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KINETIC SORPTION STUDY OF PHENOL ONTO ACTIVATED CARBON DERIVED FROM FLUTED PUMPKIN STEM WASTE (*Telfairia occidentalis Hook.* F)

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ABSTRACT

Fluted activated carbon obtained from fluted pumpkin stem waste can be harnessed as a useful adsorbent for the removal of phenol from aqueous solution. The contact time data was modeled using pseudo first - order, pseudo second order, Elovich, intra-particle and liquid - film diffusion. The kinetic data favored pseudo second-order with regression value of 0.987. Thermodynamic parameters ΔH^o, ΔS^o, and ΔG^o of the adsorption of phenol onto fluted activated carbon were negative which revealed exothermic nature of the sorption process, strong bond formation between the adsorbent and adsorbate molecules and the spontaneous nature of the adsorption with a high preference for phenol.

Keywords: phenol, fluted pumpkin, kinetics, pseudo second-order, adsorption.

INTRODUCTION

Water pollution by phenol and phenolic compounds is of great concern. Presence of phenolic compounds even at low concentration in the industrial wastewater adversely affects aquatic as well as human life directly or indirectly when disposed off to public sewage, river or surface water. Some times these form complex compounds with metal ions, discharged from other industries, which are more carcinogenic in nature than the phenolic compounds. The low volatility of phenol and its affinity to water make oral consumption of contaminated water the greatest risk to humans (USEPA, 1987; Mahvi *et al*., 2004; Prpich and Daugulis, 2005; Dursun and Kalayei, 2005, Entezari *et al*., 2005, Kujawski *et al*., 2004). The ingestion of a small amount of phenol (TLV of 5ppm) by human beings may cause nausea, vomiting, paralysis, coma, greenish of smoky coloured urine and even death from respiratory failure or cardiac arrests. Fatal poisoning may also occur by adsorption of phenol by skin, if a large area of it is exposed (Banat *et al*., 2000; Zumiriye and Yener, 2001 Banat *et al*., 2004 Sofia *et al*., 2005). The wastewater with the highest concentration of phenol (>100mg/L) is typically generated from coke processing Alzaydien and Manasreh (2009). It is therefore necessary to remove phenol completely from wastewater before being discharged into waterways. There are many methods to remove phenolic materials from aqueous solutions, e.g., steam distillation and oxidation using a strong oxidizing agent such as hydrogen peroxide. In the past several decades, extensive research has been conducted to develop innovative and promising adsorbent material for dealing with the treatment problem of contaminated industrial effluents. There is a growing interest in cost effective innovative materials and method that will be useful in the treatment of industrial waste streams (Horsfall and Spiff 2004, Horsfall and Spiff 2005, Ekpete *et al*., 2010). The study of kinetics in wastewater treatment is significant as it provides valuable insight into the reaction pathways and mechanism of sorption reactions. Kinetics describes the solute uptake rate that controls the residence time of sorbate uptake at the solid - solution interface, and is important to design appropriate sorption treatment plants, and to predict the rate at which any pollutant is removed. The pseudo-first order rate equation of Lagergren has been widely used since 1898. The use of the pseudo - first order, second order and Elovich kinetics model for the sorption of phenol has been reported by Uddin *et al*., 2007, Nagda *et al*., 2007 and Alzaydien and Manasreh (2009). The objective of this study is to carry out an investigation on the kinetics of phenol sorption onto fluted activated carbon as sorbent.

MATERIALS AND METHODS

The fluted pumpkin stem waste (*Telfairia occidentalis Hook F*) used for this study was obtained from Iwofe market Rumuolumeni Port Harcourt. The stems collected were washed thoroughly with water, cut into smaller bits rinsed with distilled water, air dried, and later oven dried at 105^{o}C for 10h. The oven-dried fluted pumpkin was carbonized to obtain the carbonized biomass.

Carbonization

Carbonization was carried out in the Plant Physiology and Anatomy Laboratory of the University of Port Harcourt, using a muffle furnace (Carbolite Sheffield England LMF4) which allows limited supply of air. Carbonization was done at 350^{o}C for two hours and allowed to cool at room temperature for three hours before activation.

