Removal Of Phenol From Industrial Wastewater Using Sawdust

Ihsan Habib Dakhil

Chemical Engineering Department /College of Engineering/Al-Muthanna University/Al-Samawa/Iraq

ABSTRACT - *The aim of present work is to study the removal of phenol presents in industrial wastewater using the local sawdust. The considered real of the four factors were (100-500) mg/l, (0.1-1) gm, (3-9) and (20-180) min for initial phenol concentration, adsorbent dose, pH and contact time, respectively, on the removal capacity has been studied. Statistical analysis of the results showed the significance of the individual factors and their interactions on both adsorption process. Box-Wilson design of experiments was adopted to find a useful relationship between the four variables and the removal efficiency. The experimental data collected by this method is successively fitted to a second order polynomial mathematical model. The optimum conditions for the removal of phenol within the experiment range of variables studies were 130 mg/l of initial phenol concentration, 0.82 gm of adsorbent dose, natural pH value of 6.7 and 120 min of contact time. Under these conditions the maximum removal efficiency was 91.6%. Batch kinetic and isotherm studies were carried out to evaluate the effect of initial phenol concentration, adsorbent dose, pH and contact time. A comparison of mathematical model applied to the adsorption of phenol was evaluated for the Langmuir and Freundlich adsorption models. It was found that the equilibrium data agree very well with the Langmuir and Freundlich models.*

KEYWORDS: *Removal, Adsorption, Phenol, Wastewater, Sawdust*

I.   INTRODUCTION

Phenol is the priority pollutant since it is toxic and harmful to organisms even at low concentrations. Beside the toxic effects, phenolic compounds create an oxygen demand in receiving waters, and impart taste and odor to water with minute concentrations of their chlorinated compounds. Surface and ground waters are contaminated by phenolics as a result of the continuous release of these compounds from petrochemical, coal conversion and phenol producing industries. Therefore, the waste waters containing phenolic compounds must be treated before their discharging into the water streams [1,2,3].

Conventional methods for the removal of phenolic pollutants in aqueous solutions can be divided into three main categories: physical, chemical and biological treatment [4]. Among them, physical adsorption method is generally considered to be the best, effective, low-cost and most frequently used method for the removal of phenolic pollutions. Therefore, the search for low cost and easily available adsorbents has led many researchers to search more economic and efficient techniques of using the natural and synthetic materials as adsorbents. Recently, using the inorganic materials as adsorbents has become one hot research field [5].

Adsorption, as a simple and relatively economical method, is a widely used technique in the removal of pollutants. Although the adsorbents used may vary due to the change in adsorption conditions depending on the type of pollutants, the properties affecting the efficiency of an adsorbent are; a large surface area, the homogeneous pore size, well defined structural properties, selective adsorption ability, easy regeneration, and multiple use. Since the synthetic adsorbents satisfying most of these conditions are relatively expensive, use of natural adsorbents is an active area of research [6].

The aim of the present work is to investigate the capability of industrial sawdust used as an adsorbent for removal of phenol from wastewater and to study the effects of initial phenol concentration, adsorbent dosage, pH value and contact time on the adsorption process, then, find then optimum conditions. In addition, the equilibrium isotherms Langmuir and Freundlich models were determined using the optimum conditions selected from the statistical design of experiments.

II.   MATERIALS AND METHODS

Materials:

Sawdust was collected from the local resource. It was boiled with distillate water and, then, filtrated and dried in an oven at 80 ^{o}C for 24 hrs. Finally, It was sieved to particle size range of 4-6 mm.

Chemicals:

The test solution was prepared by diluting stock phenol solution (1000 mg/l) to the desired concentration. A stock solution was prepared by dissolving 1.0 g of phenol (99.99% from Merk, Germany) in distillate water and diluting it to 1000 ml. The prepared range of phenol concentration varies between (100 – 500) mg/l based on most common phenol concentrations range in industrial effluents which is (100-500) mg/l [7]. The concentrations of residual phenol were measured using UV spectrophotometer equipment (Shimadzu UV/Vis 1601 Spectrophotometer, Japan). The absorbance of the colored complex of phenol with 4-aminoantipyrine was read at 500 nm [8]. The pH of each test solution was adjusted to the required value by diluting 0.5 N HCl or 0.1 N NaOH solutions with the use of pH meter to perform the measurements.

