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## Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

### Biosorption of Phenol on Dried Activated Sludge: Effect of Temperature

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Online publication date: 22 June 2010

**To cite this Article** Arslan, C. Seda and Dursun, Arzu Y.(2008) 'Biosorption of Phenol on Dried Activated Sludge: Effect of Temperature', Separation Science and Technology, 43: 11, 3251 – 3268

**To link to this Article:** DOI: 10.1080/01496390802063671

**URL:** <http://dx.doi.org/10.1080/01496390802063671>

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## Biosorption of Phenol on Dried Activated Sludge: Effect of Temperature

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**Abstract:** In this study, the effectiveness of dried activated sludge in removing phenol from aqueous solutions was examined by biosorption as a function of temperature, pH, and initial phenol concentration. Batch kinetic studies showed that an equilibrium time of 60 min was needed for the biosorption. The maximum phenol biosorption capacity was obtained as  $42.7 \text{ mg g}^{-1}$  at the temperature of  $40^\circ\text{C}$  at  $\text{pH} = 8.0$ . The Freundlich and Langmuir adsorption models were used for the mathematical description of the biosorption equilibrium and it was reported that experimental data fitted very well to the Freundlich model. Adsorption rate data were analyzed using the pseudo-first order kinetic model of Lagergren and the pseudo-second order model to determine adsorption rate constants at 10, 25, and  $40^\circ\text{C}$ . It was reported that, the pseudo-second order kinetic model provided the best correlation of the experimental data rather than the pseudo-first order model. The thermodynamic parameters such as, Gibbs free energy changes ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were determined. The results show that biosorption of phenol on dried activated sludge is an endothermic and spontaneous in nature.

**Keywords:** Biosorption, dried activated sludge, equilibrium, kinetic, phenol, thermodynamic

### INTRODUCTION

Industry creates large amounts of wastewater containing hazardous products to the environment. Among all the organic materials, phenols are important because they are used widely as raw materials for organic

Received 18 April 2007; accepted 19 February 2008.

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compounds, such as plasticizers, pharmaceuticals, dyes, and antioxidants. They exist in various concentrations in wastewaters originated from cooking, synthetic rubber, paper, oil, and gasoline etc. Phenols are toxic to microorganisms, animals, and human beings at low concentrations and they have been classified as hazardous pollutants. The maximum concentration of total phenols in drinking water is given as  $0.5 \mu\text{g L}^{-1}$  by the European Union (1). Different methods designed to remove phenols have been proposed. Traditionally, biological degradation, activated carbon adsorption, solvent extraction, and chemical oxidation are the most widely used methods for removing phenols and its derivatives from wastewaters (2–4). Application of such traditional treatment techniques needs enormous cost and continuous input of chemicals, which becomes impracticable and uneconomical and causes further environmental damage. Hence, easy, effective, economic, and ecofriendly techniques are required for fine tuning of effluent/wastewater treatment.

Biosorption is an alternative technology for the removal of contaminants such as organic pollutants and heavy metal ions from industrial effluents using inactive and dead biomasses (5–9). This term is used to indicate a number of metabolism-independent processes (physical and chemical adsorption, ion exchange, complexation, chelation and micro-precipitation) taking place essentially in the cell wall. The main attraction of biosorption are cost-effectiveness and good removal performance; raw materials which are either abundant (sea weeds) or wastes from other industrial operations (fermentation wastes, activated sludge process wastes) can be used as biosorbents presenting performances often comparable with those of ion exchange resins. The mechanism of binding by inactivated biomass may depend on the chemical nature of the pollutant (species, size, ionic charge), type of biomass, its preparation, and its specific surface properties and environmental conditions (pH, temperature, ionic strength, existence of competing organic or inorganic ligands in solution). As hydrophobic organic pollutants show a high tendency to accumulate onto microbial cells or sludge, the microbial biomass could be used as an adsorbent of biological origin for the removal of low concentration hazardous organics from the wastewater.

Probably the most abundant sources of mixed microbial biomass are the aerobic activated sludge wastewater treatment processes used for the purification of some industrial effluents and domestic wastes. Part of the microorganisms grown in such wastewater systems can be separated and utilized for the removal of pollutants as a biosorbent. Activated sludge from wastewater systems contains both bacteria and protozoa. The cell wall of bacteria essentially consists of various organic compounds such as carboxyl, chitin, acidic polysaccharides, lipids, amino acids, and other components. The protozoa are unicellular, motile, relatively large

eucaryotic cells that lack cell walls. They can absorb components through their outer membranes that contain proteins and lipids (6,10–12).

