

Adsorptive Removal of Phenol from Aqueous Solution Using Natural and immobilized Chitin by Dithiazone

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Abstract: The potential of biopolymer chitin for phenol adsorption from aqueous solution was studied. Batch kinetic and isotherm studies were carried out under varying experimental conditions of pH values, contact time, adsorbent dosage, phenol concentration, and temperature. The adsorption of phenol decreased with increasing pH. The Freundlich, Langmuir and Redlich-Peterson isotherm adsorption models were used for the mathematical description of adsorption equilibrium and it was found that the experimental data fitted very well to the Langmuir model. Batch adsorption models, based on the assumption of the pseudo-first-order pseudo-second-order and intra-particle models, were applied to examine the kinetics of the adsorption. The results showed that kinetic data followed closely to the pseudo-second-order model.

[H. A. Omar. **Adsorptive Removal of Phenol from Aqueous Solution Using Natural and immobilized Chitin by Dithiazone.** *N Y Sci J* 2012;5(8):47-55]. (ISSN: 1554-0200). <http://www.sciencepub.net/newyork>. 6

Keywords: biopolymer, phenol, adsorption, equilibrium, kinetic, immobilization.

1. Introduction

One of the major problems of the industrial waste is the great amount of wastewater produced and the high investment needed for the treatment of this effluent before it is released in the environment. In particular, phenol is present in significant concentrations, while it is highly toxic and accumulates in the environment (Hameed and Rahmab, 2008). Phenols are common contaminants in wastewater generated from oil, gasoline, coal, paper, textile, petrochemicals, pharmaceuticals, phenol producing industries and plants, which are processing phenols to plastics (Prieto et al., 2002) and (Nuhoglu and Yalcin, 2004). They are considered one of the priority pollutants in wastewater, because they are harmful to organisms even at low concentrations (Uddin et al., 2007). Human consumption of phenol contaminant water can cause severe pain leading to damage of the capillaries ultimately causing death. In the presence of chlorine in drinking water, phenols form chlorophenol, which has a medicinal taste and which is quite pronounced and objectionable. Phenol constitutes the 11th of the 126 chemicals, which has been designated as priority pollutants by the US Environmental Protection Agency (USEPA) (Nayak and Singh, 2007). The content of phenols in industrial wastewater in the range of 0.1-6800 mg L⁻¹ (Busca et al., 2008), is usually higher than the standard limit set by USEPA of 0.1 mg L⁻¹.

There are many methods to remove phenols from aqueous solution such as adsorption, microbial degradation, chemical oxidation (Santiago, et al., 2005), precipitation, ion exchange and solvent

extraction. Adsorption is an effective separation process for treating industrial and domestic effluents.

The adsorption characteristics of phenol on various adsorbents have previously been extensively investigated for many purposes of separation and purification. The adsorption of phenol from aqueous solution carried out using carbonized beet pulp (Dursun et al., 2005) active bentonites (Asheh et al., 2003), peat, fly ash and bentonite were found to adsorb phenol 46.1%, 41.6% and 42.5%, respectively, from the solution of initial concentration of approximately 1 mg/l (Vigiraraghavan and Alfaro, 1998).

Much research connected with phenol removal has been carried out using various types of biosorbents. Among them are *Spirodela polyrrhiza* (Waranusantigul et al., 2003), *Aspergillus foetidus* (Sumathi and Manju, 2000), yeasts (Aksu and Donmez, 2003) and chitin (Dursun and Kalayci, 2005).

Chitin is used as an adsorbent to remove phenol from aqueous solution. Chitin derivative have gained wide attention as effective biosorbent due to low cost and high contents of amino and hydroxyl functional groups which show significant adsorption potential for the removal of various aquatic pollutants. Chitin has widely applied in the adsorption study of heavy metal based on their chemical structures, reaction characteristics and modification properties (Meng-Wei et al., 2007). The previous literature discussed the principal results obtained during the treatment of water and wastewater utilizing chitin and chitosan-derivatives for the removal of: (a) metal cations and metal anions; (b) radionuclides; (c) different classes

of dyes; (d) phenol and substituted phenols; (e) different anions and other miscellaneous pollutants (Bhatnagar and Sillanpää, 2009).

The objective of this work was studied biopolymer chitin and immobilized chitin by dithizone as an adsorbent for adsorption of phenol, and investigated the effects of initial phenol concentration, contact time, pH values, adsorbent dosage and temperature on the adsorption of phenol on biopolymer.