III.   STATISTICAL DESIGN OF EXPERIMENTS

To study the effects of initial phenol concentration (X_1), adsorbent dosage (X_2), pH (X_3) and contact time (X_4) on the removal efficiency of phenol (Y). Box-Wilson experimental design method was used to establish a mathematical model relating the efficiency of removal of phenol to the four operating variables [15].

The needed number of experiments (N) depends on number of variable (q) and was estimated according to the following equation [9]:

$$N = 2^q + 2q + 1 \qquad \qquad ...(1)$$

Thus, for four variables process, the number of experiments needed is 29 experiments. For four variables the form of a quadratic (second order model) polynomial is illustrated by the following equation [9] :

$$Y = A_o + A_1X_1 + A_2X_2 + A_3X_3 + A_4X4 + A_5X_1^2 + A_6X_2^2 + A_7X_3^2 + A_8X_4^2 + A_9X_1X_2 + A_{10}X_1X_3 + A_{11}X_1X_4$$

$$+ A_{12}X_2X_3 + A_{13}X_2X_4 + A_{14}X_3X_4 \qquad ...(2)$$

where Y is the predicted response, X is the coded value of the independent variable and A is a coefficient. The method of least squares was applied to estimate the parameters in the polynomial equation by using Statistics–Software Windows version 7. It was made under "non-linear estimation". The obtained equation was verified by applying the F–test and analyzing the correlation coefficients (R) and variance explained (S) by comparison between the calculated and experimental values of the Y. The mathematical model can be estimated most effectively if proper experimental design is used to collect the data.

To evaluate the optimum conditions, which give the maximum response (highest removal efficiency), the fitted polynomial equation is differentiated with respect to each independent variable separately and equated to zero.

ADSORPTION PROCEDURE

The adsorption experiments were performed in isothermal batch method at 30°C ± 1°C. The experiments were conducted by adding an amount of adsorbent varied between (0.1–1) g with 100 ml of phenol solution of different initial concentration (100–500) mg/l in 250 ml stopper conical flasks. These flasks were placed on a rotating shaker with constant shaking at 150 rpm to maintain the equilibrium condition. The pH of solution was varied between (3–9) during the contact period (20–180) min. Samples were withdrawn at suitable intervals and were separated from the sorbent by centrifugation for 15 min and the percent of phenol removal (% R) by saw dust was calculated from the difference between initial concentration (C_o) and equilibrium adsorbate phenol concentration (C_e) according to the following eq. (3):

$$\% \ R = \frac{C_o - C_e}{C_o} \times 100 \qquad \qquad ...(3)$$

IV.   RESULTS AND DISCUSSION

The mathematical model that described the removal efficiency of phenol (Y) from wastewater on sawdust was examined by various physiochemical parameters such as Initial concentration of phenol (X_1), amount of adsorbent dose (X_2), pH (X_3) and contact time (X_4) which gave:

$$Y = 70.90186 - 0.057833 X_1 + 22.05761X_2 + 1.84537 X_3 + 0.040521 X_4 - 0.000011 X_1^2 - 7.3251 X_2^2 - 0.12037 X_3^2 - 0.000341 X_4^2 + 0.018333 X_1X_2 + 0.002917 X_1X_3 + 0.00015 X_1X_4 - 1.59259 X_2X_3 - 0.041667 X_2X_4 \qquad ...(4)$$

Correlation coefficient (R) = 0.98549
Variance Explained = 99.10 %

The optimum conditions for the four factors that give maximum removal efficiency are:
X_1^*: optimum initial phenol concentration = 130 mg/l
X_2^*: optimum amount of adsorbent dose = 0.82 gm
X_3^*: optimum pH solution value = 6.7
X_4^*: optimum time contact = 120 min
$Y_{max.}$: % maximum removal efficiency = 91.6 %

EFFECT OF INITIAL PHENOL CONCENTRATION

Fig.(1) shows the effect of Initial phenol concentration on the removal of phenol for different amount of adsorbent dose (0.1-1) gm and at constant optimum value of pH and contact time, 6.7 and 120 min, respectively. The result indicated that the percentage of phenol removal increases with increasing the adsorbent dose. The high sorption at the initial concentration may be due to an increased number of vacant sites on the adsorbent available at the initial stage. As concentration of initial phenol is increased there is a decrease in percentage removal of phenol. This can be attributed to the accumulation of phenol particles on the surface of adsorbent. This observation is in a good agreement with the findings of Ekpete et al. [10] and Mahvi et al. [11].