Some research in literature studied on the phenol binding ability of dried activated sludge and they investigated the effect of pH on biosorption (6,12). However, there is still a lack of the studies focusing on temperature effects on the biosorption of phenol onto dried activated sludge. The present study, deals with understanding of the temperature effects on the biosorption and one of the main objectives of the work is to investigate the feasibility of using dried activated sludge in the batch model for adsorption of phenol. The sorption phenomena were expressed by the Langmuir and Freundlich adsorption models and model constants were evaluated depending on temperature. As there is no information about the kinetic analysis of the adsorption of phenol, the experimental data was also analyzed using the pseudo-first and pseudo second-order adsorption kinetic models and kinetic constants were calculated. An understanding of the kinetics of sorption gives useful knowledge for on-site full-scale applications. Since the evaluation of the heat change of the biosorption process is very important for the reactor design, the thermodynamics of the biosorption process was also investigated.

## THEORETICAL

### Equilibrium Parameters of Adsorption

Equilibrium study on adsorption has provided information on the capacity of the adsorbent. The equilibrium established between adsorbed phased on the biosorbent and that in solution can be represented by adsorption isotherms. An adsorption isotherm is characterized 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 equilibrium can be represented by the Langmuir or Freundlich adsorption isotherms, which are widely used to analyze data for water and wastewater treatment applications.

In obtaining the Langmuir isotherm equation, several aspects of the adsorption system were presupposed in the derivation. The most important assumptions are;

- (1) All the surface of the catalyst has the same activity for adsorption,
- (2) There is no interaction adsorbed molecules and all the adsorption occurs by the same mechanism,
- (3) The extent of adsorption is less than one complete monomolecular layer on the surface (13,14).

The Langmuir equation is given by Eq. (1).

$$q_{eq} = \frac{q_{max} K_b C_{eq}}{1 + K_b C_{eq}} \quad (1)$$

where  $q_{eq}$  is adsorbed phenol quantity per gram of sorbent at equilibrium ( $\text{mg g}^{-1}$ ),  $C_{eq}$  ( $\text{mg L}^{-1}$ ) is unadsorbed phenol concentrations in solution at equilibrium,  $q_{max}$  ( $\text{mg g}^{-1}$ ) and  $K_b$  ( $\text{L mg}^{-1}$ ) are Langmuir parameters related to maximum adsorption capacity and bonding energy of adsorption respectively. A plot of  $C_{eq}/q_{eq}$  versus  $C_{eq}$  indicates a straight line of slope  $1/q_{max}$  and an intercept of  $1/K_b q_{max}$ .

The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface. It is commonly presented as Eq. (2)

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

where  $K_F$  ( $\text{mg g}^{-1}$ ) and  $n$  Freundlich parameters indicating the adsorption capacity and adsorption intensity respectively. From the linear plot of  $\ln q_{eq}$  versus  $\ln C_{eq}$ ,  $K_F$  and  $1/n$  values can be determined (14).

### Kinetic Parameters of Biosorption

In developing the procedure to obtain a mechanism and potential rate limiting step, kinetic models have been used to test experimental data. In the present study, in order to investigate the mechanism of phenol adsorption onto dried activated sludge, pseudo-first order and pseudo-second order model were considered.

The pseudo-first order rate expression of Lagergren (15) based on the adsorption capacity of the adsorbent is generally expressed as follows,

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

where  $q$  is the adsorbed phenol quantity per gram of sorbent at any time ( $\text{mg g}^{-1}$ ),  $k_1$  is the rate constant of the pseudo-first order sorption ( $\text{min}^{-1}$ ),  $t$  is time (min). The integrated form of the differential equation becomes,

$$\log(q_{eq} - q) = \log(q_{eq}) - \frac{k_1}{2.303} t \quad (4)$$

A plot of  $\log(q_{eq} - q)$  against of  $t$  should give a linear relationship with the slope of  $K_1/2.303$  and intercept of  $(\log q_{eq})$ .

The adsorption kinetics may also be described by pseudo-second order equation which based on the adsorption capacity of solid phase

(16). The equation is expressed as;

$$\frac{dq}{dt} = k_2 (\text{g mg}^{-1} \text{min}^{-1}) (q_{eq} - q)^2 \quad (5)$$

Where  $k_2$  is the rate constant of pseudo-second order sorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ). The integrated form of the differential equation becomes,

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

If the 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.

### Thermodynamic Parameters of Biosorption

The Gibbs free energy change ( $\Delta G^\circ$ ) (kJ/mol) can be determined using equilibrium constant (The Langmuir constant  $K_b$ ) (Eq. 7)

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

Where  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{K}^{-1}$ ) and  $T$  is the absolute temperature (K). The Gibbs free energy indicates the degree of spontaneity of the adsorption process and the higher negative value reflects a more energetically favorable adsorption.

