results showed that kinetic data were followed more closely the pseudo-second order model than the pseudo-first order. The thermodynamic parameters such as, equilibrium constant (*K*), Gibbs free energy changes (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) had been determined. The results show that adsorption of phenol on BPC is an endothermic and spontaneous in nature.

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Keywords: Phenol; Adsorption; Carbonisation; Beet pulp carbon (BPC); Kinetic

1. Introduction

Phenols are generally considered to be one of the important organic pollutant discharged into the environment causing unpleasant taste and odour of drinking water. The major sources of phenol pollution in the aquatic environment are wastewaters from paint, pesticide, coal conversion, polymeric resin, petroleum and petrochemicals industries [1–3]. Introducing phenolic compounds into the environment or degradation of these substances means the appearance of phenol and its derivatives in the environment.

Traditionally, biological treatment [2], activated carbon adsorption, reverse osmosis [4], ion exchange [5] and solvent extraction [6] are the most widely used techniques for removing phenols and related organic substances. Adsorption on the activated carbon is still one of the much used methods among them. Activated carbons to remove organic wastes are currently produced from a variety of starting materials such as wastes and agricultural residues [7,8], nutshells [9], wood [10], plum kernels [11], date pits [12], bentonite [13], and polymers [14]. Many researchers have shown that activated carbon is an effective adsorbent for organic compounds especially for phenolic compounds. However, its high initial cost and the need for a costly regeneration system make it less economically viable as an adsorbent. Taking these criteria into consideration, the search for a low cost and easily available adsorbent has led many investigators to search more

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Nomenclature

C	unadsorbed phenol concentration in solution at any time (mg dm^{-3})
C_{eq}	unadsorbed phenol concentration in solution at equilibrium (mg dm^{-3})
C_0	initial phenol concentration (mg dm^{-3})
ΔG°	Gibbs free energy change
ΔH°	enthalpy change of adsorption
k_1	rate constant of pseudo-first order sorption (min^{-1})
k_2	rate constant of pseudo-second order sorption ($\text{g mg}^{-1} \text{min}^{-1}$)
K	adsorption equilibrium constant ($\text{dm}^3 \text{mg}^{-1}$)
K_F	Freundlich constant
n	Freundlich adsorption constant
q	adsorbed phenol quantity per gram of adsorbent at any time (mg g^{-1})
q_{eq}	adsorbed phenol quantity per gram of adsorbent at equilibrium (mg g^{-1})
q_{max}	maximum amount of phenol per gram of BPC to form a complete monolayer on the surface (mg g^{-1})
r^2	regression correlation coefficient
R	gas constant ($=8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
ΔS°	entropy change of adsorption
T	temperature (K, $^\circ\text{C}$)
X	adsorbent concentration (g dm^{-3})

economic and efficient techniques to use agricultural waste origin, along with industrial by-products as adsorbents [3,15].

Activated carbons starting from agricultural low value by-products have the advantage of exhibiting a high adsorption capacity for organic pollutants due to their high surface area or porous structure. Besides these physical characteristics, the adsorption capacity of a given carbon produced from different sources is strongly influenced by the chemical nature of the surface and functional groups. Although studies to determine the number and the nature of the activated carbon groups given previously, the precise nature of the functional groups is not entirely established. Due to these functional groups such as carboxyls, quionens, phenols, lactones, aldehydes, and anhydrides, the carbons have an acid–base character. It is now known that the acid or base character of carbon depends on its preparation and treatment conditions where it was oxidised [3]. Despite an enormous number of papers on phenol studies [16–18] there is still lack of works of phenol adsorption onto BPC.

In this study, an agricultural low-cost by-product, beet pulp carbon was used as an adsorbent. Beet pulp is a complex material basically containing lignin and cellulose as the major constituents. Beet pulp carbon obtained from different methods to use as an adsorbent was studied for removing heavy metals such as copper and chromium ions in earlier

works [19,20]. But the studies focusing on organic pollutants adsorption on beet pulp carbon and evaluating equilibrium, kinetic and thermodynamic parameters of the process are very limited.

