

Equilibrium, kinetic and thermodynamic studies on the adsorption of phenol onto chitin

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Abstract

The adsorption of phenol onto chitin, a naturally occurring material was studied as a function of initial pH, temperature and initial phenol concentration. The highest phenol adsorption capacity was determined as 21.5 mg g^{-1} for 300 mg dm^{-3} initial phenol concentration at pH 1.0 and 40°C . Adsorption data were well described by the Freundlich Model, although they could be modeled by the Langmuir equation. The pseudo-first-order and pseudo-second-order kinetic models were applied to test the experimental data. The pseudo-second-order kinetic model provided the best correlation of the experimental data compared to the pseudo-first-order model. The thermodynamic constants of the adsorption process; ΔG° , ΔH° and ΔS° were evaluated as $-19.4 \text{ kJ mol}^{-1}$ (at 40°C), 10.2 kJ mol^{-1} and $0.093 \text{ kJ mol}^{-1} \text{ K}^{-1}$, respectively. These showed that adsorption of phenol on chitin was endothermic and spontaneous.

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1. Introduction

Phenols are common contaminants in wastewater generated from oil, gasoline, coal, paper, textile, synthetic rubber and pharmaceuticals industries. Wastewater containing these compounds presents a serious environmental problem because of their high toxicity and possible accumulation in the environment. Several methods, such as microbial degradation, adsorption, chemical oxidation, solvent extraction and reverse osmosis are being used for removing phenols from wastewater. Adsorption is an effective separation process for treating industrial and domestic effluents. Activated carbon (granular or powdered) is the most widely used adsorbent. It has the advantage of high adsorption capacity for organic compounds, but its use is usually limited due to its high cost [1–4]. Recently, considerable attention has been directed towards low cost, naturally occurring adsorbents. These novel adsorbents include a wide range of materials ranging from

by-products derived from agricultural, industrial and fishery wastes (peanut skins, wool, sugar cane bagasse, tea leaves, coffee powder, wool, rice straw, chitin, etc.) to microbial biomass [5–7].

Chitin, a homopolymer comprising β -(1-4)-linked *N*-acetyl-D-glucosamine is the second most abundant and renewable natural polymer. It is found in the exoskeletons of crabs and other arthropods and in the cell walls of some fungi [8]. Chitin is also a waste product of the crab meat canning industry and it can be extracted in large quantities from crab and shrimp shells. Chitin carries one linear amino group per glucose ring and exhibits metal ion uptake. Many studies have focused on metal binding ability of chitin and adsorption of phenol by activated carbon. However, much less is known about the adsorption equilibrium, kinetics and thermodynamics of phenol onto chitin.

The aim of this study was to investigate the phenol adsorption characteristics of chitin taking into account kinetic, equilibrium and thermodynamic aspects. The adsorption equilibrium was expressed by the Langmuir and Freundlich models. As there was no information about the kinetic analysis of the adsorption of phenol, two kinetic models were used for ana-

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Nomenclature

C	unadsorbed phenol concentration in solution at any time (mg dm^{-3})
C_0	initial phenol concentration (mg dm^{-3})
C_{eq}	unadsorbed phenol concentration in solution at equilibrium (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	Langmuir adsorption constant, adsorption equilibrium constant ($\text{dm}^3 \text{mg}^{-1}$)
K_F	Freundlich constant
n	Freundlich 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 unit weight of chitin to form a complete monolayer on the surface (mg g^{-1})
R	Universal gas constant ($8314 \text{ J mol}^{-1} \text{ K}^{-1}$)
R^2	regression correlation coefficient
ΔS°	entropy change of adsorption
T	temperature (K, °C)
X	sorbent concentration (g dm^{-3})

lyzing the experimental data. Since the evaluation of the heat change of the adsorption process is very important for reactor design, the thermodynamics of the adsorption process was also investigated.

2. Materials and methods

2.1. Adsorbent

Chitin from crushed crab shells (Sigma Chemicals Co.) was used in this study. It was sieved to separate the material into discrete particle size ranges. Previous studies showed that 147–300 μm particle sizes could be chosen as suitable size for adsorption experiments.