The temperature dependence of the free energy change is given by the following equation (17).

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

Where  $\Delta H^\circ$  is the enthalpy change of adsorption (kJ/mol). 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.

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

Eq. (9) can also be written

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

Assuming that,  $\Delta H^\circ$  is approximately independent of temperature, the slope of  $\ln K_b$  versus  $(1/T)$  plot is equal to  $(-\Delta H^\circ/R)$ . The change of

adsorption entropy with temperature can be determined from Eq. (11)

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (11)$$

Where  $\Delta S^{\circ}$  is Entropy change of adsorption (kJ/mol K)

## MATERIALS AND METHODS

### Preparation of the Biosorbent

The waste activated sludge collected from the wastewater treatment plant of Elazig city, Turkey was used in this study. The sludge was washed thoroughly with sterile distilled water, centrifuged at 5000 rpm for 5 min, and dried at 60°C for 24 h before use. For the biosorption studies, a weight amount of dried biomass was suspended in 100 mL deionized distilled water and homogenized in a homogenizer and then stored in the refrigerator.

### Chemicals

Stock solution was prepared by dissolving 1.0 g of phenol of analytical reagent grade (Merck) in 1 L of deionized-distilled water. The test solutions were prepared by diluting of the stock solution to the desired concentrations. The pH of each solution was adjusted to the required value with diluted or concentrated  $H_2SO_4$  and NaOH solutions before mixing with the adsorbent. As insignificant changes in the final equilibrium pH were observed, the uptake pH was assumed constant during the experiments.

### Biosorption Studies

This method involved agitating (150 rpm) 250 mL Erlenmeyer flasks containing 0.1 g dried activated sludge and 100 mL of phenol solutions at desired concentration, temperature, and pH. Samples (5 mL) were taken at pre-determined time intervals for determining the residual phenol concentration in the medium. Before analysis, the samples were centrifuged at 4000 rpm for 3 min and supernatant fluid analyzed for the remaining phenol. The biosorption equilibrium was reached after 60 min. All the experiments were carried out in duplicates and average values were used for further calculations.

## Analysis

The concentration of residual phenol in the biosorption media was determined spectrophotometrically. The absorbance of the colored complex of phenol and p-nitroaniline was read 470 nm (18).

## RESULTS AND DISCUSSION

Biosorption of phenol onto dried activated sludge was investigated as a function of pH, temperature and initial phenol concentration.  $C$  is unadsorbed phenol concentrations in solution at any time.  $X$  is sorbent concentration. Adsorption yield can be determined as;

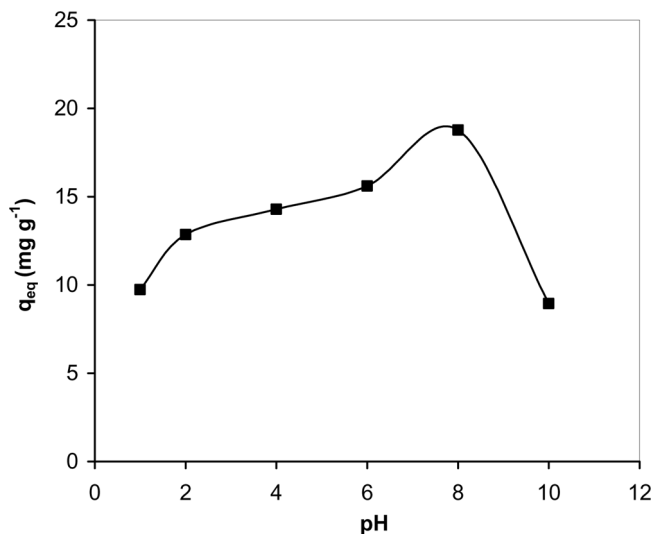
$$Ad\% = 100 \times (C_0 - C_{eq})/C_0 \quad (12)$$