Acid activation of the biomass

A carefully weighed 25.00 ± 0.01g carbonized fluted pumpkin was placed in a beaker containing 500cm^3 of 0.3M H_3PO_4. The content of the beaker was thoroughly mixed, heated until it formed a paste. The paste was put in a crucible and placed in a furnace which heated to 300^{o}C for thirty minutes. The fluted activated carbon was washed

free of acid to get a pH of 6.7 ± 0.12. This was allowed to cool, washed with distilled water, oven dried at 105°C to constant weight and ground. It was sieved with a 106µm mesh to obtain a fine powdered activated carbon which was used for the various experiments. The treatment of the adsorbent with 0.3M H_3PO_4 solution aids the removal of any debris or soluble bio molecules that might interact with phenol during sorption.

Preparation of solution

The test solutions were prepared by diluting a stock solution of phenol to the desired concentrations. A stock solution was obtained by dissolving 1.0g of phenol (obtained from Merck India), in distilled water and diluted to 1000ml. Before mixing the adsorbents, the pH of each test solution was adjusted to the required value with dilute 0.1M H_2SO_4 and 0.1M NaOH solutions. Serial dilutions of the stock solution were made to obtain specific concentrations required for the adsorption study.

Determination of contact time

0.2g of the activated carbon of 106µm mesh particle size was weighed and introduced into various 100ml conical flasks. 50ml of 100mgL^{-1} concentration of phenol solutions prepared in distilled water from the stock solution was added to the biomass. The pH of these suspensions was adjusted to 6.0. The flasks were labelled for time interval of 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 minutes. The flasks were tightly covered with cellophane and shaken for the appropriate time intervals on an electric shaker. The suspension were filtered through Whatman No 40 filter paper and centrifuged for 5minutes. The supernatants obtained were analyzed by using a Unicam UV-visible spectrophotometer at a wavelength corresponding to the maximum absorbance for phenol solution (λ_{max} = 269nm). These experiments were performed in duplicates.

Effect of temperature

50ml of phenol solutions with an initial concentration of 100mg/l was placed in several 250ml conical flasks. 0.2g activated carbon was added to these solutions. The conical flasks were labelled at temperatures of 30, 40, 50, 60, 70, 80 and 90°C, respectively. The pH of the solutions was adjusted to 6.0 by adding either HCl or NaOH. The flasks were agitated and heated on a thermostatic water bath to the appropriate temperatures for 1h. The suspensions were filtered using Whatman No 40 filter paper and then centrifuged for 5minutes. The supernatants were analysed using UV-visible spectrophotometer.

Data analysis

The percent phenol removed by the fluted activated carbon was calculated from the difference between the initial (C_o) and equilibrium (C_e) adsorbate (Phenol) concentrations, which is given in equation 1.

$$\%R = \frac{C_o - C_e}{C_o} \times 100 \quad \text{..... (1)}$$

The mass transfer properties of the adsorption of phenol on the fluted activated carbon were evaluated using different kinetic models. Pseudo - first order Pseudo second order kinetic model, Elovich kinetic model, intra-particle diffusion and liquid - film diffusion.

Adsorption thermodynamics

Experimental data on the effects of temperature on adsorption were calculated according to equations 2 and 3

$$\Delta G^0 = RTLnK \quad \text{..... (2)}$$

$$lnK = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad \text{..... (3)}$$

Where K is the thermodynamic equilibrium constant which can be determined by the method proposed by Vinod and Anirudhan (2001). In this method, a plot of ln (q_e/c_e) is made and the lines extrapolated to zero which will be used to estimate the values of ΔG^o at a given temperature. Negative values of ΔG^o will show that the process of adsorption is spontaneous. Values of ΔH^o and ΔS^o are evaluated using, the slope and intercept of plots of lnK versus 1/T.