2. Experiments

Materials and Methods

Chemicals

A stock solution of 1000 mg/l phenol was prepared by dissolving 1.0 g of analytical reagent grade phenol (Sigma Chemical Co., Germany) in 1L distilled water. The test solution of desired concentration was then prepared by diluting the stock solution. The pH of the solution was adjusted to the required value with 0.1 N HCl and 0.1 N NaOH solutions.

Immobilization of dithizone on biopolymer chitin

Preparation of chitin (Ch) and immobilized it by dithizone (Di-Ch) was described in previous work (Mudasir et al., 2008).

Adsorption experiments

Phenol solution of known concentration was treated with known weight of adsorbent, chitin (Ch) and immobilized chitin by dithizone (Di-Ch) in 24 hours contact time, at different parameters like; i) pH(2-10) at constant phenol concentration(5×10^{-4} M) and temperature ($27 \pm 1^\circ\text{C}$), ii) temperature (27, 35 and 45°C) at different phenol concentration at pH 2.0. After equilibrium establishment, the samples were centrifuged and supernatant liquid was analyzed for phenol concentration using UV-VIS spectrophotometer Shimadzu-160 (UV-visible) at λ_{max} 296 nm.

The adsorption percent (A%) of phenol was calculated from the following equation:

$$A\% = (C_o - C)/C_o \times 100 \quad (1)$$

Where C_o and C are the concentrations (mg/l) solution for phenol before and after contacting with either Chitin or immobilized chitin. The obtained data is the mean value of the three independent experimental runs.

Sorption isotherm

To study the sorption isotherm, of phenol, various concentrations ranged from 5×10^{-4} to 2.5×10^{-2} M were used. After equilibration, concentration in aqueous solution was estimated and the amount of phenol sorbed on the sorbents q_e (mg/g) was calculated from the relation:

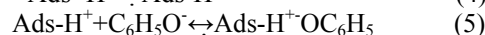
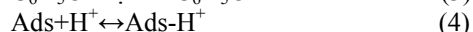
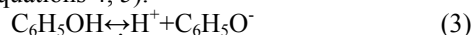
$$q_e = (C_o - C_e) V/m \quad (2)$$

Where q_e is the adsorption capacity (mg/g), C_o and C_e are the initial and equilibrium concentration (mg/L) of phenol in aqueous solution, respectively, V is the volume (L), and W is the weight (g) of the adsorbent.

3. Results and discussion

3.1. Effect of pH value

The pH value of the solution is an important controlling parameter in the adsorption process as a small variation in pH influences both the adsorbent surface and ionic species of metal in water (Waranusantigul et al., 2003). The effect of pH on the % removal of phenol on two biopolymer adsorbents (Ch and Di-Ch) has been investigated in the range 2 to 9 as shown in figure 1. The data shows that the phenol removal increased with decreasing initial pH for both biopolymer adsorbents. Chitin and dithizone immobilized chitin contain functional groups such as hydroxy, acetamido and amino those are prone to adsorb molecules by hydrogen bonds, Van der Waals interactions, and ion exchanges. Depending on the pH, the amino groups are present in protonated or neutral forms. At low pH, the ammonium groups may exert electrostatic interaction with phenolates thereby increasing the adsorption efficiency. This behavior can be explained considering the fact that variations of pH affect the ionization of phenol (Equation 3) and the surface properties of the adsorbent, denoted as Adsorption (Equations 4, 5).



Phenol is adsorbed to a lesser extent at higher pH values due to repulsive forces. Similar results have also been obtained for phenol adsorption with chitin (Dursun et al., 2005 and Milhome et al., 2009). It should be taken into account that, all experiments were conducted at pH 2.

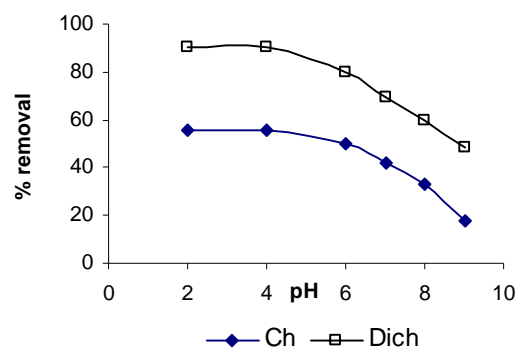


Figure 1. Effect of pH value on the removal of phenol by Ch and Di-Ch samples.

