



## ADSORPTION OF PHENOL FROM AQUEOUS SOLUTION BY WATER HYACINTH ASH

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### ABSTRACT

The potential of water hyacinth ash for phenol adsorption from aqueous solution was studied. Batch kinetic and isotherm studies were carried out under varying experimental conditions of contact time, phenol concentration, adsorbent dosage and pH. The adsorption of phenol decreased with increasing pH. The Freundlich and Langmuir 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 and pseudo-second-order models, were applied to examine the kinetics of the adsorption. The results showed that kinetic data followed closely to the pseudo-second-order model.

**Keywords:** phenol, adsorption, water hyacinth ash, equilibrium, kinetic.

### INTRODUCTION

Phenols are common contaminants in wastewater generated from oil, gasoline, coal, paper, textile, petroleum, petrochemicals, pharmaceuticals, phenol producing industries and plants, which are processing phenols to plastics. They are considered one of the priority pollutants in wastewater, because they are harmful to organisms even at low concentrations. Many phenols have been classified as hazardous pollutants because of their potential toxicity to human health. Human consumption of phenol contaminant water can cause severe pain leading to damage of the capillaries ultimately causing death. Their presence in water supplies is noticed as bad taste and odor (Mostafa, Sarma and Yousef, 1998). In the presence of chlorine in drinking water, phenols form chlorophenol, which has a medicinal taste and which is quite pronounced and objectionable. Therefore, Environmental Protection Agency regulations call for lowering phenol content in wastewater to less than 1 mg/L (Dutta, Patil and Brothakur, 1992). There are many methods, such as, adsorption, microbial degradation, chemical oxidation, precipitation, ion exchange and solvent extraction to remove phenols from aqueous solution. Adsorption is an effective separation process for treating industrial and domestic effluents. Activated carbon 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 (McKay, Prasad and Mowli, 1986; Nassar and El-Geundi, 1994; El-Geundi, 1997).

The adsorption characteristics of phenol on various adsorbents have previously been extensively investigated for many purposes of separation and purification. However, most of the work was on the adsorption behavior of activated carbon. The adsorption of phenol from aqueous solution by using carbonized beet pulp was investigated (Dursun, Cicek and Dursun, 2005). The result indicated that adsorption capacity of the adsorbent was considerably affected by initial pH, temperature and initial phenol concentration. The

equilibrium data were well described by the Freundlich model and the pseudo-second-order equation provided the better correlation for the adsorption data. In another experiment, it was reported that the adsorption of phenol onto chitin was endothermic and increased with temperature (Dursun and Kalayci, 2005). The increase in active bentonites mass or initial pH of the solution also resulted in more phenol removal from solution (Asheh, Banat and Aitah, 2003). It was also indicated that peat, fly ash and bentonite were found to adsorb 46.1%, 41.6% and 42.5% phenol, respectively, from the solution of initial concentration of approximately 1 mg/l (Vigiraghavan and Alfaro, 1998). Other adsorbents used to remove phenol from aqueous solution are bentonite (Banat, Al-Bashir, Al-asheh, and Hayajneh, 2000), silica gel, activated alumina and activated carbon (Roostaei and Tezel, 2004), titanium oxide (TiO<sub>2</sub>) (Bekkouche, Bouhelassa, Salah and Meghlaoui, 2004), activated carbon derived from solid waste such as PET, waste tires, refused derived fuel and waste generated during lactic acid fermentation from garbage (Nakagawa, Namba, Mukai, Tamon, Ariyadejwanich, and Tanthapanichakoon, 2004), powdered and granular activated carbon prepared from Eucalyptus wood (Tancredi, Medero, Möller, Piriz, Plada and Cordero, 2004), mesoporous activated carbon prepared from waste tires (Tanthapanichakoon, Ariyadejwanich, Japthong, Nakagawa, Mukai, and Tamon, 2005), aspergillus niger biomass (Rao, and Viraraghavan, 2002), pumice (Akbal, 2005) and papermill sludge (Calace, Nardi, Petronio and Pietroletti, 2002).