RESULTS AND DISCUSSIONS

Effect of contact time

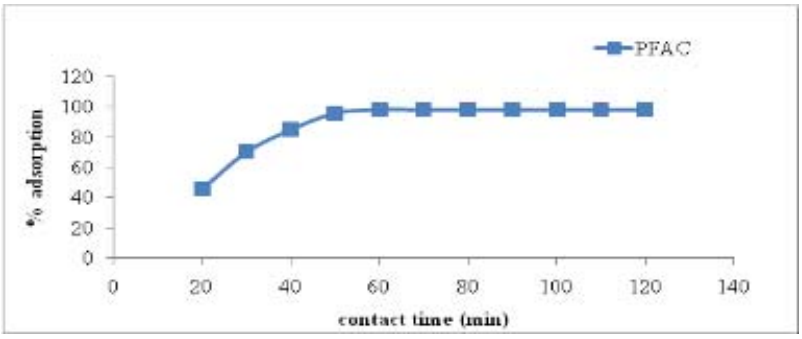

Figure-1. Effect of contact time on the percentage removal of phenol on FAC from aqueous solution. (Initial Concentration =100mg/l, pH = 6, Equilibrium Time =1hr).

As can be seen from Figure-1 that the adsorption of phenol exhibits saturation kinetics as the quantity of bound phenolic ions stagnates after approximately 60 minutes for the fluted activated carbon, this means that the possibility of further adsorption is very small. The higher sorption rate at the initial period may be due to an increased number of vacant sites on the adsorbent available at the initial stage (Vadivelan and Kumar, 2005; Tarawou *et al*., 2007). The decrease in the adsorption of phenol with time could be due to the accumulation of phenol particles in the vacant sites leading to a decrease in sorption percent at time 70 -120 minutes. The reduction in the percentage of phenol removed as a result of increased contact time was not significant, since more than 98% of phenol was removed even at contact time of 120minutes.

Sorption kinetic studies

The rate at which sorption takes place in a batch sorption process is very important in designing batch sorption systems. Consequently, it was important to establish the time dependence of such systems under various process conditions. In order to investigate the mechanism of the present biosorption process and the potential rate controlling steps, such as mass transport, pore diffusion and chemical reaction processes, kinetic models have been used to fit experimental data. The Lagergren first order, pseudo second order, intra-particle diffusion, Elovich and liquid film diffusion were used. The rate parameters of all studied models will be presented and discussed separately at the end of this kinetic modeling section.

Pseudo-first order

The linearized form of the Pseudo - first order equation is generally expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad \ldots\ldots\ldots (4)$$

Where

q_e is the amount of phenol adsorbed at equilibrium (mg/g)
q_t is the amount of phenol adsorbed at time t (mg/g)
K_1 is the first order rate constant (g/ (mg/min)

The straight line plot of log (q_e-q_t) against time (t) should give a linear relationship from which K_1 and q_e can be calculated from the slope and intercept respectively.

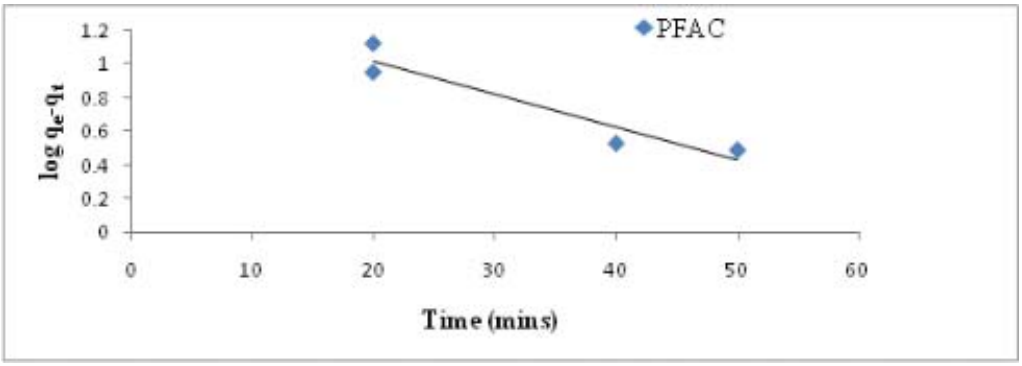

Figure-2. Effect of pseudo first order kinetic model of phenol onto FAC.

As observed in Figure-2, the pseudo-first order does not fit well over the entire sorption system despite the high sorption capacity values obtained at equilibrium Table-1. The line did not pass through the origin as expected so pseudo first order is not favoured.

Table-1. The sorption kinetic rate constants.