### Effect of Initial pH on Phenol Adsorption

A change in solution pH influences the charge properties of ionizable phenols molecules and, hence biosorption. The optimum initial pH for biosorption is also organism-dependent because of different adsorptive sites of different species of microorganisms. To find the suitable pH for the biosorption a series of experiments were performed at different initial pH values (1.0–10.0). Figure 1 shows the uptake of phenol increased with increasing initial pH up to 8 then and started decreasing with increasing pH again. As mentioned above, solution pH influences both cell surface metal binding sites and metal chemistry in water. The isoelectric point of activated sludge was usually between pH 1 and 3 (6). At pH values below the isoelectric point ( $pH < 3$ ), the overall surface charge on the cells will be positive. Above the isoelectric point, the cells would have a net negative charge. The pH also primarily affects the degree of ionization of the phenolic sorbate. The  $pK_a$  value for phenol is 9.89 and phenol could be expected to become a negatively charged phenolate ion above this pH. At highly basic pH values, a negatively charged surface site on the biosorbent does not favor for the adsorption of phenolate anions due to the electrostatic repulsion. The increase of  $OH^-$  ions with the increasing pH also cause a competition with the phenolate anions for the adsorption sites resulting in a decrease in biosorption (19).

The low pH value was obtained by using an acid solution. It introduced additional protons in the solution, which competed for the adsorption sites. This leads to an increase in water adsorption (associated water complexes) and to blocking of some of the most active phenol-adsorbing sites or blocking of some pores by water molecules. As pH increased, the





**Figure 1.** Effect of pH on the phenol biosorption ( $C_0 = 100 \text{ mg L}^{-1}$ ,  $T = 25^\circ\text{C}$ ,  $X = 1.0 \text{ g L}^{-1}$ , agitation rate = 150 rpm).

reduction of surface protonation effect takes place and the resultant surface charge decreases. Increasing the pH gradually improves the strength of the interaction, and the adsorption performance (20). Carmona et al. investigated the effect of pH on combined adsorption and ion exchange of phenol on amberlite. They reported that the higher phenol removal was observed at the higher pH values (21). It is obvious that the proposed biosorption mechanisms due to the initial pH are not sufficient to explain the efficient biosorption of phenol observed at all the pH values studied. It is thought that additional types of biosorption mechanisms such as ion exchange, complex formation, or membrane transport and physico-chemical forces such as van der Waals, H-binding are also important for the bioremoval of phenol.

The optimum pH value for this study was reported as 8.0 and this value was used in rest of the study.

### **Effect of Initial Phenol Concentration on Temperature Dependent Biosorption**

The effect of initial phenol concentration was investigated in the range of 25–300 mg L<sup>-1</sup> at 10, 25, and 40°C. Table 1 shows the change of the equilibrium biosorption capacity of the dried activated sludge with initial

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

$C_o$ (mg L <sup>-1</sup> )	10°C		25°C		40°C	
	$q_{eq}$ (mg g <sup>-1</sup> )	Ad. %	$q_{eq}$ (mg g <sup>-1</sup> )	Ad. %	$q_{eq}$ (mg g <sup>-1</sup> )	Ad. %
25	5.95	23.8	6.91	26.04	9.43	37.74
50	10.60	21.2	11.55	23.1	13.23	26.47
100	16.90	16.9	18.77	18.77	20.69	20.69
200	22.46	11.23	26.33	13.16	28.89	14.45
300	33.79	11.26	35.89	11.96	42.7	14.23

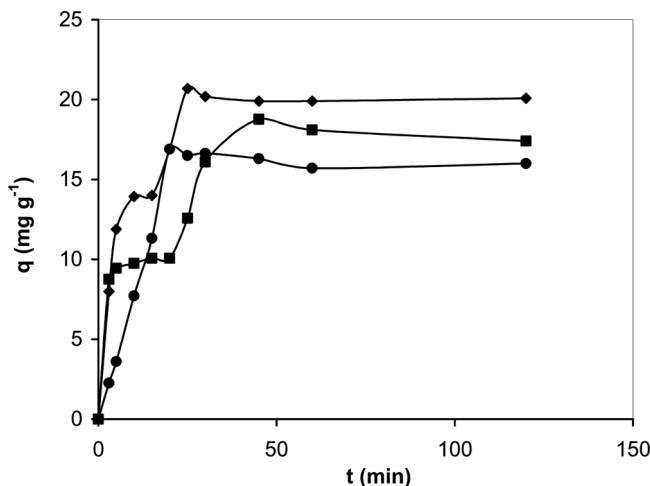
phenol concentration and temperature. When the initial pollutant concentration was increased from 25 mg L<sup>-1</sup> to 300 mg L<sup>-1</sup>, the equilibrium sorption capacity of the biosorbent increased from 5.95 to 33.79 mg g<sup>-1</sup> at 10°C. Same trend was reported for the other temperatures studied because the initial sorbate concentration provides an important driving force to overcome all mass transfer resistance. The increases of the loading capacity of the biosorbent with increasing initial phenol concentration may also be due to higher interaction between phenol and the biosorbent. As dried activated sludge offers a finite number of surface binding sites, phenol adsorption showed a saturation trend at higher initial phenol concentration. Table 1 also showed that the phenol adsorption capacity increased with increasing temperature from 10°C to 40°C. Maximum biosorption capacity was determined as 42.7 mg g<sup>-1</sup> for 300 mg L<sup>-1</sup> initial phenol concentration at 40°C.

