

Batch Studies on Phenol Removal using Leaf Activated Carbon

Dr. Susmita Mishra^{1*}, Dr. Jayanta Bhattacharya²

¹ Department of Chemical Engineering, N.I.T., Rourkela-769008, India.

² Department of Mining Engineering, I.I.T., Kharagpur-721302, India.

* Corresponding Author; Email: smishra@nitrrkl.ac.in;

Phone: +91-661-2470278; Fax: +91-661-2472926

Abstract : Removal of phenol was tested by adsorption onto activated carbon prepared from *Shorea robusta* leaf litter by chemical treatment with $ZnCl_2$. It is observed that the contact time, phenol concentration, adsorbent dose and pH significantly affect the rate of phenol adsorption from solution. Adsorption equilibrium reached within 240 minutes for concentration range 100 - 500 mg/L. Kinetics of phenol adsorption followed the first order rate equation. Adsorption equilibrium data fit most satisfactorily with the Freundlich isotherm. The adsorption of phenol on leaf litter activated carbon follows the pore diffusion process.

Keywords: Activated carbon, isotherm, adsorption, diffusion, equilibrium.

Received : 22.03.05; accepted : 03.03.08

Introduction

Activated carbon (AC) due to their extended surface area, high adsorption capacity, micro porous structure and special reactivity are widely used as adsorbents for organic waste water treatment. Phenol, a toxic organic compound is a common contaminant in water effluent of industries like coke oven units, oil refineries, plastics, leather and paint industries and paper and pulp industries [1]. At present, the importance of phenol is proven by its ever increasing production that reached 6 million tons annually in 2004. It is the basic ingredient for many synthetic organic compounds and is highly toxic and found to affect aquatic life, causing ecological imbalance. Phenol can be absorbed by our body through the respiratory organ, skin, and the alimentary canal. It is highly toxic and has harmful influences on the albumen. It can also restrain the central neural system and interact with the liver and nephridium [2]. Hence stringent discharge limits of 0.002 mg/l drinking water have been imposed by Indian standards. Thus its removal for environmentally sustainable existence is essential.

Conventional treatment methods to remove phenol from water include solvent extraction, chemical oxidation, and ozonation and biological method. Some of these methods suffer from system complexities, skilled supervision, over dosing etc. Adsorption, using activated carbon is one of the best available technologies in removing phenol from wastewater. Commonly used raw materials (precursor) for the production of activated carbon include coal, coconut shell, and wood. The limited availability of these precursors and the high regeneration cost enabled the researchers to examine

the utility of low cost and easily availability precursors. Some of these precursors like oat hulls, waste tyre rubber; fly ash, coal dust, fertilizer waste and agricultural residues have been examined [3] [4]. Since each precursor develops different surface properties due to their varying physico-chemical properties, they show wide variation in adsorption capacity with pollutants and most of them are pollution specific.

To explore the effectiveness leaf litter, a low cost easily available natural waste has been used as precursor for preparation of activated carbon. Attempts have been made to produce activated carbon from *Shorea robusta* leaf litter by $ZnCl_2$ treatment. To assess the properties of the adsorbent extensive characterization should have been carried out using standard method. The adsorption studies were carried out as a function of contact time, initial phenol concentration, carbon dose and pH. The adsorption isotherms were plotted to correlate the adsorption equilibrium data.

Materials and Methods

1. Preparation of activated carbon:

Activated carbon from withered leaf litter (*Shorea robusta*) was prepared by the procedure reported elsewhere [5]. The fallen withered leaf litter (*Shorea robusta*) was collected initially and crushed to uniform size.

It was washed thoroughly with distilled water to remove the earthy and mineral matters adhering to it. It was heated at $105^{\circ}C$ in an oven till completely dry. It was impregnated with $ZnCl_2$, followed by drying before subjecting to carbonization, in an inert atmosphere at $400-425^{\circ}C$ for 1 hour. Removal of ash

and unused $ZnCl_2$ could be achieved with dilute acid and distilled water wash. The dried material was grounded (80- 200 mesh ASTM) and stored in an airtight container.