PFAC	pseudo first order			pseudo second order			Elovich		
	k_1	q_e	R^2	k_2	q_e	R^2	α	β	R^2
	2.90 x 10^{-2}	25.94	0.904	1.69 x 10^{-3}	30.30	0.987	2.78	0.118	0.977
	intra-particle diffusion			liquid -film- diffusion					
	K_{id}	intercept	R^2	k_{id}	intercept	R^2			
	2.146	5.291	0.793	0.038	-0.297	0.967			

Pseudo-second order

The linearized form of the pseudo second-order model as expressed by Ho and Mckay (1999) was used.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$h_o = k_2 q_e^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

K_2 **(**is the second order rate constant (g/mg/min$^{1/2}$)
h_o is the initial sorption rate (mg/g/min)
q_e is the equilibrium adsorption capacity (mg/g)

Where this model is applicable, a plot of t/q_t versus t should give a linear relationship from which q_e and k_2 calculated from the slope and intercept of the plot.

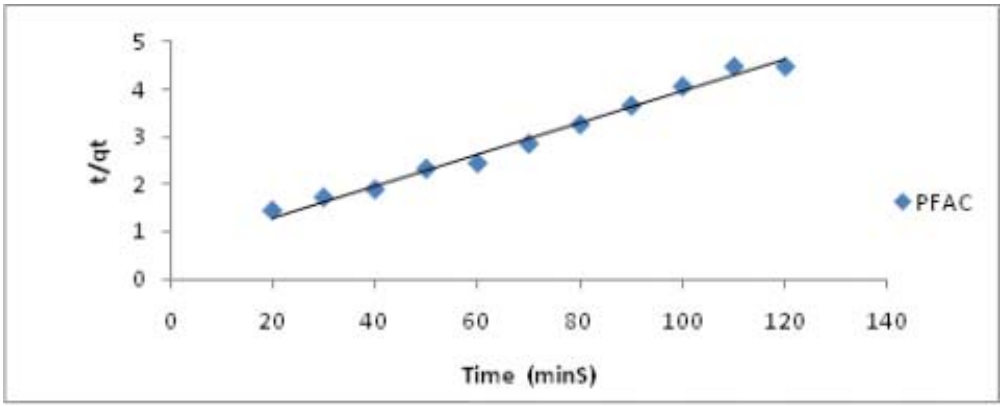

Figure-3. Effect of pseudo second- order kinetic model of phenol onto FAC.

The pseudo second order model showed the best fit to the experimental data related to the adsorption of phenol onto fluted activated carbon with the highest squared correlation coefficient (0.987). Thus this result suggest that the pseudo-second order based on the assumption that the rate limiting step might be chemical sorption involving valency forces through sharing or exchange of electrons through phenolate ions and adsorbent provides the best correlation of the dynamic data.

Elovich model

The Elovich equation is mainly applicable for chemisorptions kinetics. The equation is often valid for systems in which the adsorbing surface is heterogeneous. The Elovich model is generally expressed as:

$$\frac{dq_t}{d_t} = \alpha e^{-\beta q_t} \quad \text{.....(7)}$$

Integrating the equation for the boundary conditions gives

$$q_t - \frac{1}{\beta}\ln(\propto \beta) + \frac{1}{\beta} lnt \quad \text{.....(8)}$$

Where

α is the initial adsorption rate (mg/gmin)
β is related to the extent of surface coverage and the activation energy for chemisorption (g/mg)
Where the model is applicable, A plot of q_t versus ln t should give a linear relationship with a slope of (1/β) and an intercept of 1/β ln(αβ).