3.2. Effect of adsorbents mass

In order to investigate the effect of adsorbent mass on the removal of phenol, a series of adsorption experiments was carried out with different adsorbent mass at an initial phenol concentration of $5 \times 10^{-4} \text{M}$. Figure 2, shows the percentage removal of phenol increased with the increase in adsorbent mass. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase adsorbent mass (Riaz, et al., 2009).

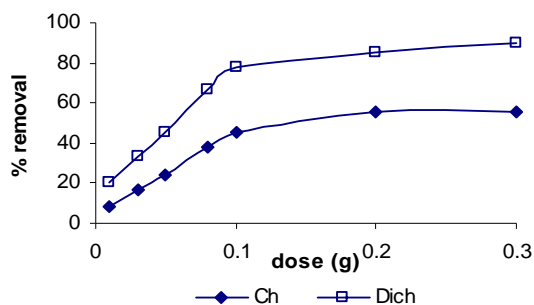


Figure 2. Effect of mass on the % removal of phenol by Ch and Di-Ch samples.

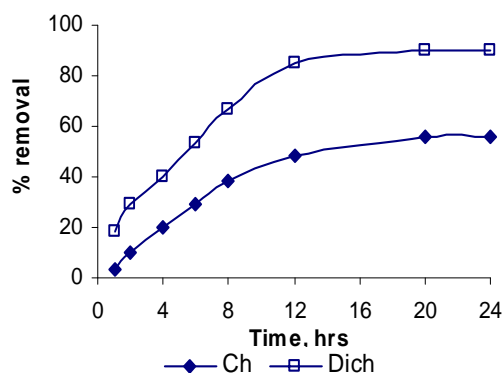


Figure 3. Effect of contact time for removal of phenol by Ch and Di-Ch samples.

3.3. Effect of contact time

Sorption of phenol as a function of time was studied at room temperature ($27 \pm 1^\circ \text{C}$) by equilibrating 0.2 g of biopolymers with concentration $5 \times 10^{-4} \text{M}$ at pH 2. The adsorbed amount of phenol at different time intervals is determined and plotted against times as shown in figure 3. The results showed that equilibrium time required for the adsorption of phenol on two samples of biopolymer Ch and Di-Ch were almost 20h. However, for subsequent experiments, the two samples were left for 24h to ensure equilibrium. These results also indicated that up to 48 and 85% of the total amount

of phenol uptake by Ch and Di-Ch respectively, was found to occur in the first rapid phase (12h). The higher sorption rate at the initial period (first 12h) may be due to an increased number of vacant sites on the adsorbent surface available at the initial stage (Mahvi et al., 2004).

3.3.1. Kinetics of adsorption

Kinetic test were conducted with two main purposes: (i) to evaluate phenol uptake rate and (ii) to define an appropriate contact time to ensure that equilibrium had been reached for adsorption isotherms. Several models have been tested to describe the kinetics of metal adsorption onto two adsorbents Ch and Di-Ch samples (Ngah et al., 2005 and Vijayaraghavan et al., 2006). Among these models, the pseudo-first-order equation Eq. (6), pseudo-second-order equation Eq. (7), and intra-particle diffusion equation Eq. (8) models, represented in figures (4-6) respectively, were selected and tested with the results obtained in this study:

$$\log (q_e - q_t) = \log q_e - K_1 t / 2.303 \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

$$q_t = K_t^{(0.5)} \quad (8)$$

Where q_e and q_t are the adsorbate concentration in the adsorbents (mg/g) at equilibrium and at time t (hour), respectively, and K_1 (h^{-1}), K_2 ($\text{g}/\text{mg hr}$) and K_t ($\text{mg}/\text{m hr}^{0.5}$) are rate constants.

Results of the linearized forms of the three evaluated models is clearly show that the pseudo-first order model is the best at describing the observed phenol adsorption for two samples under test. While no correlation was found for the pseudo-second order and intra-particle model, correlation coefficients for the pseudo-first order model were close to one (Table 1). Table 1 show that a pseudo-first order model describes satisfactorily the adsorption of phenol, suggesting that the limiting stage of adsorption is a chemical interaction between phenol and adsorbents (Dursun et al., 2005).