In this study, water hyacinth ash is used as an adsorbent to remove phenol from aqueous solution. Water hyacinth is available in the river and pond in Bangladesh. Therefore, water hyacinth ash can be used as a cost effective adsorbent for the removal of phenol from aqueous solution.

The objective of this study was to produce water hyacinth ash as an adsorbent for adsorption of phenol, to characterize it and to investigate the effects of initial



phenol concentration, contact time, pH and adsorbent dosage on the adsorption of phenol on water hyacinth ash. Equilibrium isotherm data were fitted to Langmuir and Freundlich equations and constants of isotherm equations were determined. Adsorption kinetics of phenol onto water hyacinth ash was also analyzed by using pseudo-first-order and pseudo-second-order models to data.

## MATERIALS AND METHODS

### Materials

The water hyacinth was collected from the local ponds. The roots of the collected water hyacinth were separated and washed thoroughly with water for several times to remove earthy matter and all the dirt particles. It was then dried in an oven at a temperature of 90°C for about 16 hours. The dried roots were then burned for about 1h. The remaining was then crushed, sieved and stored in plastic bottle for use.

### Chemicals

A stock solution of 1000 mg/l phenol was prepared by dissolving 1.0g 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

### Sorption experiments

#### Effect of pH

The effect of pH on the amount of phenol removal was analyzed over the pH range from 2.5 to 9. In this study, 150ml of phenol solution of 50 mg/L was taken in stopper plastic conical flask and was agitated with 1.0g of water hyacinth ash using flash shaker (Stuart Scientific Co. Ltd. Model SF1, U.K.) at room temperature (27 ± 2°C). Agitation was made for 5h at constant oscillation of 500 osc/min. The samples were then centrifuged, and the left out concentration in the supernatant solution were analyzed using a UV/VIS spectrometry (Shimadzu Model UV-1601) by monitoring the absorbance changes at a wavelength of maximum absorbance (505 nm).

#### Effect of adsorbent dosage

The effect of water hyacinth ash mass on the amount of removal of phenol solution was obtained by contacting 150ml of phenol solution of initial concentration of 70 mg/l with different weighed amount (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, and 1.6g) of water hyacinth ash in stopper conical flask. Each sample was then agitated for 5h at a constant oscillation of 500 osc/min. The samples were then centrifuged and the concentrations in the supernatant phenol solutions were then analyzed as before.

### Adsorption Equilibrium

Equilibrium studies were carried out by contacting 0.75g of water hyacinth ash with 150ml of phenol solution of different initial concentrations (40, 50, 60, 70, 80, 90, 100 and 110 mg/L) in 250ml stopper conical flasks. The samples were then shaken at a constant oscillation of 500 osc/min for 5h. After equilibrium the concentrations in the samples were analyzed as before.

### Adsorption Kinetics

Sorption kinetics experiments were carried out by contacting 200ml phenol solution of different initial concentrations ranging from 50 to 70 mg/L with 0.5g water hyacinth ash in a 250ml stoppered conical flask. The samples were then shaken at a constant oscillation speed of 500 osc/min for 5h. Samples were then pipetted out at different time intervals. The collected samples were then centrifuged and the concentration in the supernatant solution was analyzed as before.

## RESULTS AND DISCUSSION

### Effect of pH on phenol adsorption

The initial pH of adsorption medium is one of the most important parameters affecting the adsorption process. Fig. 1 shows the effect of pH on the adsorption of phenol. From Fig. 1, it was observed that the uptake of phenol by water hyacinth ash was almost constant in the pH range of 2.5-5.0. Then the adsorption decreased with increasing pH and it decreased from 7.09 mg/g at pH 5 to 3.26 mg/g at pH 9.

The pH primarily affects the degree of ionization of phenol and the surface properties of water hyacinth ash. The ionic fraction of phenolate ion ( $\phi_{ions}$ ) can be calculated from the following equation:

$$\phi_{ions} = \frac{1}{1 + 10^{pKa-pH}} \quad (1)$$

At low pH values, the surface of the water hyacinth ash would be protonated and resulted in a stronger attraction for negatively charge phenolate ions. Phenol, being weakly acidic (pKa = 10), partially ionizes in solution.