The objective of this study was to produce BPC as an adsorbent for adsorption of phenol, to characterise it and to investigate the effects of initial phenol concentration, contact time, temperature and pH. Equilibrium isotherm data were fitted to Langmuir and Freundlich equations and constants of isotherm equations were determined. Adsorption kinetics of phenol onto BPC were also analysed by using pseudo-first order and pseudo-second order models to the data. Finally, thermodynamic parameters were also evaluated using adsorption data.

2. Theoretical

2.1. Equilibrium parameters of adsorption

Equilibrium study on adsorption has provided information on the capacity of the adsorbent. An adsorption isotherm is characterised by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants. This kind of adsorption isotherm is generally fit to the Langmuir or Freundlich model [21,22]. The Langmuir model as given below is valid for monolayer adsorption onto a surface with a finite number of identical sites, which are homogeneously distributed over the adsorbent surface.

$$q_{\text{eq}} = \frac{Q^0 K C_{\text{eq}}}{1 + K C_{\text{eq}}} \quad (1)$$

where Q^0 and K are Langmuir parameters related to maximum adsorption capacity and bonding energy of adsorption respectively. A plot of $C_{\text{eq}}/q_{\text{eq}}$ versus C_{eq} indicates a straight line of slope $1/Q^0$ and an intercept of $1/KQ^0$. However, the Freundlich model as stated below is an empirical equation based on adsorption on a heterogeneous surface suggesting that binding sites are not equivalent and/or independent.

$$q_{\text{eq}} = K_F C_{\text{eq}}^{1/n} \quad (2)$$

where K_F and n are Freundlich parameters indicating the adsorption capacity and adsorption intensity respectively. From the linear plot of $\ln q_{\text{eq}}$ versus $\ln C_{\text{eq}}$, K_F and $1/n$ values can be determined.

2.2. Kinetic studies

Kinetic models have been proposed to elucidate the mechanism. 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 mechanism of phenol adsorption onto BPC,

pseudo-first order and pseudo-second order model were considered.

The pseudo-first order rate expression of Lagergren [23] based on the adsorption capacity of adsorbent is generally expressed as follows:

$$\frac{dq}{dt} = k_1(q_{\text{eq}} - q) \quad (3)$$

The integrated form of the differential equation becomes

$$\ln(q_{\text{eq}} - q) = \ln q_{\text{eq}} - k_1 t \quad (4)$$

The adsorption kinetics may also be described by pseudo-second order equation which is based on the adsorption capacity of solid phase [24]. The equation is expressed as

$$\frac{dq}{dt} = k_2(q_{\text{eq}} - q)^2 \quad (5)$$

The integrated form of the differential equation becomes

$$\frac{t}{q} = \frac{1}{k_2 q_{\text{eq}}^2} + \frac{1}{q_{\text{eq}}} t \quad (6)$$

If second order kinetic equation is applicable, the plot of t/q against t of Eq. (6) should give a linear relationship. The q_{eq} and k_2 can be determined from the slope and intercept of the plot.

2.3. Thermodynamic parameters of adsorption

The Langmuir constant K changing with temperature can be used to calculate the enthalpy (ΔH°), free energy change (ΔG°) and entropy change (ΔS°). The free energy change of the adsorption is given as

$$\Delta G^\circ = -RT \ln K \quad (7)$$

The temperature dependence of the free energy change is given by the following equation [25]:

$$d\left(\frac{\Delta G^\circ}{T}\right) = -\frac{\Delta H^\circ}{T^2} dt \quad (8)$$

Substituting Eq. (7) into Eq. (8) yields Eq. (9) and the equilibrium constant can be expressed in terms of enthalpy change of adsorption as a function of temperature.

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (9)$$

If the process is endothermic ($\Delta H^\circ > 0$), the equilibrium constant increases with temperature, if the process is exothermic ($\Delta H^\circ < 0$), the equilibrium constant decreases as temperature is raised. Eq. (9) can also be written

$$\frac{d \ln K}{d(1/T)} = \frac{-\Delta H^\circ}{R} \quad (10)$$

Assuming that, ΔH° is approximately independent of temperature, the slope of $\ln K$ versus $1/T$ plot is equal to $-\Delta H^\circ/R$. The change of adsorption entropy can be determined from the equation as $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. The Gibbs free energy

indicates the degree of spontaneity of the adsorption process and the higher negative value reflects a more energetically favourable adsorption.