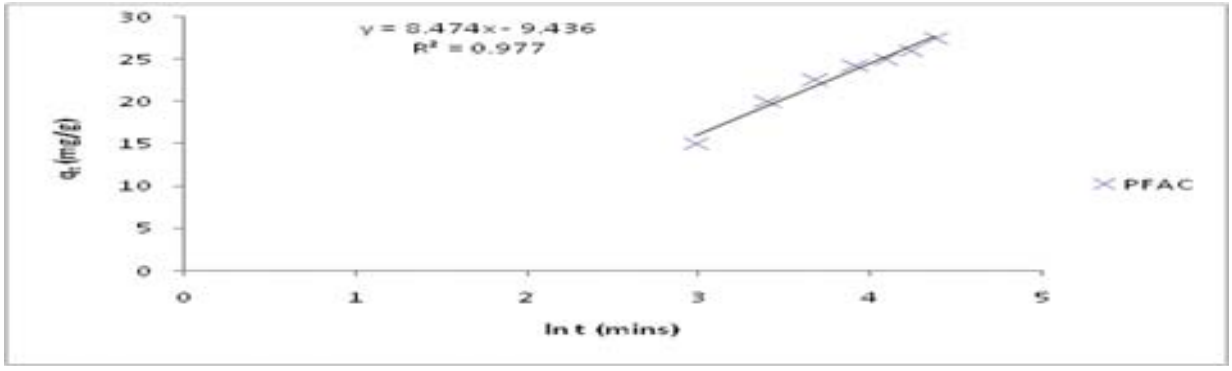

Figure-4. Effect of Elovich kinetic model of phenol onto FAC.

The Elovich model was also found to be adequate to satisfactorily explain the biosorption phenomenon with correlation coefficient value 0.977 for phenol which consolidates the chemisorption hypothesis (Ho, 2006).

Intra-particle diffusion

The possibility of intra-particle diffusion being the rate determining step was explored using the intra-particle diffusion model (Srivastava *et al*., 2006).

These involve the adsorbate transport to the surface of the adsorbent particles and the diffusion of the solute molecules into the interior of the pores, which is usually a slow process.
According to this theory

$$q_t = k_{id} t^{0.5} + C \quad \text{.....(9)}$$

Where

k_{id} is the intra particle diffusion rate constant (mg/g/min$^{1/2}$)
C (mg/g) is a constant that gives idea about the thickness of the boundary layer, i.e., the larger the value of C the greater is the boundary layer effect (Kannam and Sundaram, 2001).

If a plot of q_t versus $t^{1/2}$ gives a straight line, then the sorption process is controlled by intra-particle diffusion only and the slope gives the rate constant, k_{id}. However, if the data exhibit multi-linear plots then two or more steps influenced the sorption process.

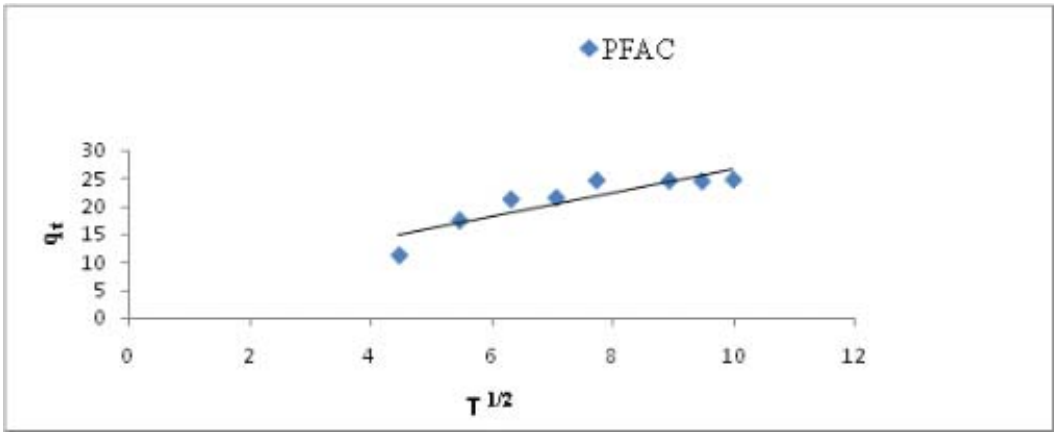

Figure-5. Effect of intra - particle diffusion kinetics of phenol onto FAC.

In Figure-5 it could be suggested that phenol diffusion onto fluted activated carbon was controlled partly by intra-particle diffusion as the graph showed a straight line though not passing through the origin. The low regression coefficient of (0.793) indicates the non-favourability of intra-particle diffusion model.

Liquid film diffusion

When the transport of the sorbate molecules from the liquid phase up to the solid phase boundary plays a major role in adsorption, then the liquid film diffusion model equation is used which is given as:

$$\ln(1 - F) = -k_{id} t \quad \text{.....(10)}$$

Where

F is the fractional attainment of equilibrium ($F = q_t/q_e$)
k_{id} is the adsorption rate constant.

A linear plot of -ln(1-F) versus t with zero intercept would suggest that the kinetics of the sorption process is controlled by diffusion through the liquid surrounding the solid sorbent.