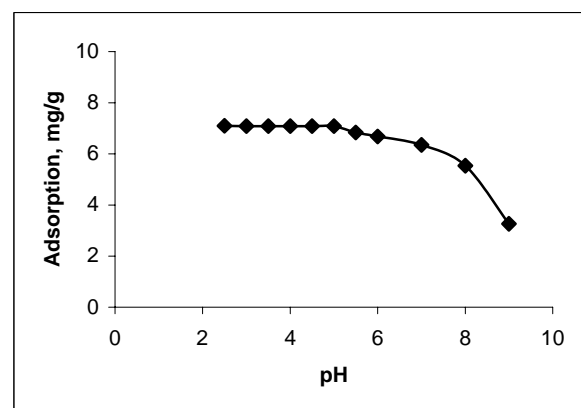


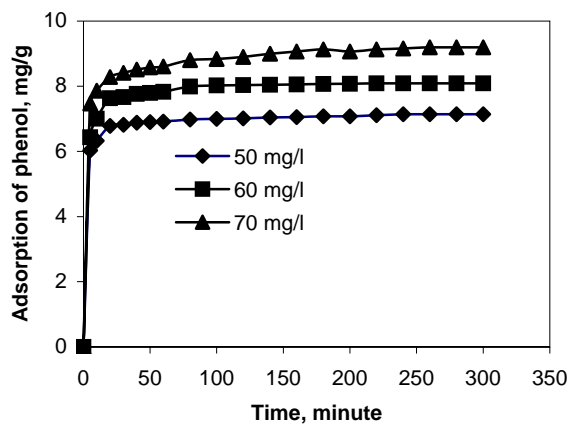
Figure-1. Effect of pH on the adsorption of phenol on water hyacinth ash.



These ions are negatively charged and are directly attracted to the protonated surface of water hyacinth ash by electro-static force. Unionized phenol molecules would also be attracted, possibly, by physical force. At high pH, OH<sup>-</sup> ions would compete with the phenol molecules for sorption sites. Sorption of excess of OH<sup>-</sup> ions could convert an initial positively charged surface of water hyacinth ash into a negatively charged surface resulting repulsion of negatively charged phenoxide ions and adsorption decreased.

#### Effect of contact time and initial concentrations

The adsorption data for the uptake of phenol versus contact time at different initial concentrations is presented in Figure-2. The results showed that equilibrium time required for the adsorption of phenol on water hyacinth ash was almost 120 minutes (2h). However, for subsequent experiments, the samples were left for 5h to ensure equilibrium. These results also indicated that up to 90-95% of the total amount of phenol uptake was found to occur in the first rapid phase (30min) and thereafter the sorption rate was found to decrease. The higher sorption rate at the initial period (first 30min) may be due to an increased number of vacant sites on the adsorbent available at the initial stage, as a result there exist increased concentration gradients between adsorbate in solution and adsorbate on adsorbent surface.



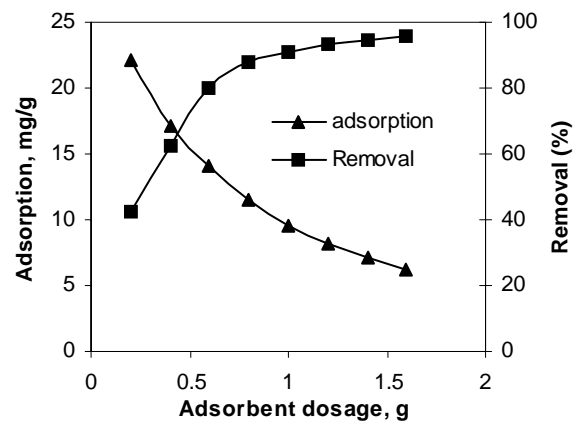
**Figure-2.** Effect of contact time and initial concentrations on the adsorption of phenol onto water hyacinth ash.