3. Materials and methods

3.1. Preparation of beet pulp carbon

The beet pulp was obtained from sugar factory in Elazığ, Turkey. This material is produced in sugar industry as a by-product. The beet pulp was dried at oven at 105°C for 1 day. It was grounded and sieved to 50–100 mesh size (0.34–0.15 mm) to separate the material into discrete particle size ranges. Then, powder of beet pulp (25 g) was placed in a horizontal ceramic tube furnace and heated up to 600°C at a rate of $5^\circ\text{C}/\text{min}$. In the meantime, nitrogen was fed into the oven by a rate of $1 \text{ dm}^3/\text{min}$. It was left at this temperature to thermally decompose to porous carbonaceous materials for 1.5 h and then allowed to cool to room temperature in nitrogen atmosphere. Carbon production yield from beet pulp was 25%. The carbon was grounded and screened through different mesh size and stored in a closed bottle to use in adsorption studies.

The surface area of BPC measured by using Micromeritics FlowSorb II-2300 was obtained by using N_2 adsorption. To determine adsorption characteristic of BPC, the iodine number was also measured.

3.2. Chemicals

Stock solution was prepared by dissolving 1.0 g of phenol of analytical reagent grade (Merck) in 1 dm^3 of double-distilled water. The test solutions were prepared by diluting of stock solution to the desired concentrations. The ranges of concentrations of phenol prepared from stock solution varied between the values of 25 and 500 mg dm^{-3} . The pH of the each solution was adjusted to the required value with 1N H_2SO_4 and 1N NaOH solutions before mixing with the beet pulp carbon. While there was no significant changes observed on pH in the equilibrium, the uptake pH was assumed constant during the experiments.

3.3. Adsorption studies

Phenol adsorption studies were performed at various initial concentrations and temperatures at constant 150 rpm shaking glass flasks of 0.25 dm^3 containing of 0.1 dm^3 phenol solution at desired concentration including 0.05 g beet pulp carbon using a rotabit shaker from Selecta. Samples (5 cm^3) were taken before mixing the carbon and phenol solution and during mixing at pre-determined time intervals for determining the residual phenol concentration in the medium. Before analysis, samples were filtered by using blue type whatman filter paper and supernatant fluid was analysed for the remaining phenol. The kinetic studies were carried

out with an initial phenol concentration of 100 mg dm^{-3} at temperature of 25°C . For equilibrium studies, the initial concentration ranged from 25 to 500 mg dm^{-3} , the experiment lasted 120 min to reach equilibrium. All the experiments were carried out in duplicates and average values were used for further calculations.

3.4. Analysis

The concentration of initial and residual phenol in the adsorption media was determined spectrophotometrically. The absorbance of the coloured complex of phenol with *p*-nitroaniline was read at 470 nm [26].

The BET surface area was determined from nitrogen adsorption isotherms using a Micromeritics FlowSorb II-2300 Surface Area Analyzer.

To determine adsorption characteristic of BPC, the iodine number (IN) of carbon was determined by shaking 0.5 g of each sample with 100 cm^3 aqueous solution of iodine ($2.7 \text{ g I}_2 \text{ dm}^{-3}$) at 25°C . The gram amount of iodine adsorbed per gram carbon was taken as iodine number.

The infrared spectrum of beet pulp was obtained with a Mattson 1000 FTIR spectrometer with a pellet of powdered potassium bromide and beet pulp.

4. Results and discussion

Some properties of the BPC used in this study are measured as BET surface area ($47.5 \text{ m}^2 \text{ g}^{-1}$), iodine number ($270 \text{ mg I}_2 \text{ g}^{-1}$) and bulk density (0.576 g cm^{-3}).