2. Characterization of activated carbon:

The activated carbon was characterized by following the standard procedure as shown in Table - 1. The moisture content of the carbon was determined by taking a known weight of the adsorbent and subjecting it to $105\pm 5^\circ C$ in an air oven for 4 hours. The residue was used to determine the ash content by igniting at $1000^\circ C$ for about 3 hours. The dried carbon was deionised with freshly boiled water. The clear solution obtained after filtration was used for pH determination using Systronics digital pH meter. Methyl blue test was conducted to determine the decolorizing power. The phenol number accounted for amount of carbon required for 90% reduction of phenol. BET apparatus was used to determine surface area of the adsorbent.

3. Batch Experiments:

The batch sorption experiments were undertaken where the adsorbent was magnetically stirred in 100 ml of phenol solution in a series of 250 ml Erlenmeyer flasks, mouth sealed tightly to prevent evaporation. The initial concentration of the corresponding phenol solution was 200 mg/L, the adsorbent/adsorbate ratio varied between 5 mg/L to 50 mg/L. The residual concentration of phenol was monitored periodically by removing the flasks at increasing time till equilibrium was achieved. The concentration of phenol was measured at 600 nm in UV/Vis spectrophotometer (Systronics, India Ltd.) using 4-aminoantipyrene method [6]. The readings were obtained in terms of optical density that was referred to the calibration chart to obtain the actual concentration. The agitation speed of 120 to 130 rpm

was maintained to keep the sorbent in suspension. To observe the effect of pH, each phenol solution was adjusted to different pH (2-12) using 0.1M NaOH and 0.1M HCl.

Results and Discussion:

The characteristics of activated carbon (LAC) obtained from withered leaf litter (Table 1) shows that that the bulk density and moisture content was less than Commercial activated carbon (CAC), which suggests that leaf litter being low strength material could not attain the pore structure with high strength as CAC after $ZnCl_2$ treatment. The ash content was moderate. The yield of activated carbon from the withered leaf was very less in comparison to CAC. The high decolorizing power indicates that it can be applied to organic adsorption. However its high phenol number suggests that higher dose of carbon would be required to attain maximum efficiency for reducing phenol as compared to CAC.

1. Effect of pH on phenol reduction:

The removal of phenol by activated carbon prepared from leaf litter increases in pH range 2-6. The reverse trend was observed beyond pH 6 (Figure 1). The uptake of phenol decreases at lower as well as higher pH [7,8]. At lower pH values the presence of H^+ ions suppresses the ionization of phenol and hence its uptake on adsorbent is reduced. At higher pH range, phenol forms salts that readily ionize leaving the negative charge on the phenolic group. At the same time the presence of OH^- ions on the adsorbent prevents the binding of phenoate ions that leads to low phenol adsorption [9]. The pH of initial phenol concentration was maintained for all the experiments at pH- 6 because of the above factor.

Table 1 : Characteristics of activated carbon [16]

| Properties | LAC | CAC |
|---------------------------|------|-------|
| Bulk Density (g/cm^3) | 0.57 | 0.72 |
| Moisture Content (%) | 4.38 | 13.04 |
| Ash Content (%) | 2.2 | 2.82 |
| Yield (%) | 20.1 | 68.4 |
| pH | 6.1 | 9.5 |
| Decolorizing Power | 74 | 70.6 |
| Phenol number | 30 | 5.3 |