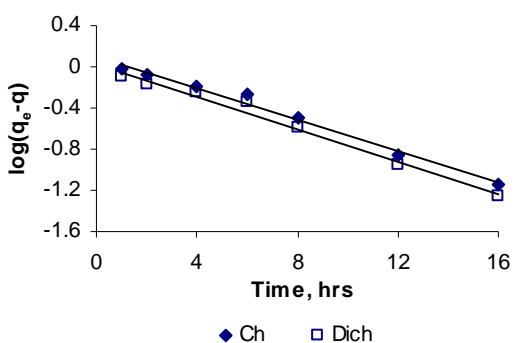


Figure 4. Pseudo-first-order plot for phenol by Ch and Di-Ch samples.

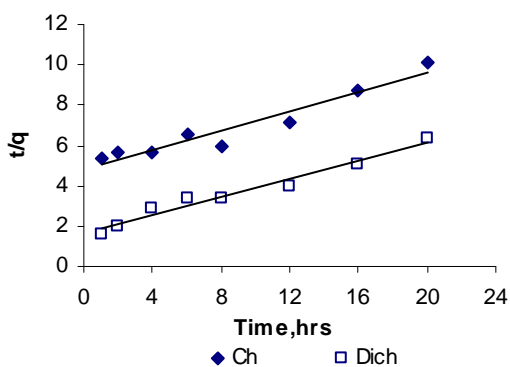


Figure 5. Pseudo-second-order plot for phenol by Ch and Di-Ch samples.

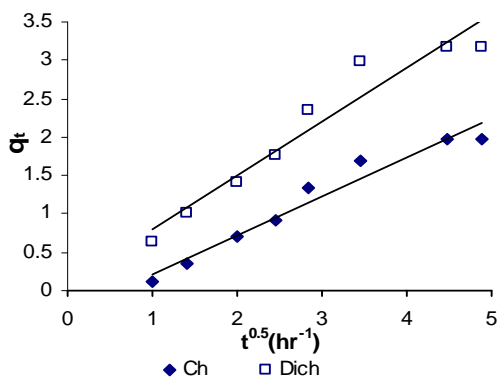


Figure 6. Intra-particle diffusion plot for phenol by Ch and Di-Ch

Table 1. Kinetic models for phenol sorbed by Ch and Di-Ch Samples.

Sample	First-order rate		Second-order rate		Intra-particle	
	$K_1(\text{mg/g}\cdot\text{hr}^{-1})$	R^2	$K_2(\text{mg/g}\cdot\text{hr}^{-1})$	R^2	$K_3(\text{mg/g}\cdot\text{hr}^{-1})$	R^2
Ch	0.177	0.987	0.012	0.922	0.508	0.957
Di-Ch	0.182	0.986	0.031	0.968	0.697	0.934

3.4. Adsorption isotherm

The effect of phenol concentration on its sorption by Ch and Di-Ch biopolymers were studied under the optimized conditions of shaking time, pH and the amount of adsorbents. The phenol concentration has been tested, at different temperature (27, 35 and 45°C), in the concentration range of 5×10^{-4} to 2.5×10^{-2} M. The adsorption (figure 7) was almost constant up to 2×10^{-2} M phenol; beyond this concentration the adsorption decreased gradually with the increase of phenol concentration. This can be explained in terms of the relatively smaller number of active sites at a higher concentration of phenol. Temperature exerts a significant influence on the adsorption of phenol as a small change in temperature produces a large effect on interactive forces between phenol and two biopolymers. This is due to high temperature leads to higher affinity of phenol for binding sites on the biopolymers (Goyal, et al., 2003).

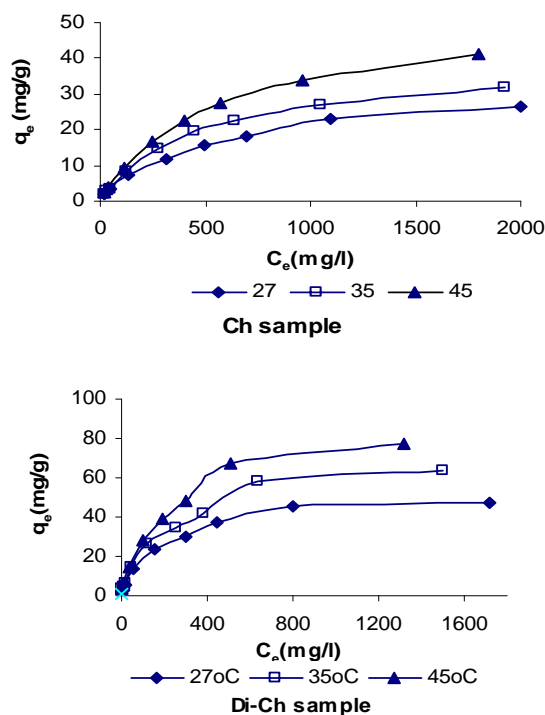


Figure 7. Effect of different concentration of phenol on the adsorption of biopolymers.