The biosorption yields determined at different initial phenol concentrations were also compared in Table 1. At lower concentrations, all sorbate ions present in the adsorption medium could interact with the binding sites so higher adsorption yields were obtained. At higher concentrations, lower adsorption yield were observed because of the saturation of the adsorption sites. So increasing phenol concentration generally caused a decrease in the biosorption yield. The maximum adsorption yields were determined as 23.8%, 26.0%, and 37.7% at 25 mg L<sup>-1</sup> initial phenol concentration for 10, 25, and 40°C respectively. The adsorption yields were also influenced by temperature and increased with increasing temperature. The increase of the adsorption yield and adsorption capacity at increased temperature indicated that the sorption of phenol onto dried activated sludge is endothermic in nature. This effect may be attributed to the enlargement of the pore size or the creation of some new active sites on the adsorbent surface due to bond rupture (22,23).

The comparison of the biosorption capacity of dried activated sludge used in this study ( $42.7 \text{ mg g}^{-1}$  for  $300 \text{ mg L}^{-1}$  initial phenol concentration at  $40^\circ\text{C}$ ) with those obtained in the literature shows that dried activated sludge is effective for this purpose. Thawornchaisit and Pakulanon (12) investigated the effect of pH and initial phenol concentration on biosorption of phenol on dried activated sludge at  $32 \pm 2^\circ\text{C}$ . They reported that the biosorption capacity was strongly influenced by the pH of the aqueous solution with an observed maximum phenol removal at pH around 6–8. Wu and Yu (9) studied on the biosorption of phenolic compounds from aqueous solutions by non-living *Phanerochaete chrysosporium* mycelial pellets. They observed the highest biosorption capacity of the microorganism as  $1.1 \text{ mg g}^{-1}$  for phenol. The effect of pH on the equilibrium uptake of phenol and nickel(II) ions by dried aerobic activated sludge was studied in a batch system by Aksu and Akpinar (23). They found the binding capacity value as  $49.8 \text{ mg g}^{-1}$  at pH: 1.0, T:  $25^\circ\text{C}$ ,  $100.8 \text{ mg L}^{-1}$  initial phenol concentration. Z. Aksu and J. Yener (6) investigated the effect of initial pH, initial pollutant concentration on biosorption of phenol, *o*-chlorophenol, and *p*-chlorophenol from aqueous solutions on dried activated sludge. The maximum loading capacity of biosorbent was found to be  $86.1 \text{ mg g}^{-1}$  for phenol. Al-Asheh et al. (24) investigated the adsorption of phenol onto activated bentonites. They found equilibrium uptake of phenol between 9.9 and  $8.2 \text{ mg g}^{-1}$  for different types of activated bentonites. A raw lignitic coal was investigated to determine its potential as an adsorbent for phenol removal from wastewaters by Polat et al. (25). They found the adsorption capacity of lignite as  $10 \text{ mg g}^{-1}$ . Vipulanandan (26) determined phenol adsorption capacity of kaoline as  $5 \mu\text{mol g}^{-1}$ . The adsorption of phenol onto chitin was studied by Dursun and Kalayci (27). They reported the maximum biosorption capacity of chitin as  $21.49 \text{ mg g}^{-1}$  for  $300 \text{ mg L}^{-1}$  initial phenol concentration at  $40^\circ\text{C}$ . Batch adsorption of phenol on a polymeric adsorbent was performed by Pan et al. (28) and the equilibrium adsorption capacity was determined as  $1.0 \text{ mmol g}^{-1}$ . The beet pulp, a major low value byproduct of the sugar industry was used to prepare carbon for phenol adsorption by Dursun et al. (29). The maximum phenol adsorption capacity was obtained as  $89.5 \text{ mg g}^{-1}$  at the temperature of  $60^\circ\text{C}$  at pH = 6.0.

### Effect of Contact Time

Figure 2 shows the biosorption of phenol onto dried activated sludge as a function of contact time at 10, 25, and  $40^\circ\text{C}$ . Biosorption studies were carried out for 2 hours and it was observed that, a larger amount of



**Figure 2.** The adsorption curves of phenol ( $C_0 = 100 \text{ mg L}^{-1}$ ,  $\text{pH} = 8.0$ ,  $X = 1.0 \text{ g L}^{-1}$ , agitation rate = 150 rpm and ●, ■, ▲ show uptake values at 10, 25, and 40°C respectively).

phenol was removed in the first 30 min of contact time. Equilibrium was established in 60 min for all the temperatures studied.