Fig. (2) shows the same effect but for different pH value and optimum conditions of adsorbent dose (0.82 gm), optimum contact time (120 min). Also, it can be seen that the percent of removal is favored at pH value near 6.7.

Fig. (3) shows the same effect but for different contact time and optimum conditions of adsorbent dose (0.82 gm) and pH value (6.7). The results showed that more than 90% of the phenol was adsorbed within a period of 100 min. The maximum uptake of phenol was observed within 120 min.

EFFECT OF ADSORBENT DOSAGE

Fig. (4) shows the effect of adsorbent dose on the removal of phenol for different initial phenol concentrations (100-500) mg/l and at constant optimum pH value of 6.7 and constant optimum contact time of 120 min. The result showed that the percentage removal of phenol increases with the increase in adsorbent dosage. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increasing adsorbent dosage. This agrees with the finding of Uddin et al. [12].

Fig. (5) shows the same effect but for different pH value and optimum conditions of initial phenol concentration (130) mg/l and optimum contact time (120 min). The result showed that the percentage of phenol removal increases with increasing the adsorbent dose.

Fig. (6) shows the same effect but for different contact times and optimum conditions of initial phenol concentration (130) mg/l and optimum pH value (6.7). It can be, also, seen that increasing the contact time shall increase the percentage removal of phenol. Similar results were obtained by Ekpete et al [10] and Tagreed [13]. The results also clearly indicated that the removal efficiency increases up to the optimum dosage beyond which the removal efficiency is negligible.

EFFECT OF PH VALUE

The effect of pH value on the percentage removal of phenol at optimum values of the others factor is shown in Fig.s (7, 8, 9). From these figures it can be shown that the removal of phenol increases slightly with increasing the pH value from 3 to 6, then, fast decreases at pH 7-9. In general, the phenol uptake decreases at low and high pH values. At low pH values, the uptake of phenol is less due to the presence of H^+ ions suppressing the ionization of phenol and hence its uptake on polar adsorbent is reduced. In the high pH range, phenol forms salts which are readily ionized leaving negative charge on the phenolic group. At the same time the presence OH^- ions on the adsorbent prevents the uptake of phenolate ions. Similar behavior has been reported during the adsorption onto activated carbon by Ekpete et al. [10], onto rise husk by Mahvi et al. [11] and onto agriculture waste by Tagreed [13].

EFFECT OF CONTACT TIME

The effect of contact time on the percentage removal of phenol at optimum conditions of the others factor is the presented in Fig.s (10,11,12). These figures show the removal of phenol increases with increasing mixing contact time attains equilibrium in 120 min. After this period the removal of phenol versus time curves are smooth and continue leading to saturation. These results indicated that the sorption process can be considered very fast because of the large amount of phenol attached to the sorbent within the first 80 min of adsorption. The higher sorption rate at initial period can be attributed to the increase of number of vacant site on the adsorbent available at the initial stage. This result is in agreement with those obtained by Uddin et al. [12] and Ekpete et al. [10].