The sorption isotherm is represented in figure.7 and the results were also subjected to analysis in terms of Freundlich, Langmuir and Redlich-peterson adsorption isotherms. The Freundlich adsorption isotherm was capable of describing the data over the entire concentration range tested (figure 8); while the Langmuir adsorption isotherm was capable of describing the data in the concentration range from 10^{-3} to $2.5 \times 10^{-2} \text{M}$ (figure 8).

The Freundlich isotherm was tested in the linearized form:

$$\text{Log}q_e = \text{log}K_F + 1/n \text{log} C_e \quad (9)$$

Where, K_F and $1/n$ are characteristic constants for the adsorption system. From the straight line obtained on plotting $\log q_e$ versus $\log C_e$ (figure 8), the values of K_F and $1/n$ were deduced respectively from the intercept and the slope of the straight line and tabulated in Table 3. High values of $1/n$ signify that strong adsorption forces are operative on the surface. Moreover, a relatively higher value of K_F further confirms the higher affinity of phenol for the adsorbent. The affinity of phenol may be due to its low hydration energy and/or strong electrostatic interaction with the exchanger sites. The $1/n$ value, which reflects the intensity of sorption, for two sorbents as seen from Table 3. The higher fractional value of $1/n$ ($0 < 1/n < 1$) signifies that the surface of Ch and Di-Ch is heterogeneous in nature (Khalid et al., 2000).

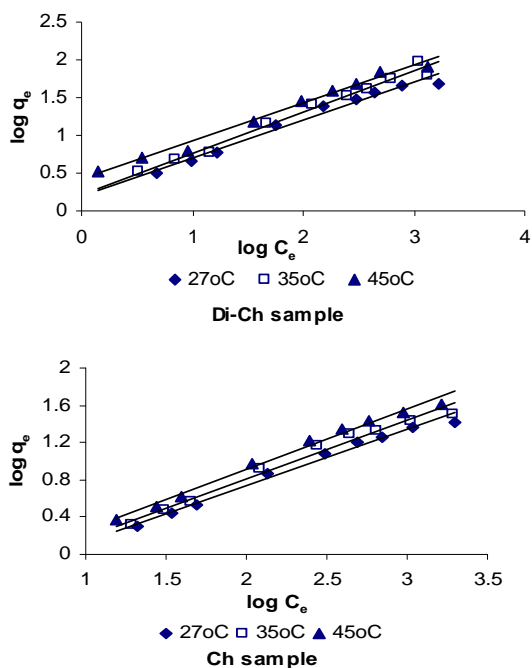


Figure 8. Freundlich adsorption isotherm for phenol by Ch and Di-Ch biopolymer.

The modified Langmuir model tested in this study is:

$$C_s/q_e = 1/K_L Q_o + C_s/Q_o \quad (10)$$

Where, K_L and Q_o are the Langmuir constants, their values are related to the physical properties of the system and reflect the energy of adsorption and the solute adsorptivity respectively. Q_o is generally called the monolayer capacity. On plotting C_s/q_e vs. C_s a straight line was obtained, (figure 9). Q_o and K_L were obtained from the slope and intercept of the straight line respectively. The values Q_o , K_L and correlation coefficients are tabulated in Table 3. The validity of the Langmuir isotherm over the specified concentration range indicates monolayer coverage of surface of biopolymer.

The essential characteristics are the Langmuir adsorption isotherm which expressed in terms of a dimensionless separation factor (R_L) can be calculated from the following equation:

$$R_L = 1/1 + bC_o \quad (11)$$

Where b is the Langmuir constant and C_o is the initial phenol concentration (mgL^{-1}). The parameter (R_L) is related to the shape of the isotherm according to the following adsorption characteristics; $R_L > 1$ represents unfavorable adsorption; $R_L = 1$ corresponds to a linear relationship; $0 < R_L < 1$ is favorable nature of adsorption and $R_L = 0$ is irreversible (Kim et al., 2002). R_L values presented in Table 2 indicate favorable adsorption of phenol for all initial concentration at three different temperatures (27, 35 and 45°C). All values of R_L calculated for Ch and Di-Ch vary between 0 and 1 indicating that adsorption is favorable for both adsorbents.