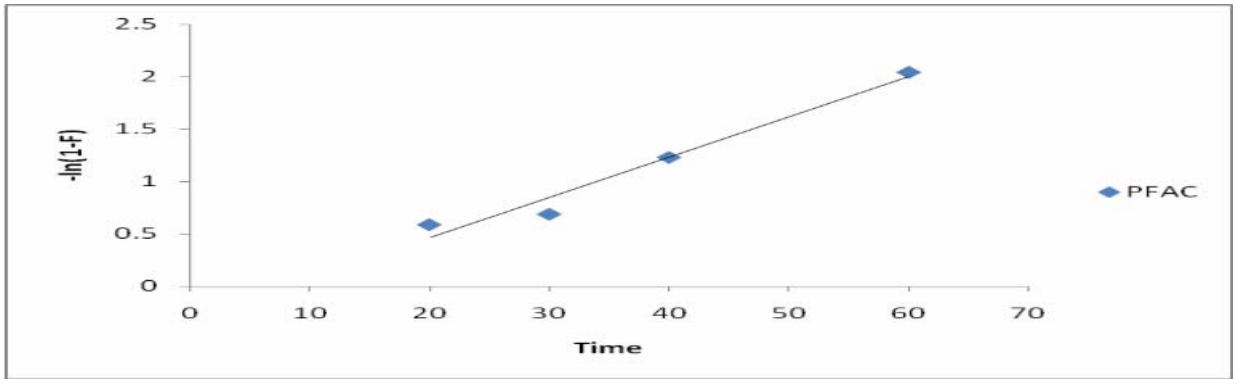

Figure-6. Effect of liquid film diffusion kinetics of phenol onto FAC.

Figure-6 revealed that the intercept value was close to the origin indicating the significance of liquid film diffusion in rate determination of the sorption process. Table-1 showed that the liquid film regression value of phenol onto fluted activated carbon was 0.967 thus showing the relevance of film diffusion as a rate determining factor in the sorption process.

Table-2. Thermodynamic parameters of phenol onto fluted activated carbon (FAC).

Temp (^oC)	**ΔH^o** (KJ/mol)	**ΔS^o** (KJ/mol)	**ΔG^o** (KJ/mol)
30	-12.05	-0.072	-3.784
40			-3.873
50			-3.998
60			-4.123
70			-4.246
80			-4.411
90			- 4.498

Table-2 showed the thermodynamic parameters of this work, the negative values of ΔH^o, revealed exothermic nature of the sorption process and the negative values of ΔS^o indicate strong bond formation between the adsorbent and adsorbate molecules. The negative values of ΔG^o confirms the feasibility of the process and the spontaneous nature of the adsorption with a high preference for phenol and suggest some structural changes in phenol and carbon interaction (McKay and Poots, 1980: Ho *et al*., 2005) Thus, confirming a chemical sorption, as was earlier suggested in pseudo-second order studies of this work.

CONCLUSIONS

Sorption of phenol was demonstrated using fluted activated carbon. The needed time to reach equilibrium state was one hour. Five kinetic models were considered the deduced parameters and constants had shown that the pseudo second - order model is the most appropriate theory to satisfactorily describe the studied sorption process followed by Elovich model. Such tendency would predict that the rate limiting step might be chemical adsorption (chemisorption) probably followed by an intraparticle diffusion phenomenon in later stages.

REFERENCES

Alzaydien S. A. and Manasreh W. 2009. Equilibrium, kinetic and Thermodynamic studies on the adsorption of phenol onto activated phosphate rock. International Journal of Physical Sciences. 4: 172-181.

Banat F.A. Al-Bashir B. Al-Asheh S and Hayajneh O. 2000. Adsorption of Phenol by bentonit. Environmental Pollution. 107: 391-98.

Banat F.S. Al-asheh and Al-Makhhammeh L. 2004. Utilization of raw and activated date pit for the removal of phenol from aqueous solutions, Chem. eng. Techno. l27: 80-86.

Dursun A. and Kalayei S. 2005. Equilibrium, kinetic and thermodynamic studies on adsorption of phenol onto chitin, J. of Hazardous Materials. B123. pp. 151-157.