This increased in concentration gradients tends to increase in phenol sorption at the initial stages. As time precedes this concentration is reduced due to the accumulation of phenol particles in the vacant sites leading to a decrease in the sorption rate at the larger stages from 30 to 300 min (Vadivelan and Kumar, 2005). It was also seen that an increase in initial concentration resulted in increased phenol uptake.

#### Effect of adsorbent dosage

In order to investigate the effect of mass of adsorbent on the adsorption of phenol, a series of adsorption experiments was carried out with different adsorbent dosage at an initial phenol concentration of 70

mg/L. Figure-3 shows the effect of adsorbent dosage on the removal of phenol.



**Figure-3.** Effect of adsorbent dosage on the adsorption of phenol on water hyacinth ash.

The percentage removal of phenol increased with the increase in adsorbent dosage. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase adsorbent dosage. But amount of phenol adsorbed per unit mass of water hyacinth ash decreased with increase in adsorbent dosage.

#### Adsorption Equilibrium

Equilibrium study on adsorption provides information on the capacity of the adsorbent. 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. 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 modeling of the adsorption data is the Langmuir equation, which is valid for monolayer sorption onto a surface with a finite number identical site and is given by eq. (2).

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} \quad (2)$$

Where  $q_0$  and  $K_L$  are Langmuir parameters related to maximum adsorption capacity and free energy of adsorption, respectively.  $C_e$  is the equilibrium concentration in the aqueous solution and  $q_e$  is the equilibrium adsorption capacity of adsorbent. The linearized form of Langmuir equation can be written as

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_0 K_L} \cdot \frac{1}{C_e} \quad (3)$$

The Langmuir constant  $q_0$  and  $K_L$  can be calculated by plotting  $1/q_e$  versus  $1/C_e$ .



The Freundlich model is an empirical equation based on sorption on heterogeneous surface. It is given as

$$q_e = K_f C_e^{\frac{1}{n}} \quad (4)$$

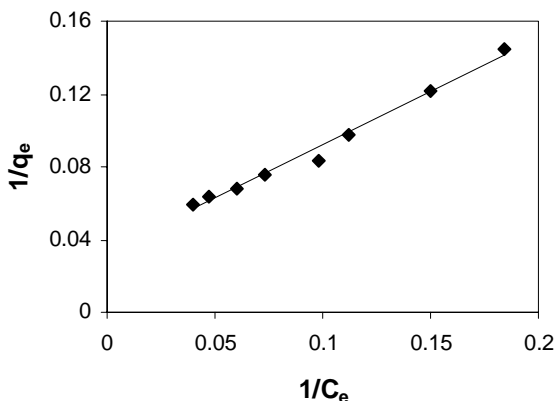
Where  $K_f$  and  $n$  are the Freundlich constants that indicate adsorption capacity and adsorption intensity, respectively.

The linear form of Freundlich isotherm can be written as

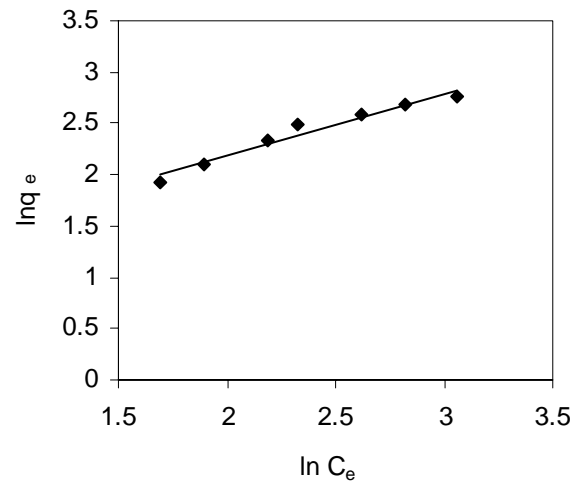
$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

The value of  $K_f$  and  $n$  can be calculated by plotting  $\ln q_e$  versus  $\ln C_e$ .