Table 2. R_L values for adsorption of phenol by Ch and Di-Ch biopolymers.

Temp.	Samples	R_L Concen. M			
		10^{-3}	2.5×10^{-3}	5×10^{-3}	10^{-2}
27°C	Ch	0.999	0.999	0.998	0.997
	Di-Ch	0.999	0.998	0.997	0.994
35°C	Ch	0.999	0.999	0.998	0.997
	Di-Ch	0.999	0.998	0.996	0.995
45°C	Ch	0.999	0.998	0.998	0.997
	Di-Ch	0.995	0.998	0.996	0.995

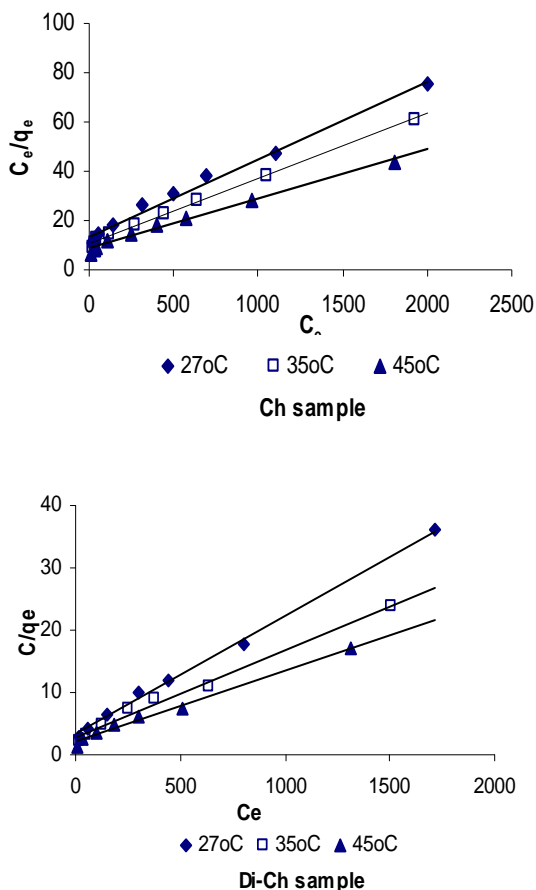


Figure 9. Langmuir adsorption isotherm for phenol

Redlich- Peterson developed an isotherm model which describes the equilibrium for heterogeneous surfaces and is expressed by a more general formula than both Langmuir and Freundlich isotherms with three isotherm constants K , Q and β as:

$$\ln(kC_e/q_e - 1) = \ln b_R + \beta \ln C_e \quad (12)$$

where, K , b_R and β ($0 < \beta < 1$) are the Redlich- Peterson parameters. Plotting $\ln[K(C_e/q_e)-1]$ against $\ln C_e$ yields a straight line of slope = β and intercept = b_R as shown in figure 10.

A general trial and error procedure which is applicable to computer operation was developed to determine the coefficient of determination ' r^2 ' for a series of values of K for the linear regression of $[(K C_e/q_e)-1]$ and to obtain the best value of K yields a maximum optimized value ' r^2 '. The quality of the fit of the experimental data to the isotherm equation is assessed by the magnitude of the correlation coefficient for the regression. The Redlich-Peterson isotherm constant is shown in Table 3. From Table 3, it is clear that the isotherm giving an ' r^2 ' value closest to unity provides the best fit. The solubility of a phenol is an essential property to enable the phenol

to penetrate into the porous structure of the chitin (Annadurai, et al 2007).