V.   ADSORPTION EQUILIBRIUM

Several models have been published in the literature to describe experimental data of adsorption isotherms. The Langmuir and Freundlich models are the most frequently employed models. In this work, both models were used to describe the relationship between the phenol adsorbed and optimum conditions. The equilibrium isotherms were determined at 30 ^{o}C under optimized conditions. The Langmuir adsorption isotherms is often expressed as [9]:

$$q_e = \frac{q_o \ K_l \ C_e}{1 + K_l \ C_e} \qquad \qquad \dots (5)$$

where q_o and K_l are Langmuir parameters related to maximum adsorption capacity (mg of solute per gm of adsorbent) and free energy of adsorption, respectively. C_e is the equilibrium concentration in the solution (mg/l) and q_e is the equilibrium adsorption capacity of adsorbent (mg of adsorbate per gm of adsorbent). The linear form of the Langmuir isotherm model is given by [11]:

$$\frac{1}{q_e} = \frac{1}{q_o} + \frac{1}{q_o \ K_l} \cdot \frac{1}{C_e} \qquad \qquad \dots (6)$$

The Langmuir constant q_o and K_l can be calculated from the intercept and slope of the linear plot of experimental data of $1/q_e$ versus $1/C_e$ as shown in Fig.(13).

The essential characteristics of the Langmuir isotherm can be expressed in term of a dimensionless constant separation factor for equilibrium parameter, R_L, which is defined by eq. (7) [14]:

$$R_L = \frac{1}{1 + K_l \ C_o} \qquad \qquad \dots (7)$$

Hall et al. [17] showed, using mathematical calculation, that the parameter, R_L indicates the shape of isotherm as summarized in Table (1).

The Freundlich model is an empirical based on sorption on heterogeneous surface. It is given by eq. (8) [6]:

$$q_e = K_f \ . \ C_e^{1/n} \qquad \qquad \dots (8)$$

where K_f and n are the Freundlich constants that indicate the adsorption capacity and intensity, respectively. The linear form of Freundlich model can be written as:

$$ln \ q_e = ln \ K_f + \frac{1}{n} \ ln \ C_e \qquad \qquad \dots (9)$$

The value of K_f and n are evaluated from both intercept and slope, respectively, of the linear plot of the experimental data of $ln \ q_e$ versus $ln \ C_e$ as illustrated in Fig. (14).

Fig.(13) and Fig.(14) show the Langmuir and Freundlich curves for phenol adsorption onto saw dust, respectively. The isotherm constants and correlation factors are summarized in Table (2). In general, R^2 values, which are a measure of goodness of fit show that both Langmuir and Freundlich isotherm models could adequately describe the adsorption data. From Table (3), it can be seen that the values of correlation factor R^2 is close to unity for both models which indicates the good representation of the experimental results by using linear Langmuir or Freundlich isotherms.

VI.   CONCLUSION

In this study, the adsorption of phenol from wastewater was investigated using sawdust as adsorbent. The result indicated that the percentage removal of phenol was considerably affected by initial phenol concentration, amount of adsorbent dose, pH value and mixing contact time. The results showed that the percentage of removal increased with increasing amount of adsorbent dosage. The results also indicate that the uptake of phenol took place at natural pH value and equilibrium is happed at 120 min. The Langmuir and Freundlich adsorption models were used for the mathematical description of the adsorption model. The obtained results showed that the adsorption equilibrium data fit very well to both models.

REFERENCES

[1].   Li Z., Burt T. and Bowman R.S., "Sorption of Ionizable Organic Solutes by Surfactant Modified Zeolite", Environ. Sci. Technol., 34, (2000), 3756-3760.

[2].   Yapar S., Klahre P. and Klumpp E., "Hydrotalcite as A potential Sorbent for the Removal of 2,4 Dicholorophenol", Turkish Journal of Engineering and Environmental Sciences, 28, (2004), 4-48.

[3].   Akcay M., "Characterization and Determination of The Thermodynamic and Kinetic Properties of P-cp Adsorption onto Organophilic Bentonite from Aqueous Solution", J. Colloid Interf. Sci., Vol. 280, (2004), 299-304.

[4].   Hao O. J., Kim H. and Chiang P. C., "Decolorization of Wastewater" , Crit. Rev. Environ. Sci. Technol., Vol. 30, (2000), 449-505.

[5].   Roostaei N. and Tezel F. H., "Removal of Phenol from Aqueous Solutions by Adsorption", J. Environ. Manage., Vol. 70, (2004), 157-164.

[6].   Banat, F.A., Al-Bashir B., Al-Asheh S., and Hayajneh O., "Adsorption of Phenol by Bentonite", Environmental Pollution, 107, (2000), 390-398.