Adsorption data for the uptake of phenol onto BPC was investigated at various initial concentration, temperature and pH. The results are given as the units of adsorbed phenol quantity per gram of adsorbent at any time (q , mg g^{-1}) and at equilibrium (q_{eq} , mg g^{-1}), unadsorbed phenol concentration in solution at any time (C , mg dm^{-3}) and at equilibrium (C_{eq} , mg dm^{-3}). Adsorption yield is given as: $[\text{Adsorp. \%} = 100 \times (C_0 - C_{\text{eq}})/C_{\text{eq}}]$.

4.1. Effect of contact time

Fig. 1 shows the adsorption of phenol onto BPC as a function of contact time at 25 , 40 and 60°C . Adsorption studies were carried out for 2 h and it was observed that, the amount of adsorbed phenol increased linearly with time at the beginning of adsorption. Then attained saturation called the equilibrium time. A larger amount of phenol was removed in the first 80 min of contact time and the equilibrium was established in 120 min at all temperatures studied.

4.2. Effect of initial pH of phenol adsorption

The most critical parameter affecting the adsorption process in the removal of phenol by the activated carbon is the

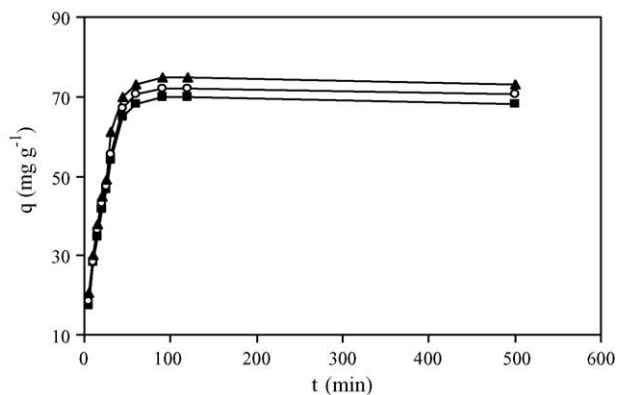


Fig. 1. Phenol adsorption curves at given conditions: $C_0 = 100 \text{ mg dm}^{-3}$, $\text{pH} = 6.0$, $X = 0.5 \text{ g dm}^{-3}$ and agitation rate = 150 rpm at the temperatures: (■) 25°C , (○) 40°C , (▲) 60°C .

pH of the adsorption medium. Fig. 2 shows the effect of solution pH on the adsorption of phenol on the BPC at given conditions. Adsorption increased with increasing pH up to 6.0 and started decreasing with increasing pH again. It is known that activated carbons have strong heterogeneous surfaces. The heterogeneity of their surfaces stems from two sources known as geometrical and chemical ones. Chemical heterogeneity is associated with different functional groups and chemical nature of the surface is the most important factor – apart from the porous structure – that determines its adsorption properties [3]. Coughlin and Ezra reported that [27], the oxidized carbon due to the oxidation atmosphere was mainly carboxyl and hydroxyl ones, and small quantity of carbonyl groups. Fig. 3 shows, the IR spectrum of beet pulp. As seen from the figure, beet pulp contains several functional groups such as hydroxyl peak at 3408 cm^{-1} , carbonyl peak at 2925 cm^{-1} and asymmetric carboxylate peak at 1630 cm^{-1} . Mattson et al. [28] indicated that, phenol and its derivatives adsorb on activated carbon via a “donor–acceptor complex” mechanism that involves carbonyl surface-oxygen groups acting as electron donor, and the aromatic ring of the solute acting as acceptor.

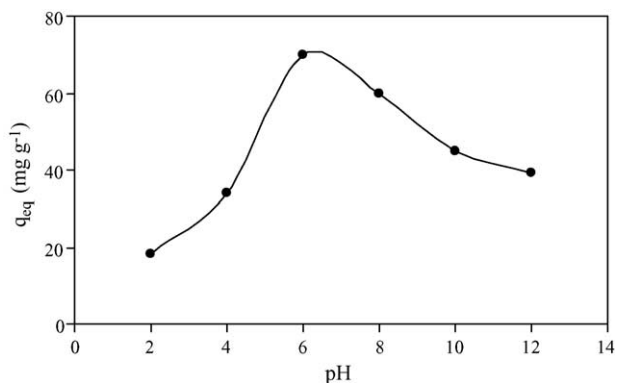


Fig. 2. Effect of pH on the phenol adsorption ($C_0 = 100 \text{ mg dm}^{-3}$, $T = 25^\circ\text{C}$, $X = 0.5 \text{ g dm}^{-3}$, agitation rate = 150 rpm).