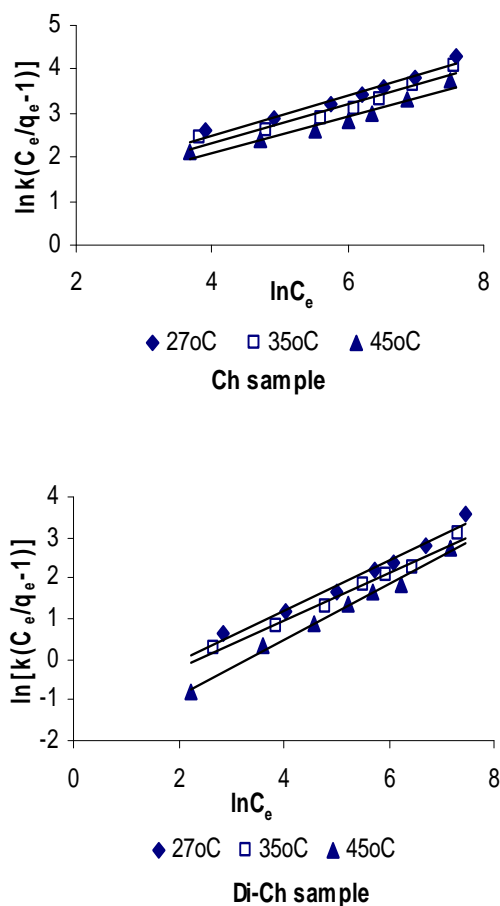


Figure 10. Redlich-Peterson adsorption isotherm for Phenol by Ch and Di-Ch biopolymer.

Comparison of various low-cost adsorbents

A comparison of the maximum phenol adsorption capacity, Q_o , of biopolymer chitin with those of other low cost adsorbents reported in the literature is given in Table 4. The adsorption capacity of biopolymer chitin and chitin immobilized by dithizone is relatively high when compared with other biosorbents.

Table 3. Isotherm parameters and correlation factors of phenol sorbed by Ch and Di-Ch

Isotherms	Sample/ Temp.	Parameters			
		$Q_0(\text{mg/g})$	K_L	R^2	
Langmuir	Ch	27	32.79	0.002	0.995
		35	38.31	0.0024	0.999
		45	51.28	0.00021	0.996
	Di-Ch	27	52.63	0.006	0.997
		35	72.46	0.005	0.991
		45	88.49	0.005	0.990
Freundlich	Ch	27	0.63	0.60	0.987
		35	0.65	0.62	0.980
		45	0.68	0.65	0.989
	Di-Ch	27	1.21	0.50	0.978
		35	1.24	0.55	0.986
		45	1.52	0.50	0.988
Redlich-Peterson	Ch	27	β 0.45	$b_R(\text{L/mg})$ 2.0	R^2 0.966
		35	0.44	1.72	0.927
		45	0.41	1.61	0.943
	Di-Ch	27	0.62	0.28	0.985
		35	0.59	0.25	0.983
		45	0.68	0.10	0.993

Table 4. Comparison of maximum adsorption capacity of different adsorbents for phenol

Adsorbents	$Q_0(\text{mg/g})$	T(°C)	Ref.
Chitin	32.79	27±1	This work
Chitin	51.28	45±1	This work
Chitin immobilized	52.63	27±1	This work
Chitin immobilized	88.49	45±1	This work
Chitin	1.96	28±2	18
Chitosan	1.26	28±2	18
Chitin	25.06	40	8
Rice husk	4.50	40	27
Bentonite	1.71	20	28
Natural Ziolite	34.50	25	29
Activated carbon (commercial)	49.72	25	30
Biomass	0.33	21±1	31
Water hyacinth ash	30.49	27±2	4
Burned Water hyacinth (BWH)	30.49	27±2	5

3.5. Thermodynamic parameters

The effect of temperature on the adsorption equilibrium was investigated under isothermal conditions in the three temperatures (27, 35 and 45°C). The experimental results showed that the magnitude of adsorption is proportional to the solution temperature. In order to gain insight into the mechanism involved in the adsorption, the variation in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) for the adsorption are calculated as follows:

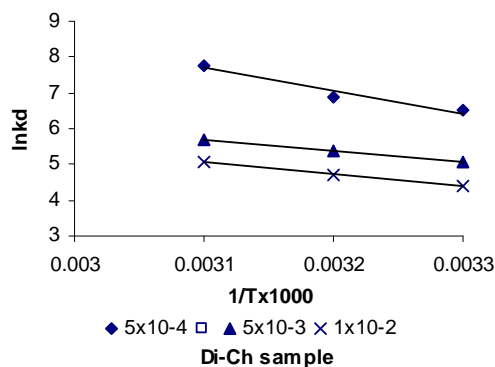
$$\Delta G^\circ = -RT \times \ln(K) \quad (13)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (14)$$

where R is the universal gas constant and T is the temperature (K). The calculated ΔG° values based on Eq. (14) are -16.2, -17.7, and -20.3 kcal/mol, respectively, for corresponding temperatures of 27, 35 and 45°C at phenol concentration 5×10^{-4} M (Table 5). As mentioned in the kinetic experiments, the increase in adsorption with temperature is attributed to the increased diffusion rate of phenol into the Ch and Di-Ch. The negative value of ΔG° confirms that the adsorption process is spontaneous with a high preference of phenol for the Ch and Di-Ch. The decrease in ΔG° with temperature implies more efficient adsorption at higher temperatures as represented in Table 5. Note that the rate of adsorption indeed increases with increasing temperature as shown in the results of kinetic experiments.