2.2. 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 stock solution to the desired concentrations. The pH of the each solution was adjusted to the required value with dilute

or concentrated H_2SO_4 and NaOH solutions before mixing with the adsorbent. As negligible changes in the final equilibrium pH were observed, the uptake pH was assumed constant during the experiments.

2.3. Adsorption studies

This method involved agitating (150 rpm) 250 cm^3 Erlenmeyer flasks containing 0.1 g chitin and 100 cm^3 of phenol solutions at desired concentration, temperature and pH. Samples (5 ml) were taken before mixing the chitin and phenol solution and at predetermined time intervals for determining the residual phenol concentration in the medium. Before analysis, samples were filtered and supernatant fluid analyzed for the remaining phenol. The adsorption equilibrium was reached after 100 min. All the experiments were carried out in duplicates and average values were used for further calculations.

In the first stage of the adsorption studies, the initial pH of adsorption medium was changed from 1 to 10 to obtain optimum initial pH value. Then, the initial phenol concentration was varied from 25 to 300 mg dm^{-3} at 10, 25 and 40 °C to determine the effect of initial phenol concentration on the equilibrium uptake of phenol.

2.4. Analysis

The concentration of residual phenol in the adsorption media was determined spectrophotometrically. The absorbance of the colored complex of phenol and *p*-nitroaniline was read at 470 nm [9].

3. Results and discussion

Adsorption of phenol onto chitin was investigated as a function of pH, temperature and initial phenol concentration. The results are given as the units of adsorbed phenol quantity per gram of sorbent at any time and at equilibrium q and q_{eq} (mg g^{-1}), respectively; unadsorbed phenol concentration in solution at any time and at equilibrium C and C_{eq} (mg dm^{-3}), respectively; and adsorption yield (Ad (%)) = $100 \times (C_0 - C_{\text{eq}})/C_{\text{eq}}$.

3.1. Effect of initial pH on phenol adsorption

The initial pH of adsorption medium is one of the most important parameters affecting the adsorption process. Fig. 1 shows that, the uptake of phenol increased with decreasing initial pH and was the greatest at pH 1.0. The pH primarily affects the degree of ionization of the phenol and the surface properties of chitin. At low pH values, the functional groups of chitin would be protonated and result in a stronger attraction for negatively charged ions in the adsorption medium. Phenol being weakly acidic would be partially ionized in solution. These ions will be negatively charged and will be

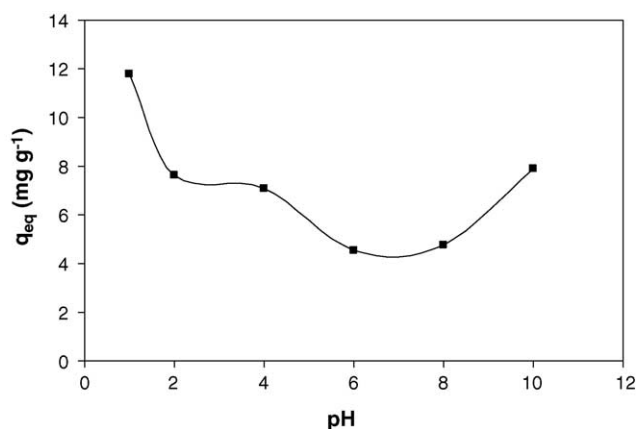


Fig. 1. Effect of pH on the phenol adsorption ($C_0 = 100 \text{ mg dm}^{-3}$, $T = 25^\circ \text{C}$, $X = 1.0 \text{ g dm}^{-3}$, agitation rate = 150 rpm).

directly attracted due to electrostatic forces by the protonated amino groups of the chitin. As the pH increased, the overall surface charge of the chitin became negative and adsorption decreased.

3.2. Effect of initial phenol concentration on temperature dependent adsorption

Table 1 shows that, the equilibrium sorption capacity of the sorbent increased with increasing initial phenol concentration up to 300 mg dm^{-3} because the initial sorbate concentration provided an important driving force to overcome all mass transfer resistance. The increases of loading capacity of chitin with increasing initial phenol concentration may also be due to higher interaction between phenol and chitin. As chitin offered a finite number of surface binding sites, phenol adsorption showed a saturation trend at higher initial phenol concentration.