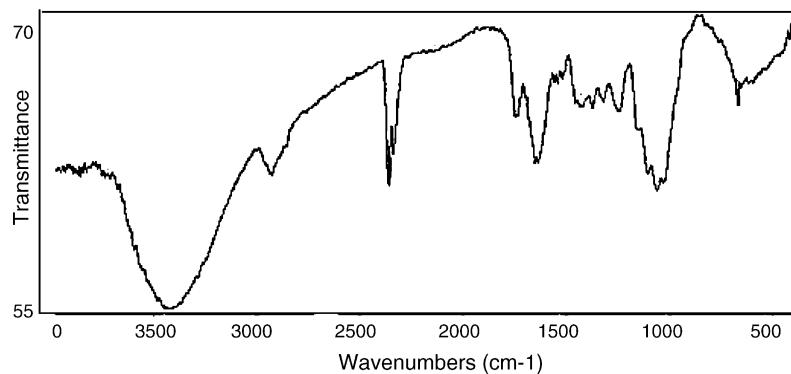


Fig. 3. IR spectra of the beet pulp.

Owing to the amphoteric character of the carbon surface, i.e., to the acidic and/or basic functional groups, the surface properties may be influenced by the pH value of the adsorption medium. The surface charge of carbon is a function of pH of the solution. The pH value, at which the surface charge is zero, is called the point of zero charge (PZC). For typical amphoteric carbons, the surface is positively charged at $\text{pH} < \text{pH}_{\text{PZC}}$ and negatively charged at $\text{pH} > \text{pH}_{\text{PZC}}$ [3]. pH also affects the degree of ionisation of phenol in adsorption medium. In this study, the amount adsorbed decreases at both high and low pH values. The $\text{p}K_{\text{a}}$ value for phenol is 9.89. Phenol could be expected to become negatively charged phenolate ion above this pH and repulsion between the surface layer and the anionic phenolate results in reduced adsorption [29]. The low pH value was obtained by using an acid solution. It introduced additional protons in the solution, which competed for the carbonyl sites, so the adsorption was reduced at low pH. Similar result was given by Liu and Pinto for granule and spherical activated carbon [30]. They reported that, the decrease in phenol adsorption from $\text{pH} = 6.3$ to 3.07 was due to the increased H^+ adsorption on the carbonyl sites, which suppresses phenol adsorption on these sites. On the other hand, the decrease in the phenol amount adsorbed from $\text{pH} = 6.3$ to 11.35 was attributed to both greater solubility of dissociated phenol at $\text{pH} > \text{p}K_{\text{a}}$ and increased repulsion forces between the dissociated form of the adsorbate and the carbon surface.

4.3. Effect of initial phenol concentration on temperature-dependent adsorption

The initial phenol concentration provides an important driving force to overcome all mass transfer limitations of phenol between the aqueous and solid phases. Thus a higher initial phenol concentration will enhance the adsorption process. The effect of initial phenol concentration was investigated in the range of 25–500 mg dm^{-3} at 25, 40 and 60 °C. Table 1 shows the change of the equilibrium adsorption capacity of the BPC with initial phenol concentration and temperature. It was indicated that q_{eq} values increased with both increasing

initial phenol concentrations and increasing temperature. The maximum equilibrium adsorption capacity values were determined as 85.0, 88.0, and 89.5 mg g^{-1} for 500 mg dm^{-3} initial phenol concentration at 25, 40 and 60 °C respectively. The adsorbent showed saturation at high phenol concentration as the adsorbent offers a limited number of surface binding sites. Table 1 also demonstrated that, the adsorption yield decreased with increasing initial phenol concentration while it showed opposite trend with increasing temperature. The maximum phenol adsorption yield of the BPC was determined as 70.0% for 25 mg dm^{-3} initial phenol concentration at 60 °C. The increase of the adsorption capacity and adsorption yield at increased temperature indicated that the adsorption of phenol onto the BPC is endothermic in nature and may involve physical adsorption as well as somewhat chemical adsorption.