Figure-4 and Figure-5 show the Langmuir and Freundlich curves for phenol adsorption onto water hyacinth ash, respectively. The isotherm constants and correlation coefficients are shown in Table-1. From Figure-5 and Figure-6, it was observed that the equilibrium data were very well represented by the Langmuir isotherm equation when compared to the Freundlich equation. The sorption equilibrium data fitted Langmuir and Freundlich equations with correlation coefficients values of 0.9941 and 0.9625, respectively. The best fit of equilibrium data in the Langmuir isotherm expression predicted the monolayer coverage of phenol onto water hyacinth ash. From Table-1 it was also observed that the maximum sorption capacity of water hyacinth ash for phenol was found to be 30.49 mg/g.



**Figure-4.** Langmuir isotherm for phenol adsorption on water hyacinth ash.



**Figure-5.** Freundlich isotherm for phenol adsorption on water hyacinth ash.

**Table-1.** Equilibrium constants for methylene blue onto water hyacinth ash.

Freundlich isotherm parameters			Langmuir isotherm parameters		
$K_f$	$n$	$r^2$	$q_0$ (mg/g)	$K_L$	$r^2$
2.6289	1.6428	0.9625	30.49	0.0555	0.9882

#### Adsorption kinetics

Kinetic models are used to examine the rate of the adsorption process and potential rate-controlling step. In the present work, the kinetic data obtained from batch studies have been analyzed by using pseudo-first-order and pseudo-second-order models.

The first order equation of Lagergren is generally expressed as follows (Lagergren, 1998):

$$\frac{dq}{dt} = k_1(q_e - q) \quad (6)$$

where  $q_e$  and  $q$  are the amounts of methylene blue adsorbed ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$  (min), respectively, and  $k_1$  is the rate constant of pseudo-first-order sorption ( $\text{min}^{-1}$ ).

The integrated form of Eq.(6) becomes

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (7)$$

A plot of  $\ln(q_e - q)$  against  $t$  should give a linear relationship with the slope  $k_1$  and intercept of  $\ln q_e$ .

The pseudo-second-order kinetic rate equation is expressed as follows (Ho and McKay, 1999)

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (8)$$

Where  $k_2$  is the rate constant of pseudo-second-order sorption ( $\text{g mg}^{-1}\text{min}^{-1}$ ). The integrated form of Eq. (8) becomes

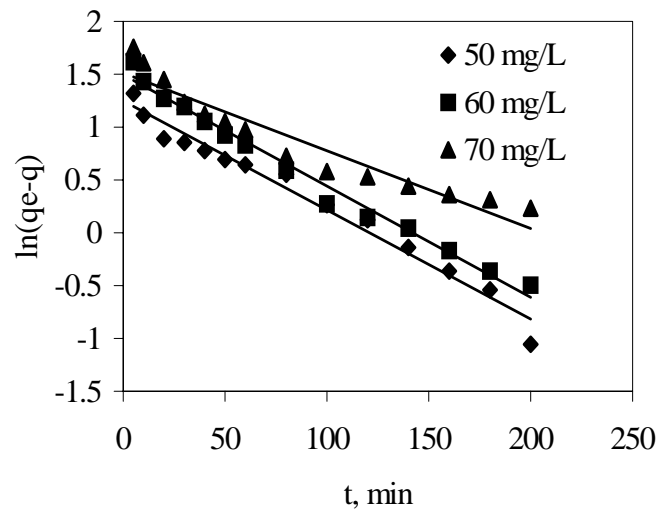


$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

If the second order kinetic equation is applicable, the plot of  $t/q$  against  $t$  of Eq. (9) should give a linear relationship. The  $q_e$  and  $k_2$  can be determined from the slope and intercept of the plot.

The plot of linearized form of the pseudo first-order equation is shown in Figure-6. The pseudo first-order rate constant  $k_1$ , amount of phenol adsorbed at

equilibrium, and correlation coefficient are shown in Table-2. The results showed that, the correlation coefficients obtained for all initial concentrations,  $C_0$  were higher than 0.9. Although the correlation coefficient values were higher than 0.9, the experimental  $q_e$  did not agree with the calculated ones, obtained from the linear plots. Therefore, pseudo-first-order kinetic model did not describe the adsorption results of phenol onto water hyacinth ash.