The maximum adsorption yields were determined as 21.4, 23.7 and 29.1% at 25 mg dm^{-3} initial phenol concentration for 10, 25 and 40°C , respectively (Table 1). The adsorption yield showed a decreasing trend as the initial phenol concentration was increased. 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 yields were observed because of the saturation of the adsorption sites.

Table 1

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

C_0 (mg dm ⁻³)	10 °C		25 °C		40 °C	
	q_{eq} (mg g ⁻¹)	Adsorption (%)	q_{eq} (mg g ⁻¹)	Adsorption (%)	q_{eq} (mg g ⁻¹)	Adsorption (%)
25	5.36	21.4	5.93	23.7	7.36	29.1
50	7.20	14.4	7.71	15.4	9.44	18.9
100	10.35	10.4	11.80	12.0	15.83	15.8
200	13.45	6.7	17.59	8.8	18.01	9.0
300	18.90	6.3	19.50	6.5	21.49	7.2

The equilibrium uptake of phenol by chitin was also affected by temperature. The effect of temperature on the equilibrium sorption capacity of chitin was also presented in Table 1. It was indicated that phenol adsorption capacity increased with increasing temperature from 10 to 40°C . Similar results were observed for phenol adsorption yields of chitin and the adsorption yields increased with increasing temperature. The increase of the adsorption yield and adsorption capacity at increased temperature indicated that the sorption of phenol onto chitin is endothermic in nature and may involve not only physical but also chemical sorption. This effect may be attributed to the enlargement of pore size or creation of some new active sites on the adsorbent surface due to bond rupture [10–13]. The endothermic nature of adsorption for several pollutants on different sorbents has also been reported in previous studies, i.e., the sorption of lead(II) on cellulose-based sorbent, sphagnum moss peat [14], the cadmium(II) and lead(II) adsorption by spent grain [15] and sorption of copper(II) onto tree fern [16].

Al-Asheh et al. investigated the adsorption of phenol onto activated bentonites. They found equilibrium uptake of phenol between 9.9 and 8.2 mg g^{-1} for different types of activated bentonites [17]. Vipulanandan determined phenol adsorption capacity of kaolin as $5 \text{ } \mu\text{mol g}^{-1}$ [18]. Batch adsorption of phenol on a polymeric adsorbent was performed by Pan et al. [19] and equilibrium adsorption capacity was determined as 1.0 mmol g^{-1} . In the present work, the maximum phenol adsorption capacity of chitin was obtained as 21.49 mg g^{-1} for 300 mg dm^{-3} initial phenol concentration at 40°C . This result confirmed that the adsorption capacity of chitin was relatively high when compared with other adsorbents.

3.3. Adsorption kinetics

Before the adsorption equilibrium studies of phenol could commence, it was necessary to determine the equilibrium contact time required for phenol (the time required to reach the equilibrium state after contact with the sorbent). Results given in Fig. 2 clearly showed that initial sorption of phenol occurred very rapidly and reached equilibrium in 100 min for 100 mg dm^{-3} initial phenol concentration at all temperatures studied. The variation of the unadsorbed phenol concentration in the solution was negligible after 100 min of contact time.

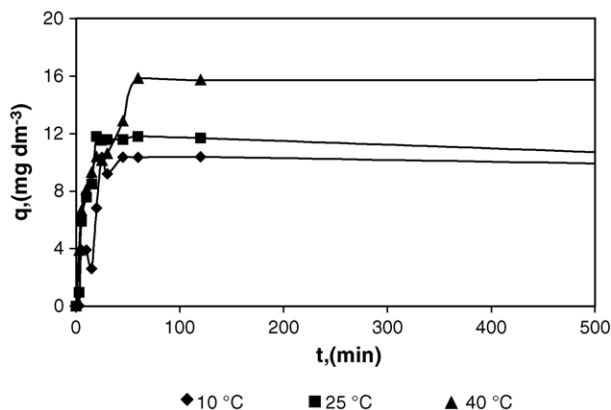


Fig. 2. The adsorption curves of phenol ($C_0=100\text{ mg dm}^{-3}$, pH 1.0, $X=1.0\text{ g dm}^{-3}$, agitation rate = 150 rpm and (◆), (■) and (▲) show uptake values at 10, 25 and 40 °C, respectively).