The typical range of bonding energy for an ion-exchange mechanism is 1.91–3.82 kcal/mol (Ho et al., 2002). It is to be noted that ΔG° values up to (20 kJ/mol) are consistent with electrostatic interaction between adsorption sites and the metal ion (physical adsorption) while ΔG° values more negative than (40 kJ/mol) involve charge sharing or transfer from the adsorbent surface to the metal ion to form a coordinate bond (Abia et al., 2006). The values of ΔG° obtained in this work, range from -11.0 to -20.3 kcal/mol indicating that ion-exchange may not play a significant role in the adsorption process. It may be suggested that a surface complex reaction is the major mechanism responsible for the phenol adsorption process.

Figure 11. presents the Van't Hoff plots of $\ln(K)$ versus $1/T$ and the values of ΔH° and ΔS° were determined from the slope and the intercept respectively. Thermodynamically, the values of ΔG° are negative and the values of ΔH° and ΔS° are positive, suggesting that the adsorption is a spontaneous process at high temperature and endothermic Petrucci (1989).



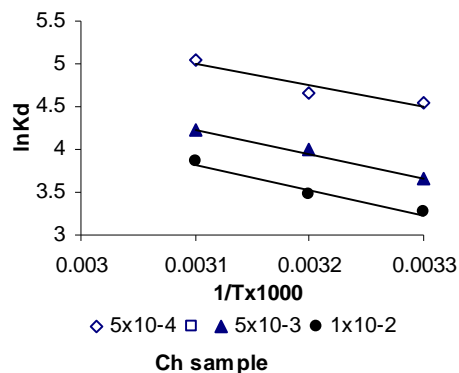


Figure 11. Variation of $\ln K_d$ with $1/T$ for phenol by Ch and Di-Ch biopolymers

Table 5. Thermodynamic parameters for phenol by Ch and Di-Ch biopolymers.

Concn. M/l	T	ΔH° (K/mol)		ΔS° (K/mol)		ΔG° (K/mol)	
		Ch	Di-Ch	Ch	Di-Ch	Ch	Di-Ch
5X10 ⁻⁴	300	}0.30	0.77	}1.53	3.31	-11.4	-16.2
	308					-12.0	-17.7
	318					-13.4	-20.3
5x10 ⁻³	300	}0.34	0.37	}1.57	1.84	-9.1	-12.6
	308					-10.2	-13.7
	318					-11.2	-15.0
1x10 ⁻²	300	}0.36	0.39	}1.56	1.82	-8.2	-11.0
	308					-8.9	-12.1
	318					-10.2	-13.4

4. Conclusion

The results indicated that adsorption capacity of the biopolymers (Ch and Di-Ch) was considerably affected by the initial pH, initial phenol concentration, contact time and the adsorbent dosage. The uptake of phenol took place at pH in the range of 2 – 9. Then the adsorption of phenol decreased with increasing the pH. The amount of phenol adsorbed increased with increasing the adsorbent dosage. Langmuir, Freundlich and Redlich-Peterson models could be used to describe phenol sorption equilibrium and kinetic data of two biopolymers also gave a better fit. The equilibrium data fitted very well in Langmuir isotherm equation, confirming the monolayer sorption capacity of phenol onto biopolymers with a monolayer sorption capacity of 32.79 and 52.63 mg/g for Ch and Di-Ch respectively, at 27°C. The pseudo-first-order and the pseudo-second-order kinetic models were used to analyze the data obtained for phenol adsorption onto biopolymer. The result indicated that the pseudo-first-order equation provided the better correlation for the adsorption data. Adsorption studies were also performed at different temperatures. The numerical value of ΔG° decreased with an increase in temperature, indicating that the adsorption was more favorable at higher temperature. The positive values of ΔH° corresponded to the endothermic nature of the

process. Natural biopolymer can be immobilized by dithizone to improve its adsorption capacity.

This study has demonstrated that the low-cost adsorbent, biopolymer, could be efficiently utilized for the removal of phenol from aqueous solution.

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6/13/2012