**Figure-6.** Pseudo-first-order kinetics for the adsorption of phenol onto water hyacinth ash.

**Table-2.** Pseudo-first-order kinetic constants for the adsorption of phenol onto water hyacinth ash.

$C_0$ (mg/L)	$q_{e, exp}$ (mg/g)	$q_{e, cal}$ (mg/g)	$k_1$ ( $\text{min}^{-1}$ )	$r_1^2$
50	13.48	3.48	0.0103	0.9751
60	15.30	4.46	0.0105	0.9853
70	16.65	4.53	0.0074	0.9124

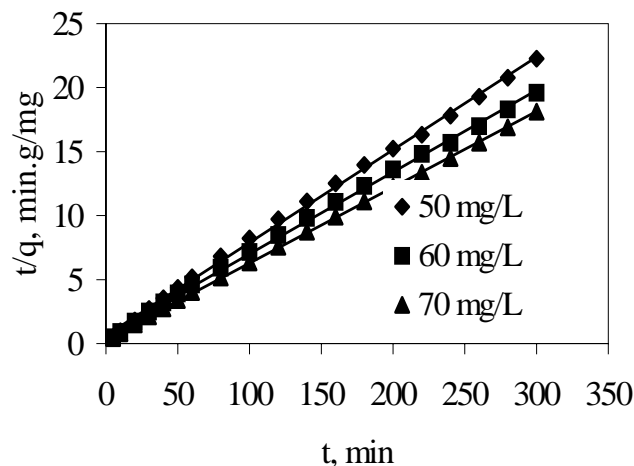
Figure-7 shows the linearized form of the pseudo-second-order kinetic model. The pseudo-second-order constant  $k_2$ , amount of phenol adsorbed at equilibrium  $q_e$ , and the corresponding correlation coefficient values are given in Table-3. From Table-3, it was noticed that the  $r_2^2$  values were found to be higher than that of  $r_1^2$  at all initial

phenol concentrations. The theoretical  $q_e$  values were closer to the experimental  $q_e$  values. 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 water hyacinth ash in contrast to the pseudo-first-order model.

**Table-3.** Pseudo-second-order kinetic constants for the adsorption of methylene blue onto water hyacinth ash.

$C_0$ (mg/L)	$q_{e, exp}$ (mg/g)	$q_{e, cal}$ (mg/g)	$k_2$ (g/mg min)	$r_2^2$
50	13.48	13.79	0.0083	0.9985
60	15.30	15.65	0.0067	0.9987
70	16.65	16.86	0.0099	0.9997





**Figure-7.** Second order kinetics for adsorption of phenol onto water hyacinth ash.

## CONCLUSIONS

In this study, the adsorption of phenol from aqueous solution was investigated using water hyacinth ash as an adsorbent. The results indicated that adsorption capacity of the adsorbent was considerably affected by initial pH, initial phenol concentration, contact time and adsorbent dosage. The results showed that the amount of phenol adsorbed increased with increasing initial phenol concentration. The result also indicated that the uptake of phenol took place at a pH in the range of 2.5-5. Then the adsorption of phenol decreased with increasing pH.

Equilibrium data fitted very well in a Langmuir isotherm equation, confirming the monolayer sorption capacity of phenol onto water hyacinth ash with a monolayer sorption capacity of 30.49 mg/L.

The pseudo-first-order and pseudo-second-order kinetic models were used to analyze the data obtained for phenol adsorption onto water hyacinth ash. The result indicated that the pseudo-second-order equation provided the better correlation for the adsorption data.

## REFERENCES

Akbal, F. 2005. Sorption of phenol and 4-chlorophenol onto pumice treated with cationic surfactant. *J. Env. Management*. Vol. 74, pp. 239-244.

Asheh, S. A., Banat, F. and Aitah, L. A. 2003. Adsorption of phenol using different types of activated bentonites. *Sep. and Purification Tech.* Vol. 33, pp. 1-10.

Banat, F. A., Al-Bashir, BAl-asheh., S. and Hayajneh, O. 2000. Adsorption of phenol by bentonite. *Env. Poll.* Vol. 107, pp. 391-398.