4.4. Adsorption equilibrium depending on temperature

In this study, the adsorption equilibrium of phenol on BPC was modelled using Langmuir and Freundlich isotherms. Their isotherm plots obtained at three different temperatures presented in Figs. 4 and 5. The Langmuir and Freundlich adsorption constants evaluated from the isotherms and correlation coefficients are given in Table 2. As seen from the

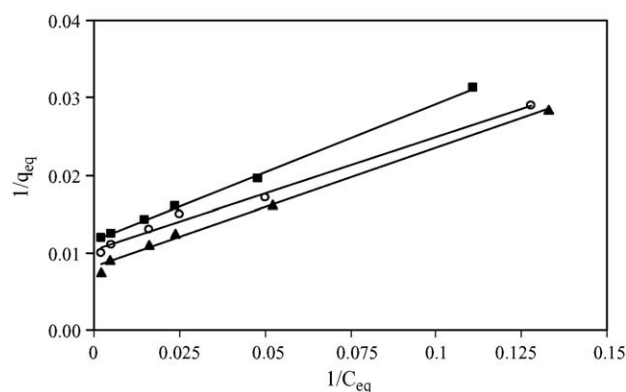


Fig. 4. The linearised Langmuir adsorption isotherm of phenol: (■) 25 °C, (○) 40 °C, (▲) 60 °C.

Table 1
The equilibrium uptake capacities and adsorption yields obtained at different initial concentrations and temperatures

C_0 (mg L ⁻¹)	25 °C		40 °C		60 °C	
	q_{eq} (mg g ⁻¹)	Adsorp. %	q_{eq} (mg g ⁻¹)	Adsorp. %	q_{eq} (mg g ⁻¹)	Adsorp. %
25	32.0	64.0	34.4	68.8	35.0	70.0
50	58.0	58.0	60.0	60.0	61.8	61.8
75	65.0	43.3	66.0	44.0	67.0	44.7
100	70.0	35.0	72.0	36.0	75.0	37.5
250	79.5	15.9	81.2	16.2	83.0	16.6
500	85.0	8.5	88.0	8.8	90.0	9.0

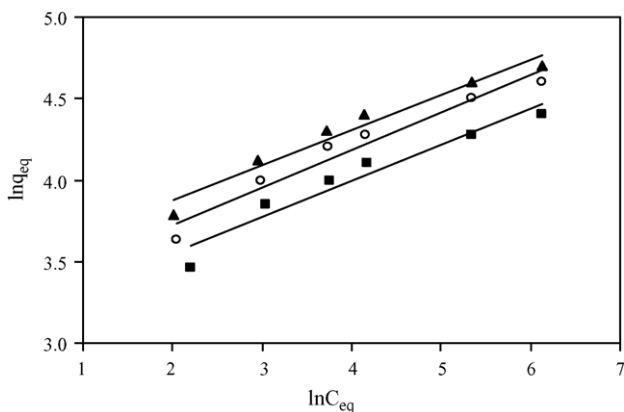


Fig. 5. The linearised Freundlich adsorption isotherm of phenol: (■) 25 °C, (○) 40 °C, (▲) 60 °C.

table, although correlation coefficients (>0.991) of both equations are considerably well obtained at all temperatures, the Freundlich model exhibited better fit to the adsorption data than the Langmuir model.

The magnitude of K_F and n of the Freundlich isotherm constants showed the tendency of phenol uptake from the adsorption medium with high capacity of the BPC especially at 60 °C. The highest K_F value was determined as 29.35 at this temperature. All n values were greater than unity, indicating that phenol was favourably adsorbed by BPC at all temperatures studied. Both the q_{max} and K values determined from Langmuir equation increased from 88.76 to 90.61 and from 0.064 to 0.090 with increasing temperature from 25 to 60 °C respectively. The maximum capacity, q_{max} defines the total capacity of the adsorbent for phenol. The other Langmuir constant, K indicates the affinity for the binding of phenol. The higher value of K found at 60 °C showed strong bonding of phenol to the BPC at this temperature.