### Determination of Equilibrium Model Constants

Langmuir and Freundlich adsorption isotherms are used to describe the sorption phenomena of phenol to dried activated sludge. To determine the equilibrium isotherms for both equations; initial phenol concentrations were varied from  $25 \text{ mg L}^{-1}$  to  $300 \text{ mg L}^{-1}$  while the adsorbent concentration was kept constant ( $1.0 \text{ g L}^{-1}$ ) at 10, 25, and 40°C. The linearised isotherms are presented in Figs. 3, 4. The isotherm constants and correlation coefficients are tabulated in Table 2. As seen from the table, the isotherms appeared to follow the Freundlich model more closely than the Langmuir model at all the temperatures studied. The Freundlich equation is based on a monolayer adsorption by the adsorbent with a heterogeneous energy distribution of active sites. The surface of the biological materials was expected to have heterogeneous energies for adsorption, so a good fit was obtained. The values of the Freundlich constants increased with increasing temperature and the highest  $K_F$  value was reported as  $2.11 \text{ mg g}^{-1}$  at 40°C. All  $n$  values were found high enough for adsorption ( $> 1.0$ ).

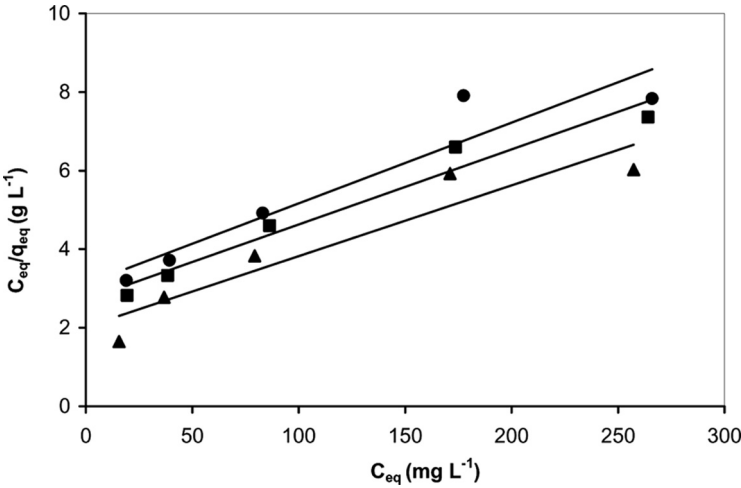


Figure 3. The linearized Langmuir adsorption isotherm of phenol.

The maximum capacity  $q_{max}$  determined from the Langmuir isotherm defines the adsorption capacity when the surface is fully covered with phenol. The adsorption capacity of the biosorbent increased with increasing the temperature and maximum  $q_{max}$  values were determined

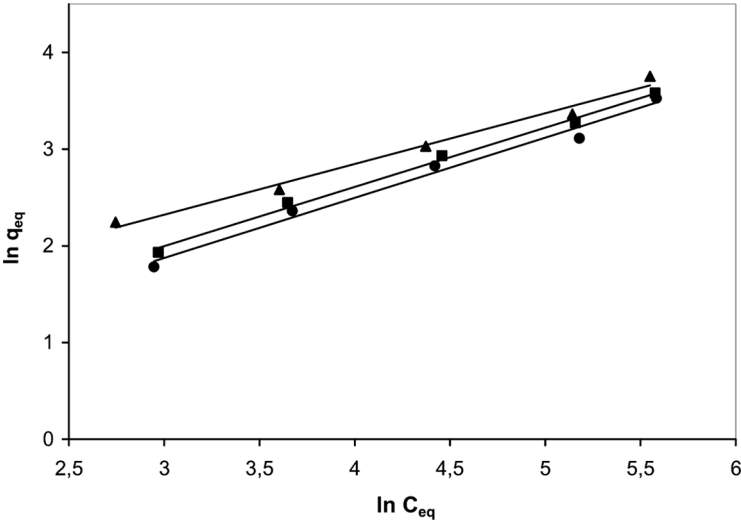


Figure 4. The linearized Freundlich adsorption isotherm of phenol.