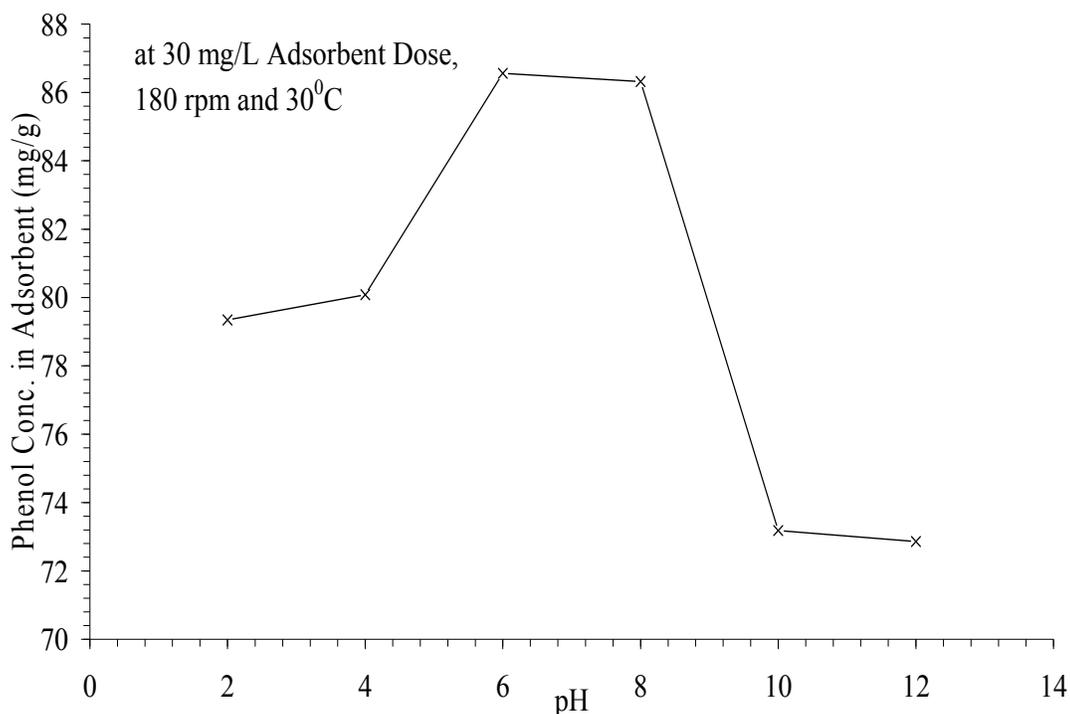


Figure 1 : Rate of phenol adsorbed at varying pH

2. Effect of carbon dose:

It is observed that with the increase in the dose of adsorbent the concentration of phenol in the remaining solution decreases (Figure- 2). The adsorption of phenol is site specific. It is due to the availability of more surface area with more functional groups at higher carbon dosage. Due to the hydrophobic (solvent-disliking) characteristics of the phenol molecules and higher affinity of the solute for the solid adsorbing surface, the molecules of phenol get adsorbed on the surface. However, with the increase in the amount of adsorbent, the sites for phenol adsorption increase. But the maximum removal (87 %) of phenol from the aqueous solution could be achieved at 30mg/L carbon dose. With further increase in carbon amount the concentration of phenol in the solution did not show any marked variation. It may also be due to shortage of phenol concentration at carbon dosage greater than 30 mg/L. The above observation conforms to adsorption of phenol using palm seed coat activated carbon [10].

3. Effect of initial phenol concentration

It is observed that with the increase in initial phenol concentrations the amount of phenol

adsorption increases. It is because as the initial concentration of phenol increases, the concentration gradient, which is the main driving force for the mass transfer increases. Thereby the rate of mass transfer increases leading to high adsorption rate [11]. But beyond 10 minutes there is little change in equilibrium concentration (Figures: 3). At higher concentration above 300 mg/L, the adsorption of phenol decreases that may be attributed to saturation of adsorption sites. More than 80 % phenol gets reduced in 30 minutes at concentration (100 mg/L – 500 mg/L). It indicates that the carbon obtained has highly active sites with well-developed micro pores, which is responsible for phenol adsorption.

The equilibrium studies were performed at optimized carbon dose, pH and fixed temperature of 30°C at an agitation of 120 rpm. It is observed that maximum reduction (80%) is achieved within first 30 minutes and achieved equilibrium within two hours (Figure-3). The curve leading to saturation indicates the possibility of monolayer coverage of phenol on the surface of the LAC.