[7].   Kartal, O.E., Erol, M., and Oguz, H., "Photocatalytic Destruction of Phenol by TiO_2 Powder", Chem. Eng. Tech., 24, (2001), 645-649.

[8].   APHA, AWWA, and WEF, "Standard Methods for the Examination of Water and Wastewater", 20th Edn. Washington DC, (1998).

[9].   Montogomery, D.G., "Design and Analysis of Experiments", 2nd ed., John Wiley, (1984).

[10].   Ekpete, O.A., Horsfall, M. and Tarawou, T., "Potential of Fluid and Commertial Activated Carbons for Phenol Removal in Aqueous Systems", ARPN Journal of Engineering and Applied Sciences, Vol. 5, No. 9, (2010), 39-47.

[11].   Mahavi, A. , Maleki, A. and Eslami, A., " Potential of Rise Husk and Rise Husk Ash for Phenol Removal in Aqueous Systems", American Journal of Applied sciences, 14, (2004), 321-326.

[12].   Uddin, M. T., Islam, M. S. and Adedin, M. Z., "Adsorption of Phenol from Aqueous Solution by Water Hyacinth Ash", ARPN Journal of Engineering and Applied Sciences, Vol. 2, No. 2, (2007).

[13].   Tagreed, L. A., "Removal of Phenol From Aqueous Solution By Agriculture Waste", Eng.& Tech. Journal, Vol. 28, No. 19, (2010).

[14].   Hall K. R. and Vermeylem T., "Pore and Solid Diffusion Kinetics in Fied Bed Adsorption Under Constant Pattern Conditions", J. Eng. Chem. Fundam., 4, (1966), 212-219.

[15].   Box, G. E. and Hunter, J. C., "Multifactor Experimental Design for Exploring --Response surface", Ann. Math, vol.28, (1957), p.195.

Table (1) Constant parameter, R_L

R_L Value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$R_L = 0$	Irreversible
$0 < R_L < 1$	Favorable

Table (2) Parameters of Langmuir and Freundlich isotherm models

Langmuir Constants			Freundlich Constants		
q_o	K_l	R^2	K_f	$1/n$	R^2
105.93	0.004928	0.9996	1.091	1.2735	0.9975