Table 2
Isotherms constants for phenol adsorbed on BPC

T (°C)	Langmuir model			Freundlich model		
	q_{max}	K	r^2	K_F	n	r^2
25	89.96	0.0639	0.988	25.58	4.64	0.998
40	88.87	0.0836	0.992	28.01	4.91	0.998
60	90.61	0.0896	0.991	29.35	5.13	0.997

4.5. Kinetic modelling of phenol adsorption

The Lagergren's pseudo-first order and pseudo-second order kinetic models were applied to analyse the adsorption kinetics and to determine the specific rate constant of adsorption process of phenol on BPC. Fig. 6 shows the linearised plots of pseudo-first order rate expression obtained at three different temperatures. The values of various kinetic parameters are tabulated in Table 3. The results showed that the plots were linear with high correlation coefficients (>0.974). The magnitude of k_1 and q_{eq} increased from 0.0512 to 0.0521 dm⁻³ min⁻¹ and from 69.58 to 73.14 mg g⁻¹ respectively with the rise in temperature from 25 to 60 °C.

Using pseudo-second order kinetic model, $1/q$ was plotted versus t at the same temperatures (Fig. 7). The values of second order adsorption rate constant, k_2 , were calculated. Theoretical and experimental q_{eq} and correlation coefficients are also given in Table 3. The values of k_2 and q_{eq} exhibited similar trend with k_1 and increased with increasing temperature. The highest value of k_2 was determined as 5.5×10^{-4} g mg⁻¹ min⁻¹ at 60 °C. Table 3 shows the correlation coefficients for the second order kinetic model which were higher than that of obtained for the first order model. The theoretical q_{eq} values were closer to the experimental q_{eq} values. It was concluded that the adsorption of phenol on to BPC process obeyed second order kinetic model.

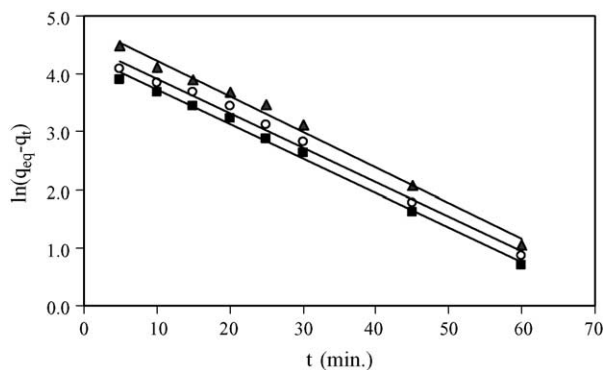


Fig. 6. Pseudo-first order adsorption kinetics of phenol at various temperatures: (■) 25 °C, (○) 40 °C, (▲) 60 °C.

Table 3

Change of the pseudo-first order and pseudo-second order reaction rate constants with temperature

T ($^{\circ}\text{C}$)	$q_{\text{eq,exp}}$ (mg g^{-1})	First order kinetic model			Second order kinetic model		
		k_1 ($\text{dm}^{-3} \text{min}^{-1}$)	$q_{\text{eq,cal}}$ (mg g^{-1})	r^2	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	$q_{\text{eq,cal}}$ (mg g^{-1})	r^2
25	70.0	0.0512	69.58	0.983	5.35×10^{-4}	88.92	0.995
40	72.0	0.0529	72.84	0.974	5.24×10^{-4}	91.46	0.995
60	75.0	0.0521	73.17	0.982	5.50×10^{-4}	93.823	0.994

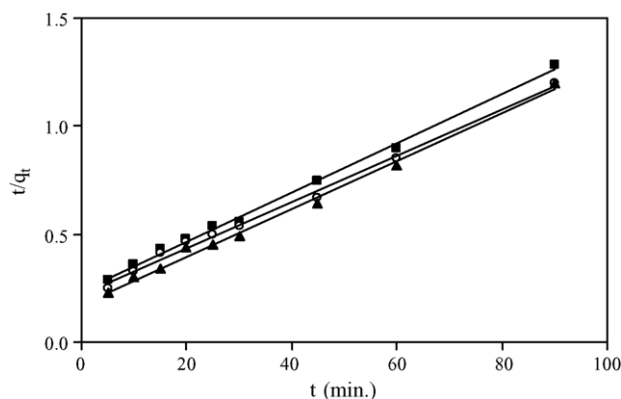
Fig. 7. Pseudo-second order adsorption kinetics of phenol at various temperatures: (■) 25 $^{\circ}\text{C}$, (○) 40 $^{\circ}\text{C}$, (▲) 60 $^{\circ}\text{C}$.