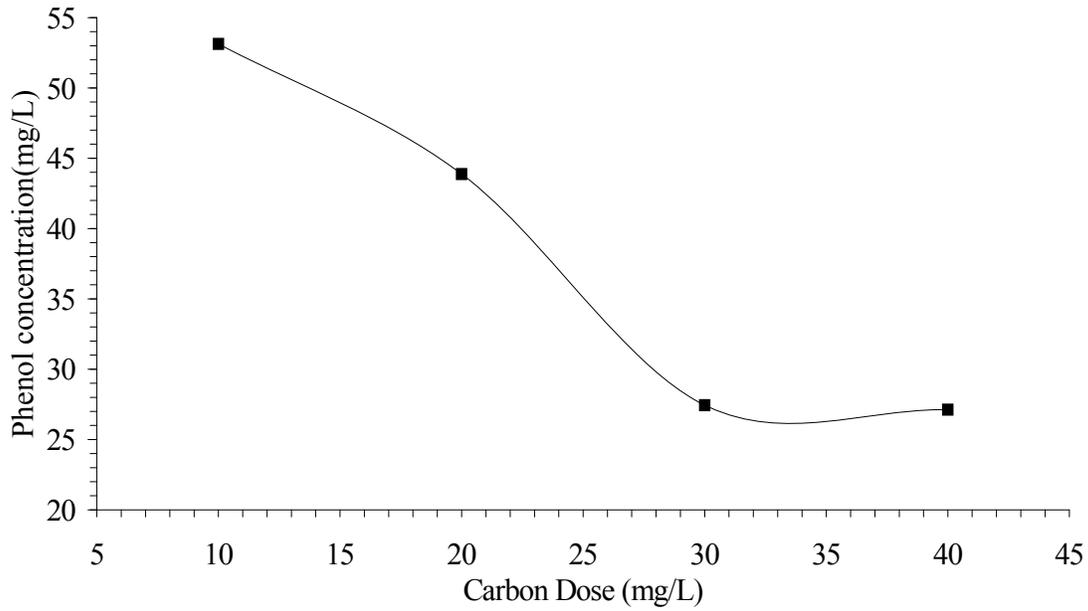


Figure 2 : Influence of carbon dose on phenol reduction at initial phenol concentration 100 mg/L and contact time 3 hours at 30 °C

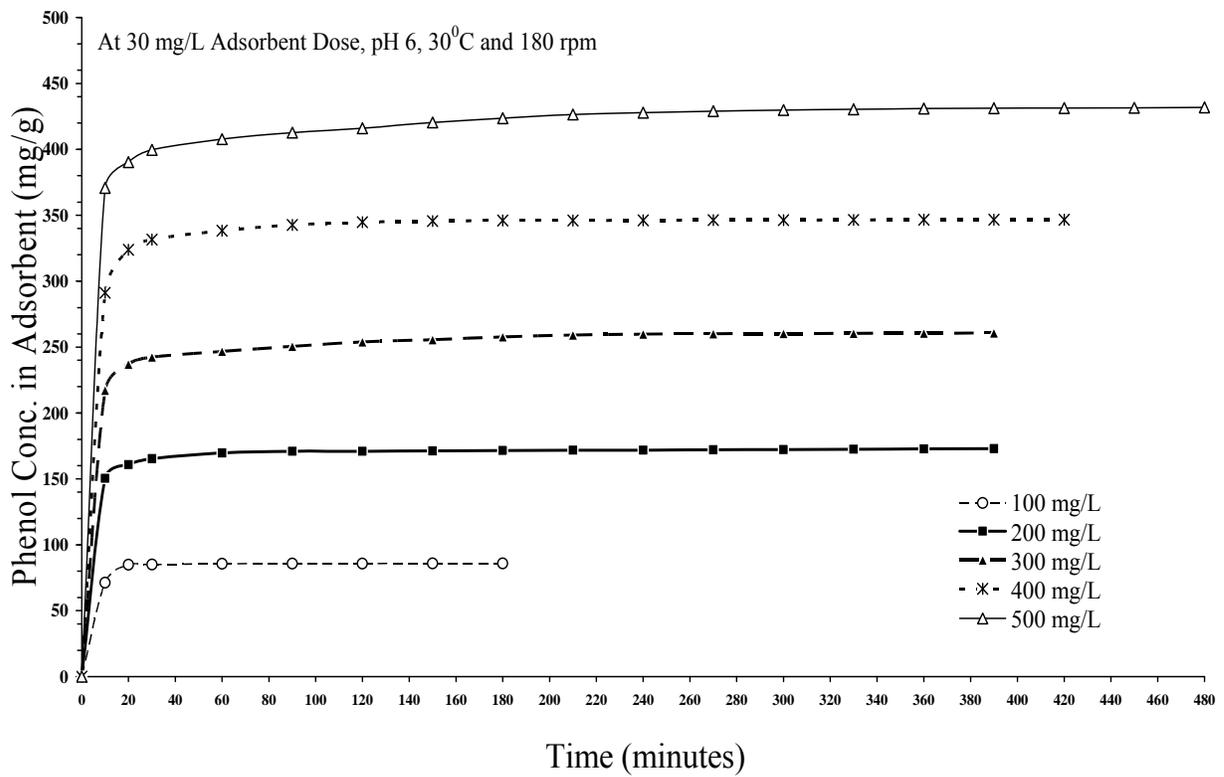


Figure 3 : Effect of initial phenol concentration on rate of phenol reduction

4. Adsorption Isotherms:

The isotherms are the theoretical models that are used to correlate the experimental equilibrium data. Freundlich isotherm model was used in this adsorption study. The equation is given by

$$q_e = K_f C_e^{1/n} \quad (\text{A})$$

The linearised form may be shown as

$$\text{Log} q_e = \text{Log} K_f + \frac{1}{n} \text{Log} C_e \quad (\text{B})$$