**Table 2.** Isotherms constants for phenol biosorbed on dried activated sludge

$T$ ( $^{\circ}\text{C}$ ) $q_{\text{max}}$	Langmuir Model			Freundlich Model		
	( $\text{mg g}^{-1}$ )	$K_b$ ( $\text{L mg}^{-1}$ )	$R^2$	$K_F$ ( $\text{mg g}^{-1}$ )	$n$	$R^2$
10	48.54	0.0066	0.899	1.01	1.61	0.984
25	52.35	0.0070	0.889	1.18	1.63	0.995
40	55.55	0.0088	0.961	2.11	1.91	0.985

as  $55.55 \text{ mg g}^{-1}$  at  $40^{\circ}\text{C}$ . A high  $K_b$  value indicates the affinity for binding of phenol. When the adsorption is endothermic, an increase in  $T$  results in an increase in  $K_b$ . The highest value of  $K_b$  was found at  $40^{\circ}\text{C}$ .

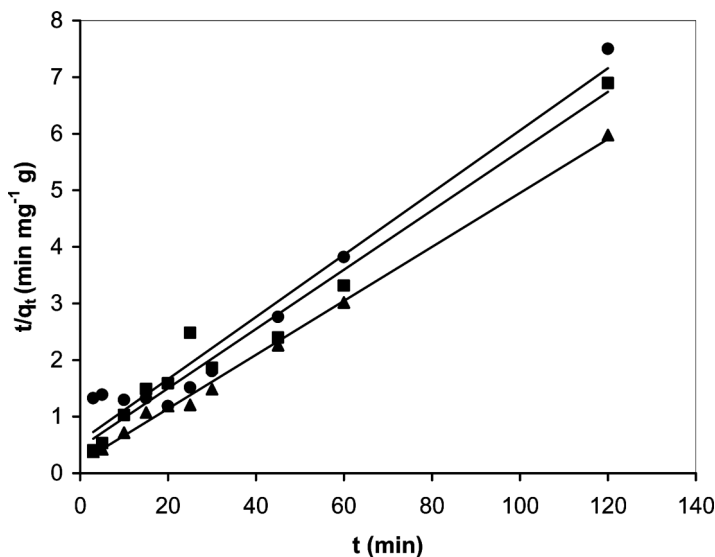
### Determination of Kinetic Constants

In order to analyze the biosorption kinetics of the system, a series of experiments were carried out with constant initial phenol concentration of  $100 \text{ mg L}^{-1}$  at different temperatures. The pseudo-first and second-order kinetic models were applied to the data. The results showed that, the correlation coefficients for the first order kinetic model were very low (Table 3). The theoretical  $q_{\text{eq}}$  values found from this model did not give reasonable values so the pseudo-first order model did not describe the biosorption results of phenol onto dried activated sludge.

The plots of the linearized form of the pseudo-second order equation are shown in Fig. 5. Kinetic constants and correlation coefficients are compared in Table 3. As seen from the table, the values of the correlation coefficient were very high and the theoretical  $q_{\text{eq}}$  values were much closed to the experimental  $q_{\text{eq}}$  values. In view of these results, it can be said that the pseudo-second order kinetic model in contrast to the pseudo-first order model, provided a good correlation for the biosorption.

**Table 3.** Change of the pseudo-first and second order reaction rate constants with temperature

$T$ ( $^{\circ}\text{C}$ )	$q_{\text{eq,exp}}$ ( $\text{mg g}^{-1}$ )	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
		$k_1$ ( $\text{min}^{-1}$ )	$q_{\text{eq,cal}}$ ( $\text{mg g}^{-1}$ )	$R^2$	$K_2$ ( $\text{g mg}^{-1} \text{ min}^{-1}$ )	$q_{\text{eq,cal}}$ ( $\text{mg g}^{-1}$ )	$R^2$
10	16.90	0.0230	8.61	0.572	0.0054	18.21	0.959
25	18.77	0.0198	3.48	0.232	0.0060	19.08	0.970
40	20.69	0.0258	5.61	0.502	0.0124	20.96	0.996



**Figure 5.** Pseudo-second order adsorption kinetics of phenol at different temperatures.

### Determination of Thermodynamic Constants of Biosorption

The Gibbs free energy changes for the biosorption process were calculated by using the equilibrium constants obtained from Langmuir model and tabulated in Table 4. As seen from the table all the Gibbs free energy change values are negative. A negative value of  $\Delta G^\circ$  indicates the feasibility of the process and spontaneous nature of the biosorption. The standard enthalpy change of biosorption determined from the  $\ln K_b$  versus  $1/T$  plot (Fig. 6) was  $7.164 \text{ kJ mol}^{-1}$ . The positive value of  $\Delta H^\circ$  suggests the endothermic nature of biosorption. The entropy change of the biosorption at  $40^\circ\text{C}$  was determined as  $0.079 \text{ kJ mol}^{-1} \text{ K}^{-1}$  and the positive value of  $\Delta S^\circ$  confirms the increased randomness at the solid–solution interface during biosorption.