3.4. Equilibrium modelling

Equilibrium data can be analyzed using commonly known adsorption isotherms, which provide the basis for the design of adsorption systems. The most widely used isotherm equation for modelling of the adsorption data is the Langmuir equation, which is valid for monolayer sorption onto a surface with a finite number of identical sites and is given by Equation (1).

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

where K is the adsorption equilibrium constant including the affinity of binding sites ($\text{dm}^3\text{ mg}^{-1}$) and q_{max} is the maximum amount of phenol per unit weight of chitin to form a complete monolayer on the surface (mg g^{-1}). It represents a practical limiting adsorption capacity when the surface is fully covered with phenol. q_{max} and K can be determined from the linear plot of $C_{\text{eq}}/q_{\text{eq}}$ versus C_{eq} [20,21].

The Freundlich model is an empirical equation based on sorption on a heterogenous surface. It is given as:

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

where K_F and n are the Freundlich constants that indicate relative capacity and adsorption intensity, respectively. The Freundlich equation can be linearized by taking logarithms and constants can be determined [21].

To determine the equilibrium isotherms, initial phenol concentrations were varied from 25 to 300 mg dm^{-3} , while the adsorbent concentration was kept constant (1.0 g dm^{-3}) at 10, 25 and 40 °C. The linearized isotherms are presented in Figs. 3 and 4. The isotherm constants and correlation coefficients are tabulated in Table 2. Although the equilibrium data fitted well to both of the adsorption models, the Freundlich Model exhibited a slightly better fit to the adsorption data than the Langmuir Model. The values of Freundlich constants increased with increasing temperature and the highest K_F value was reported as 2.29 at

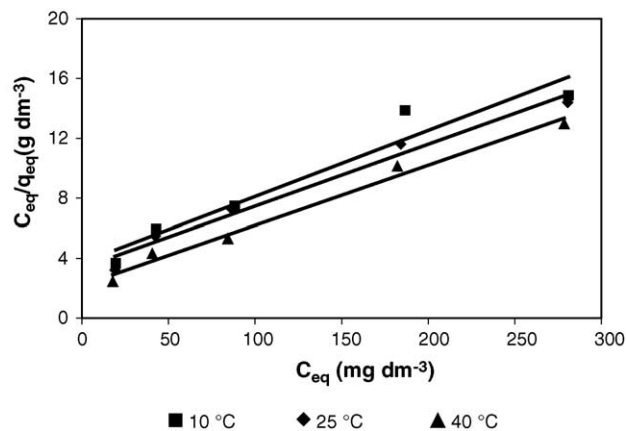


Fig. 3. The linearized Langmuir adsorption isotherm of phenol.

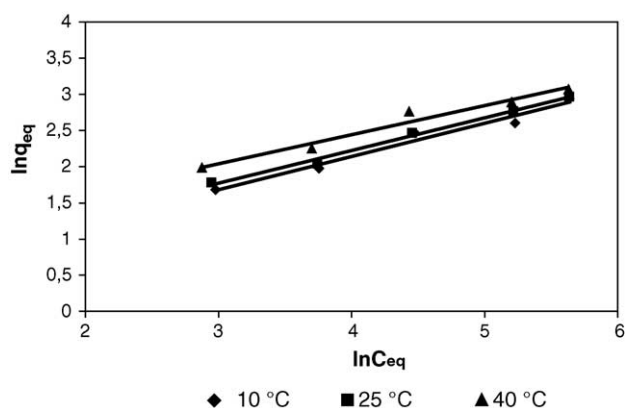


Fig. 4. The linearized Freundlich adsorption isotherm of phenol.

40 °C. All n values were found high enough for adsorption (>1.0).

Values of q_{max} and K at different temperatures are also tabulated in Table 2. The maximum capacity, q_{max} defined the total capacity of chitin for phenol adsorption and increased with increasing temperature. Its maximum value was determined as 25.06 mg g^{-1} at 40 °C. The increase of sorption equilibrium constant with temperature showed that there was a chemical interaction between adsorbent and adsorbate.