Ekpete O.A. Horsfall M. Jnr. and Tarawou T. 2010. Potentials of fluted and commercial activated carbons for phenol removal in aqueous solution. ARPN Journal of Engineering and Applied Sciences. 5(9):39-47.

Entezari M. P. Petrier and Devidal P. 2005. Sonochemical degradation of phenol in water a comparison of classical equipment with a new cylindrical reactor ultra son. Sonochem. 10(2): 103-108.

Ho Y. S. and Mckay G. 1999. Comparative sorption kinetic studies of dye and aromatic compounds onto fly ash. J. Environ. Sci. Health. A34 (35): 1179-1204.

Ho Y.S. 2006. Review of second-order models for adsorption systems. J. Hazard mater. B136, pp. 681-689.

Ho Y.S. Chiang T.H and Hseuh Y.M. 2005. Removal of basic dyes from aqueous solution using tree fern as a biosorbent. Process Biochem. 40: 119-124.

Horsfall M. Jnr. and Spiff A. I. 2004. Adsorption of metal ions from mixed metal solutions by caladium bicolor (wild cocoyam) biomass. Journal of Corrosion Science and Technology. 2: 120 -126.

Horsfall M. Jnr. and Spiff A. I. 2005. Equilibrium sorption study of Al^{3+}, Co^{2+} and Ag^{+} in aqueous solutions by fluted pumpkin (*Telfairia occidentalis Hook* F.) waste biomass. Acta chim. Slov. 52: 174-181.

Kannam N. and Sundaram S. 2001. Kinetics and mechanism of removal of methylene blue by adsorption on various carbons comparative study. Dyes and Pigm. 51: 25-40.

Kujawski WA. Warzawsk T. Ratajczak T. Porebski .and Zostraws C. 2004. Sep purify.Technol. 40: 123-134.

Lagergren S. 1898. About the theory of so called adsorption of soluble substances. K. Sven. Vetenskapsakad. Hanl. 24(4): 1-39.

Mahvi A. Maleki A. and Eslami A. 2004. Potential of rice husk and rice husk ash for phenol removal in aqueous systems. American Journal of Applied Sciences. 1(4): 321-326.

Mckay G. Poots V.J.P. 1980. Kinetics and diffusion processes in colour removals from effluent using wood as an adsorbent. J. Chem. Tech. Biotechnol. 30(1): 279-292.

Nagda. G. Diwan M. and Ghole S. 2007. Potential of Tendu leaves refuse for phenol removal in aqueous systems. Applied Ecology and environmental research. 5(2): 1-9.

Prpich G. Daugulis A. 2005. Enhanced biodegradation of phenol by a microbial consortium in a solid. liquid two phase partitioning bioreactor. Biodegradation.16: 329 - 339.

Sofia A. Tzayhri G. Guillermo O. Madel S. and Brenda P. 2005. Adsorption of phenol and dichlorophenol from aqueous solutions by porous clay heterostructure (PCH). J. Mex. Chem. Soc. 49(3): 287-291.

Srivastava V.C. Swammy M. M. Mall I.D. Prasad B. and Mishra I.M. 2006. Adsorptive removal of Phenol by Bagasse flies ash and activated carbon: equilibrium, kinetics and thermodynamics: Colloids Surf. A Physicochem Eng. Aspects. 272: 89-104.

Tarawou T. Horsfall M. Jnr. and Jose V. L. 2007. Adsorption of methyl red by water hyacinth (eichornia crassipes). Biomass. Chemistry and Biodiversity. (4): 2236-2245.

Uddin M. Islam M. and Abedin M. 2007. Adsorption of phenol from aqueous solution by water hyacinth. ARPN Journal of Engineering and Applied Sciences. 2(2): 11-16.

U.S.E.P.A. 1987. Health and Environmental Effects profile for Phenol. EPA/600/x-87/121-Enviromental Criteria and Assessment and Development Cincinnati. OH.

Vadivelan V. A. 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. 286: 90-100.

Vinod V. P. and Anirudhan T.S. 2001. Sorption of Tanic acid on Ziroconium pillard clay. J. Chem. Technol. Biotechnol. 77: 92-101.

Zumriye A. and Yener J. 2001. A comparative adsorption / bio sorption study of mono-chlorinated phenols onto various sorbents. Waste Management. 21: 695-701.