Bekkouche, S., Bouhelassa, M., Salah, N. H. and Meghlaoui, F. Z. 2004. Study of adsorption of phenol on titanium oxide (TiO<sub>2</sub>). *Desalination*. Vol. 166, pp. 355-362.

Calace, N., Nardi, E., Petronio B. M. and Pietroletti, M. 2002. Adsorption of phenols by pepermill sludge. *Environ. Poll.* Vol. 118, pp. 315-319.

Dursun A. Y. and Kalayci, C. S. 2005. Equilibrium, Kinetic and thermodynamic studies on adsorption of phenol onto chitin. *J. of hazardous materials*. Vol. B123, pp. 151-157.

Dursun, G., Cicek H. and Dursun, A.Y. 2005. Adsorption of phenol from aqueous solution by using carbonized beet pulp. *J. Hazardous materials*. Vol. B125, pp. 175-182.

Dutta, N. N., Patil, G. S and Brothakur, S. 1992. Phase transfer catalyzed extraction of phenolic substances from aqueous alkaline stream. *Separation Sci. and Tech.* Vol. 27, p. 1435.

El-Geundi, M. S. 1997. Adsorbents of industrial pollution control, *Adsorot. Sci. Technol.* Vol. 15, pp. 777-787.

Ho, Y.S. and Mckay, G. 1999. Pseudo-second-order model for sorption process. *Process Biochem.* Vol. 34, pp. 451-465.

Lagergren, S. 1998. Zur theorie der sogenannten adsorption geloster stoffe, *Kungliga Svenska Vetenskapsakademiens. Handlingar*. Vol. 24, pp. 1-13.

McKay, G., Prasad, G. R. and Mowli, P. R. 1986. Equilibrium studies for the adsorption of dyestuffs from aqueous solutions by low-cost materials. *Water Ail Soil Pollut.* Vol. 29, pp. 273-283.

Mostafa, M. R., Sarma, S. E. and Yousef, A. M. 1989. Removal of organic pollutants from aqueous solution: Part 1. Adsorption of phenols by activated carbon. *Idian Journal of Chem.* Vol. 28A, pp. 946-948.

Nakagawa, K., Namba, A., Mukai, S. R., Tamon, H., Ariyadejwanich, P. and Tanthapanichakoon, W. 2004.



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Adsorption of phenol and reactive dye from aqueous solution on activated carbons derived from solid wastes. *Water Research*. Vol. 38, pp. 1791-1798.

Nassar, M. M. and El-Geundi, M. S. 1994. Comparative cost of color removal from textile effluents using natural adsorbents. *J. Chem. Technol. Biotechnol.* Vol. 61, pp. 307-317.

Rao, J. R. and Viraraghavan, T. 2002. Biosorption of phenol from an aqueous solution by *Aspergillus niger* biomass. *Bioresource Technology*. Vol. 85, pp. 165-171.

Roostaei, N. and Tezel, F. H. 2004. Removal of phenol from aqueous solutions by adsorption. *J. Env. Management*. Vol. 70, pp. 157-164.

Tancredi, N., Medero, N., Möller, F., Piriz, J., Plada C. and Cordero, T. 2004. Phenol adsorption onto powdered

and granular activated carbon, prepared from Eucalyptus wood. *J. Colloid Interface Sci.* Vol. 279, pp. 357-363.

Tanthapanichakoon, W., Ariyadejwanich, P., Japthong, P., Nakagawa, K., Mukai, S. R. and Tamon, H. 2005. Adsorption-desorption characteristics of phenol and reactive dyes from aqueous solution on mesoporous activated carbon prepared from waste tires. *Water Research*. Vol. 39, pp. 1347-1353.

Vadivelan, V. and Kumar, K.V. 2005. Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. *J. Colloid and Interface Science*. Vol. 286, pp. 90-100.

Vigiraraghavan, T. and Alfaro, F. M. 1998. Adsorption of phenol from wastewater by peat, fly ash and bentonite. *J. Hazardous materials*. Vol. 57, pp. 59-70.