3.5. Kinetic modelling

Kinetic models are used to examine the rate of the adsorption process and potential rate-controlling step, i.e., mass transfer or chemical reaction. The capability of pseudo-first-

Table 2
Isotherms constants for phenol adsorbed on chitin

T (°C)	Langmuir Model			Freundlich Model		
	q_{max}	K	R^2	K_F	n	R^2
10	22.68	0.0119	0.937	1.35	2.18	0.973
25	24.15	0.0124	0.977	1.51	2.21	0.993
40	25.06	0.0181	0.986	2.29	2.48	0.965

order and pseudo-second-order kinetic models were examined in this study.

The pseudo-first-order equation of Lagergren is generally expressed as follows [22]:

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

where k_1 is the rate constant of pseudo-first-order sorption (min^{-1}). Integrating this equation for boundary conditions: $t = 0$ to t and $q = 0$ to q gives

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

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 pseudo-second-order kinetic rate equation is expressed as [23]:

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

where k_2 is the rate constant of pseudo-second-order sorption ($\text{g mg}^{-1} \text{min}^{-1}$). For the same boundary conditions, the integrated form of Equation (5) becomes

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

The second-order rate constant can be determined from the intercept of the linearized pseudo-second-order rate equation.

A series of contact time experiments was carried out with constant initial phenol concentration of 100 mg dm^{-3} at 10, 25 and 40°C . The plots of linearized form of the pseudo-first-order equation are shown in Fig. 5. k_1 , q_{eq} values and correlation coefficients are compared in Table 3. The results showed that, the correlation coefficient for the first-order kinetic model obtained at 10 and 25°C was very low and they increased with increasing temperature. The theoretical q_{eq} values found from this model did not give reasonable values; so pseudo-first-order model did not describe the adsorption results of phenol onto chitin.

Fig. 6 shows the linearized form of the pseudo-second-order model. The values of correlation coefficient were very high and the theoretical q_{eq} values were closer to the experimental q_{eq} values (Table 3). In the view of these results, it can be said that the pseudo-second-order kinetic model provided a good correlation for the adsorption of phenol onto chitin in contrast to the pseudo-first-order model.

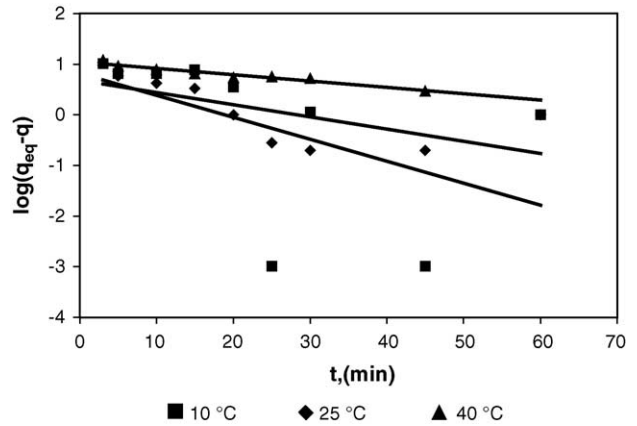


Fig. 5. Pseudo-first-order adsorption kinetics of phenol at different temperatures.

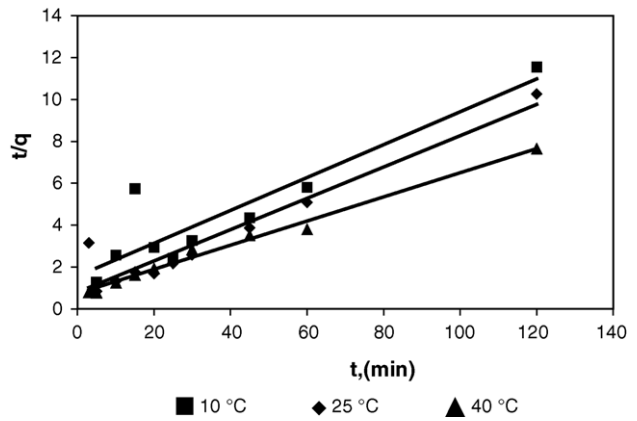


Fig. 6. Pseudo-second-order adsorption kinetics of phenol at different temperatures.