Table (3) Constant parameter, R_L, for Langmuir Isotherm

C_o (mg/l)	R_L
100	0.669
200	0.503
300	0.403
400	0.336
500	0.288
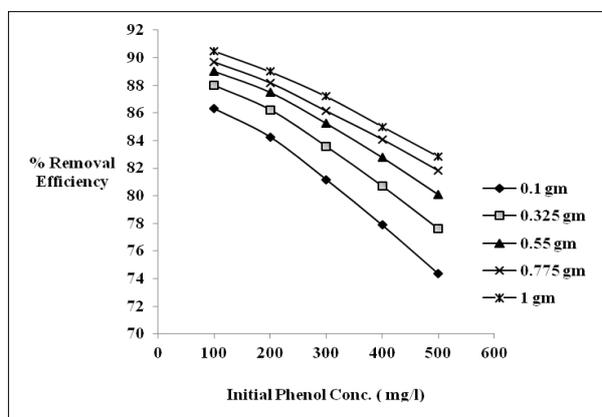
Fig. (1) Effect of initial phenol concentration at different adsorbent doses
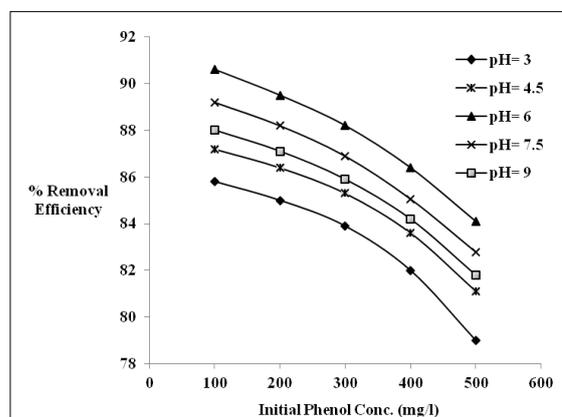
Fig. (2) Effect of initial phenol concentration at different pH values
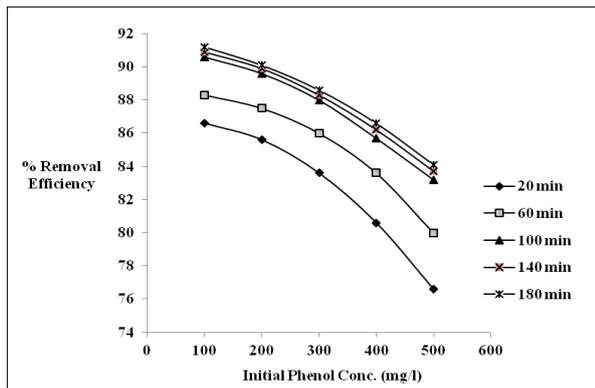
Fig. (3) Effect of initial phenol concentration on removal efficiency at different contact times
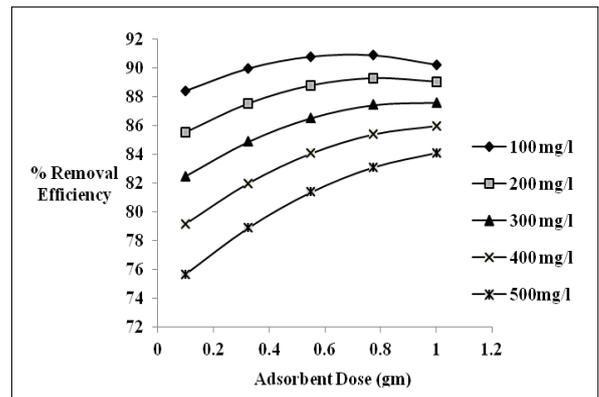
Fig. (4) Effect of adsorbent dose on removal efficiency at different Initial phenol concentrations