**Table 4.**  $\Delta G^\circ$  values for adsorption of phenol at different temperatures

$T (^\circ\text{C})$	$K_b (\text{L mg}^{-1})$	$-\Delta G^\circ (\text{kJ mol}^{-1})$
10	0.0066	15.141
25	0.0070	16.094
40	0.0089	17.513

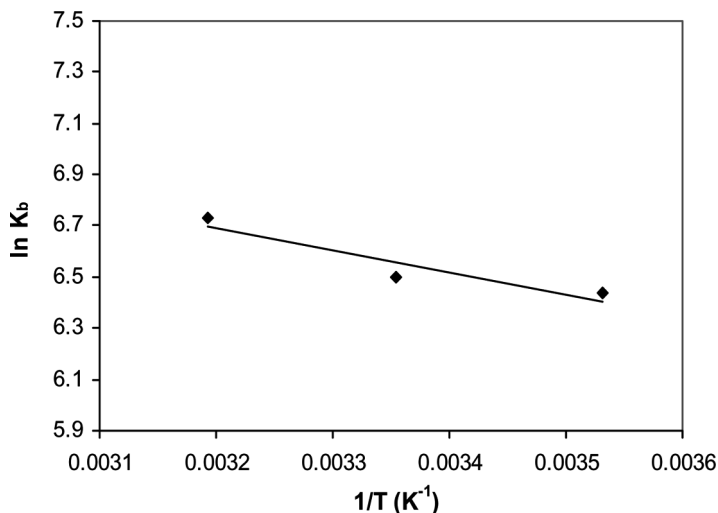


Figure 6.  $\ln K_b$  vs.  $1/T$  plot.

## CONCLUSION

In this study, the adsorption of phenol from aqueous solutions was investigated using dried activated sludge. It was seen that initial pH, temperature, and initial phenol concentration highly affected the biosorption capacity of the sorbent. Biosorption capacity increased as phenol concentration and temperature increased.

The equilibrium of biosorption of phenol onto the biosorbent was tested using Langmuir and Freundlich equations. The equilibrium data were well described by the Freundlich model.

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

The thermodynamic constants of adsorption were also evaluated. The negative value of  $\Delta G^\circ$  confirms the spontaneous nature adsorption process. The positive value of  $\Delta S^\circ$  showed the increased randomness at the solid-solution interface during biosorption and the positive value of  $\Delta H^\circ$  indicated the adsorption process was endothermic.

## ACKNOWLEDGEMENTS

The authors wish to thank FÜBAP (The research Foundation of Firat University), for the financial support of this study (Project no: FÜBAP 806).



## NOMENCLATURE

$C$	Unadsorbed phenol concentration in solution at any time ( $\text{mg L}^{-1}$ )
$C_{eq}$	Unadsorbed phenol concentration in solution at equilibrium ( $\text{mg L}^{-1}$ )
$C_0$	Initial phenol concentration ( $\text{mg L}^{-1}$ )
$q$	Adsorbed phenol quantity per gram of biosorbent at any time ( $\text{mg g}^{-1}$ )
$q_{eq}$	Adsorbed phenol quantity per gram of biosorbent at equilibrium ( $\text{mg g}^{-1}$ )
$q_{max}$	Maximum amount of phenol per unit weight of the biosorbent to form a complete monolayer on the surface ( $\text{mg g}^{-1}$ )
$K_b$	Adsorption equilibrium constant ( $\text{L mg}^{-1}$ )
$K_F$	Freundlich constant ( $\text{mg g}^{-1}$ )
$k_1$	Rate constant of pseudo-first order sorption ( $\text{min}^{-1}$ )
$k_2$	Rate constant of pseudo-second order sorption ( $\text{g mg}^{-1} \text{min}^{-1}$ )
$n$	Freundlich constant
$R$	Universal gas constant ( $8.314 \text{ J mol}^{-1} \text{K}^{-1}$ )
$R^2$	Regression correlation coefficient
$T$	Temperature ( $\text{K}, ^\circ\text{C}$ )
$t$	Time (minute)
$X$	Sorbent concentration ( $\text{g L}^{-1}$ )
$\Delta G^\circ$	Gibbs free energy change ( $\text{kJ/mol}$ )
$\Delta H^\circ$	Enthalpy change of adsorption ( $\text{kJ/mol}$ )
$\Delta S^\circ$	Entropy change of adsorption ( $\text{kJ/mol K}$ )

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