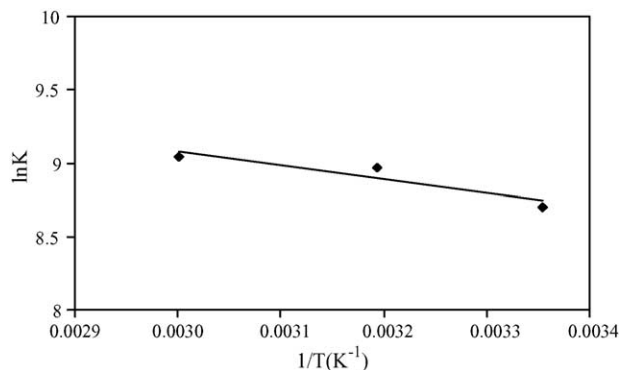
Table 4

 ΔG° values for adsorption of phenol at various temperatures

T ($^{\circ}\text{C}$)	K ($\text{dm}^3 \text{mg}^{-1}$)	$-\Delta G^{\circ}$ (kJ mol^{-1})
25	0.0639	21.57
40	0.0836	23.36
60	0.0896	25.04

4.6. Determination of thermodynamic parameters

The equilibrium constants obtained from Langmuir equation at 25, 40 and 60 $^{\circ}\text{C}$ were used to determine the Gibbs free energy changes [25]. Table 4 shows the Gibbs free energy values for the adsorption process. The negative sign of ΔG° indicates the spontaneous nature of phenol adsorp-

Fig. 8. $\ln K$ vs. $1/T$ plot.

tion onto BPC. The Gibbs free energy and the entropy changes at 60 $^{\circ}\text{C}$ were determined as $-25.04 \text{ kJ mol}^{-1}$ and $0.095 \text{ kJ mol}^{-1} \text{ K}^{-1}$ respectively. The enthalpy change of adsorption was obtained as 6.35 kJ mol^{-1} from Fig. 8. The positive value of ΔH° suggests the endothermic nature of adsorption while the positive value of ΔS° shows the increasing randomness at the BPC–solution interface during the adsorption.

5. Conclusions

In this study, the adsorption of phenol from aqueous solutions was investigated using a carbonised beet pulp in the inert nitrogen atmosphere. The results indicated that adsorption capacity of the adsorbent was considerably affected by initial pH, temperature and initial phenol concentration. The optimum pH value was found to be 6.0. The results showed that phenol adsorption increased with temperatures up to 60 $^{\circ}\text{C}$ and initial phenol concentrations up to 500 g dm^{-3} .

The equilibrium, kinetic and thermodynamic parameters for the adsorption of phenol onto BPC was also determined. The negative sign of ΔG° confirms the spontaneous nature adsorption process. The positive sign of ΔS° shows the increased randomness at the solid–solution interface during adsorption and the positive sign of ΔH° indicates that adsorption process is endothermic.

The Langmuir and Freundlich adsorption equations were used to express the adsorption phenomenon of the phenol. The equilibrium data were well described by the Freundlich model.

The pseudo-first order and pseudo-second order kinetic models were used to analyse data obtained for phenol adsorption onto BPC. The results indicated that the pseudo-second order equation provided the better correlation for the adsorption data.

It can be concluded that the carbonised product from beet pulp is an efficient adsorbent for the removal of phenol from aqueous solution.

Acknowledgement

The authors wish to thank FÜBAP (The Research Foundation of Fırat University), for the partly financial support of this study (Project no.: FÜBAP 929).

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