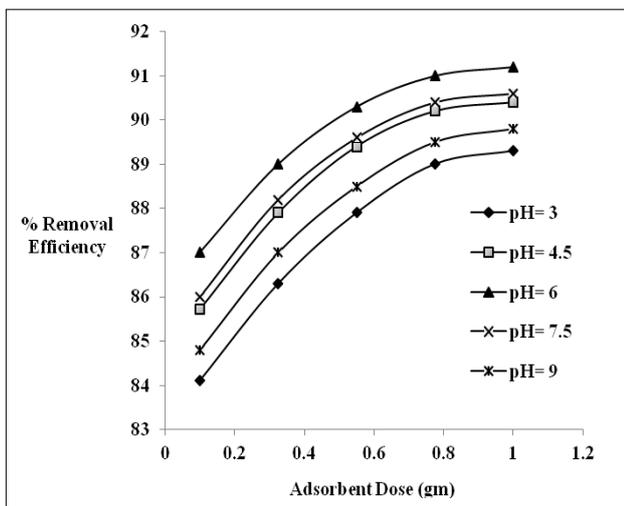
Fig. (5) Effect of adsorbent dose on removal efficiency at different pH values
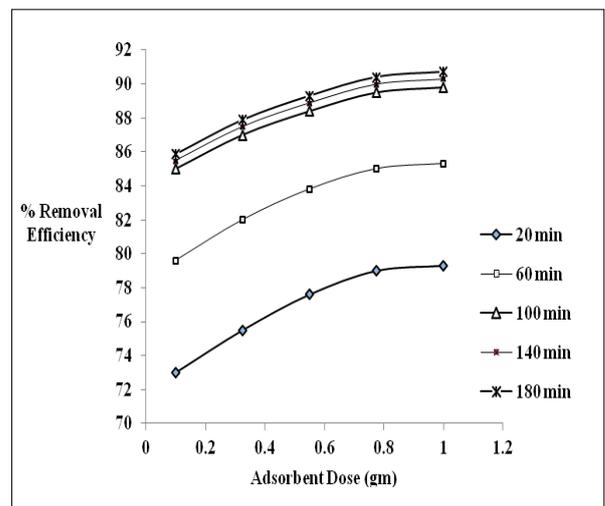
Fig. (6) Effect of adsorbent dose on removal efficiency at different contact times
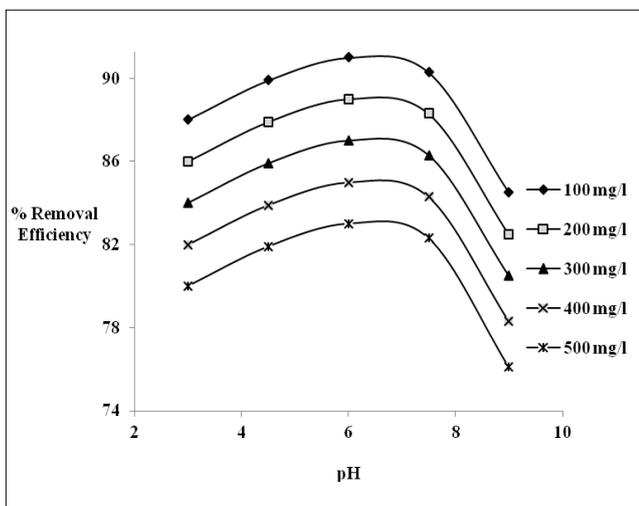
Fig. (7) Effect of pH value on removal efficiency at different initial Phenol concentrations
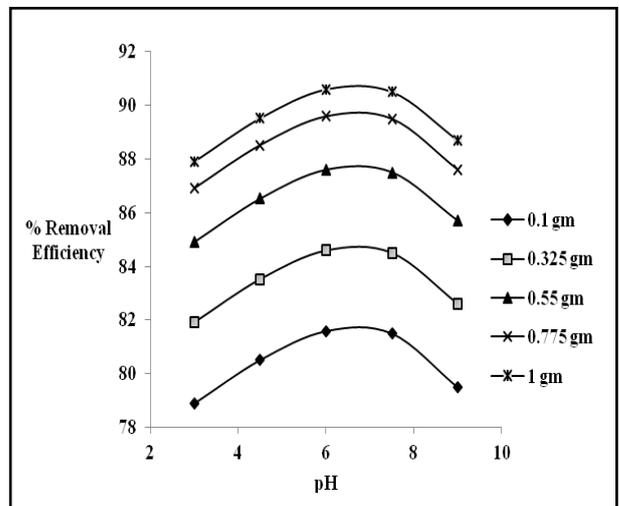
Fig. (8) Effect of pH value on removal efficiency at different adsorbent doses
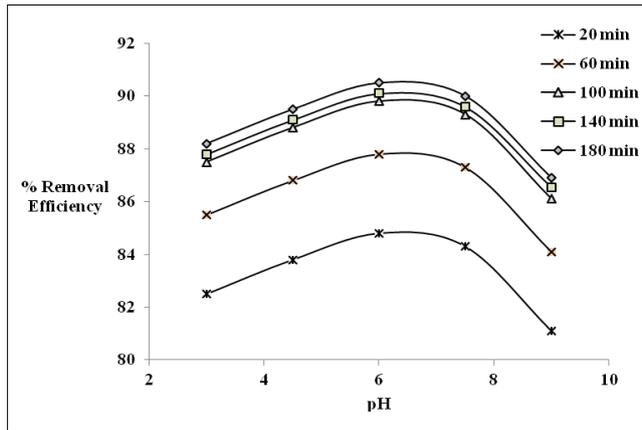
Fig. (9) Effect of pH value on removal efficiency at different contact times