3.6. Determination of thermodynamic parameters

In engineering practice, entropy and energy factors should be considered in order to determine what processes will occur spontaneously. The Gibbs free energy change ΔG° , indicates the degree of spontaneity of the adsorption process and higher negative value reflects a more energetically favorable adsorption. The Gibbs free energy change of adsorption is defined as

$$\Delta G^\circ = -RT \ln K \tag{7}$$

where R is the universal gas constant ($8314 \text{ J mol}^{-1} \text{K}^{-1}$) and T is the absolute temperature (K). [24,25]. The magnitude of the heat of adsorption can be calculated by thermodynamic

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

T ($^\circ\text{C}$)	$q_{eq,exp}$ (mg g^{-1})	First-order kinetic model			Second-order kinetic model		
		k_1 (min^{-1})	$q_{eq,cal}$ (mg g^{-1})	R^2	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	$q_{eq,cal}$ (mg g^{-1})	R^2
10	10.35	0.099	6.60	0.257	0.0039	12.74	0.836
25	11.8	0.055	4.78	0.473	0.0071	13.39	0.914
40	15.83	0.029	11.04	0.937	0.0045	17.36	0.987

Table 4
 ΔG° values for adsorption of phenol at different temperatures

T (°C)	K (dm ³ mg ⁻¹)	$-\Delta G^\circ$ (kJ mol ⁻¹)
10	0.0119	16.51
25	0.0124	17.49
40	0.0181	19.36

methods. The effect of temperature on the equilibrium constant is determined by Equation (8).

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (8)$$

ΔH° is enthalpy change of adsorption and for an endothermic adsorption process ΔH° is positive. For an exothermic process, it is negative. After integration and necessary rearrangements, Equation (8) gives

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (9)$$

and

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

where ΔS° is entropy change of adsorption. ΔH° and ΔS° can be determined from the slope and intercept of the plot of $\ln K$ versus $1/T$ [22,23].

The equilibrium constants obtained from the Langmuir Model at 10, 25 and 40 °C were used to determine the Gibbs free energy changes. Table 4 shows the Gibbs free energy values for the adsorption process. The negative value of ΔG° showed the spontaneous nature of phenol adsorption onto chitin. The standard enthalpy and the entropy changes were determined as 10.19 kJ mol⁻¹ and 0.0929 kJ mol⁻¹ K⁻¹ from the $\ln K$ versus $1/T$ plots (Fig. 7), respectively. The positive value of ΔH° suggested the endothermic nature of adsorption, while positive values of ΔS° showed the increasing randomness at the chitin-solution interface during the adsorption [10,25].

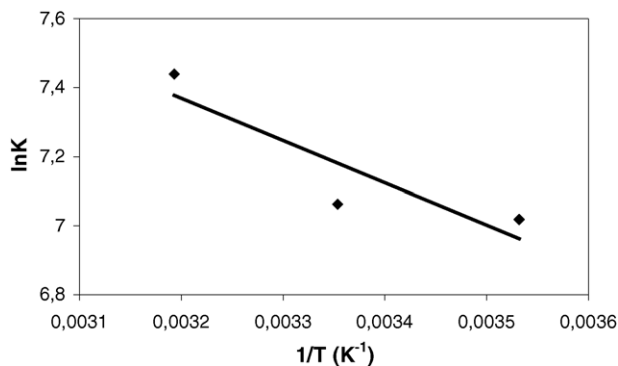


Fig. 7. $\ln K$ vs. $1/T$ plot.

4. Conclusions

In this study, the ability of chitin to bind phenol was tested using equilibrium, kinetic and thermodynamic aspects. The results indicated that, adsorption capacity of the sorbent was affected by pH, temperature and initial phenol concentration. The optimum pH value was determined to be 1.0. It was found that phenol adsorption increased with temperature up to 40 °C and initial phenol concentration up to 300 g dm⁻³.

The Langmuir and Freundlich adsorption models were used to express the sorption phenomenon of the sorbate. The equilibrium data were well described by the Freundlich Model.

The kinetics of phenol adsorption onto chitin was examined using the pseudo-first and pseudo-second-order kinetic models. The results indicated that the pseudo-second-order equation provided the best correlation of the sorption data.

The negative value of ΔG° confirmed the spontaneous nature adsorption process. The positive value of ΔS° showed the increased randomness at the solid-solution interface during adsorption and the positive value of ΔH° indicated the adsorption process was endothermic.