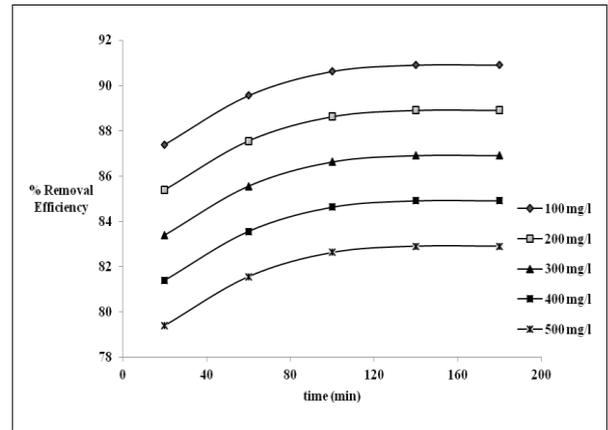
Fig. (10) Effect of contact time on removal efficiency at different initial phenol concentrations
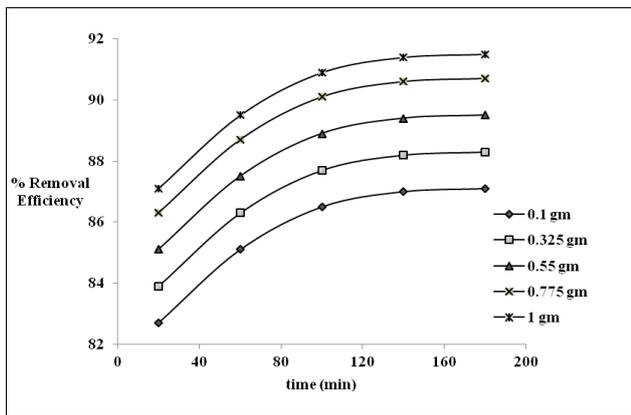
Fig. (11) Effect of contact time on removal efficiency at different adsorbent doses
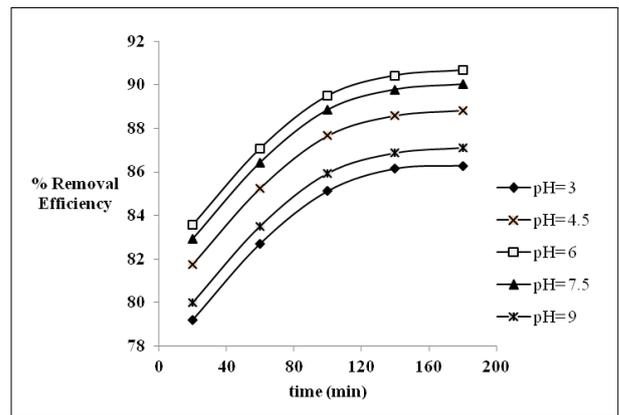
Fig. (12) Effect of contact time on removal efficiency at different pH values
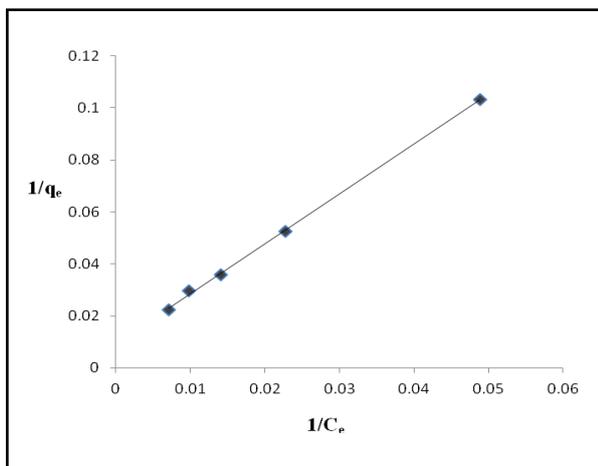
Fig. (13) Langmuir isotherm for phenol adsorption on sawdust
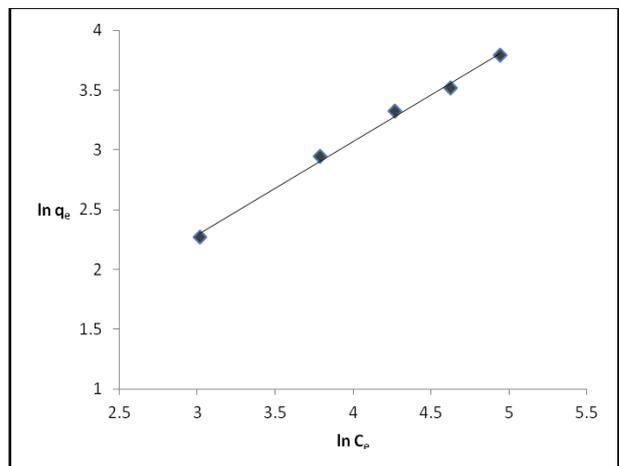
Fig. (14) Freundlich isotherm for phenol adsorption on sawdust