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References

- [1] A.K. Bhattacharya, C. Venkobachar, Removal of cadmium (II) by low cost adsorbents, J. Environ. Eng. ASCE 110 (1984) 110–122.
- [2] G. Mckay, G.R. Prasad, P.R. Mowli, Equilibrium studies for the adsorption of dyestuffs from aqueous solutions by low-cost materials, Water Air Soil Pollut. 29 (1986) 273–283.
- [3] M.M. Nassar, M.S. El-Geundi, Comparative cost of color removal from textile effluents using natural adsorbents, J. Chem. Technol. Biotechnol. 61 (1994) 307–317.
- [4] M.S. El-Geundi, Adsorbents for industrial pollution control, Adsorpt. Sci. Technol. 15 (1997) 777–787.
- [5] A.Y. Dursun, The effect of pH on the equilibrium of heavy metal biosorption by *Aspergillus niger*, Fresenius Environ. Bull. 12 (11) (2003) 1315–1322.
- [6] Y. Orhan, H. Büyükgüngör, The removal of heavy metals by using agricultural wastes, Water Sci. Technol. 28 (1993) 247–255.
- [7] M.M. Nassar, Y.H. Magdy, Removal of different basic dyes from aqueous solutions by adsorption on palm-fruit bunch particles, Chem. Eng. J. 66 (1997) 223.
- [8] R.C.W. Berkeley, Chitin, Chitosan and their degradative enzymes, in: R.C.W. Berkeley, C.W. Gooday, D.C. Elwood (Eds.), Microbial Polysaccharides, Academic Press, New York, 1979, pp. 205–236.
- [9] F.D. Snell, L.S. Ettore, Encyclopedia of Industrial Chemical Analysis, vol. 17, Interscience Publishers, 1973, pp. 1–8.
- [10] Z. Aksu, Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel (II) ions onto *Chlorella vulgaris*, Process Biochem. 38 (2002) 89–99.

- [11] D. Mohan, V.K. Gupta, S.K. Srivastava, S. Chander, *Colloid Surf. A177* (2001) 169.
- [12] A. Shukla, Y.-H. Zhang, P. Dobey, J.L. Margrave, S.S. Shukla, *J. Hazard. Mater.* 95 (2002) 137.
- [13] J.P. Chen, M. Lin, *Water Res.* 35 (2001) 2385.
- [14] Y.S. Ho, D.A.J. Wase, C.F. Forster, Removal of lead ions from aqueous-solution using sphagnum moss peat as adsorbent, *Water SA* 22 (3) (1996) 219–224.
- [15] K.S. Low, C.K. Lee, S.C. Liew, Sorption of cadmium and lead from aqueous solutions by spent grain, *Process Biochem.* 6 (2000) 59–64.
- [16] Y.S. Ho, C.T. Huang, H.W. Huang, Equilibrium sorption isotherm for metal ions on tree fern, *Process Biochem.* 37 (2002) 1421–1430.
- [17] S. Al-Asheh, F. Banat, L. Abu-Aitah, Adsorption of phenol using different types of activated bentonites, *Sep. Purif. Technol.* 33 (2003) 1–10.
- [18] C. Vipulanandan, Effect of clays and cement on the solidification/stabilization of phenol-contaminated soils, *Waste Manage.* 15 (1995) 399–406.
- [19] B.C. Pan, Y. Íxong, Q. Su, A.M. Li, J.L. Chen, Q.X. Zhang, Role of amination of a polymeric adsorbent on phenol adsorption from aqueous solution, *Chemosphere* 51 (2003) 953–962.
- [20] I. Langmuir, The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.* 38 (11) (1916) 2221–2295.
- [21] J.M. Smith, *Chemical Engineering Kinetics*, third ed., McGraw-Hill, Singapore, 1981.
- [22] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, *Kungliga Svenska Vetenskapsakademiens handlingar* 24 (1998) 1–39.
- [23] Y.S. Ho, G. McKay, Pseudo-second-order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.
- [24] F. Daniels, R.A. Alberty, *Physical Chemistry*, fourth ed., Wiley, USA, 1975.
- [25] J.M. Smith, H.C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, fourth ed., McGraw-Hill, Singapore, 1987.