Where, C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed (mg/g) at equilibrium time, K_f and n are Freundlich constants. The result shows that the experimental studies, at optimum pH, temperature and adsorbent dose fit well in the Freundlich isotherm (Figure-4). This isotherm correlates the amount of phenol adsorbed per unit mass of the adsorbent (x/m) and the equilibrium concentration of phenol in the solution (C_e). The K and n are the adsorption capacities and intensity of adsorption respectively. The linear plot of x/m vs C_e shows the applicability of this isotherm. The K value of $0.216(\text{mg/g} (\text{L/mg})^n)$ and $n = 0.99$ shows that the reported results are well in agreement with values

reported by several others [12]. However the adsorption capacity is low.

5. Kinetic model:

A simple mass transfer model was developed to analyse the rate data obtained from the phenol reduction studies. The basic assumptions included;

1. The particles of adsorbents to be spherical and identical in physico- chemical properties
2. The bulk liquid phase concentration is uniform at any instant of time that is achieved by thorough mixing.
3. The total rate of adsorption equals to the rate of adsorbate disappearance from the solution. Consequently the concentration of solid phase rises with time
4. The adsorption process is also considered to be reversible

A simple first order reversible kinetic model has been developed with K_f as forward rate constant and K_b as backward rate constant for the rapid stage zone of phenol reduction. The reversible process is expressed as

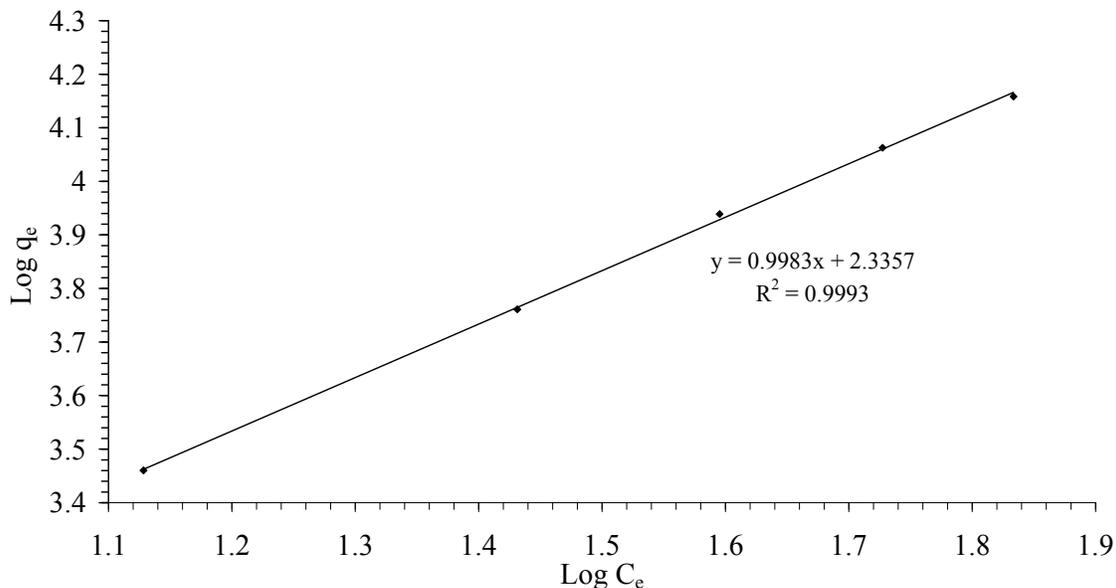


Figure 4 : Freundlich Isotherm at pH 6 and temperature 30°C

Where P is the product and R is the reactant. If the first order reversible kinetic is valid and X represents the amount of phenol conversion at any time, then equation (1) may be expressed as

$$\begin{aligned}\frac{dP}{dt} &= -\frac{dC_R}{dt} = \frac{dX}{dt} = K_f C_P - K_b C_R \\ &= K_f (C_{P_0} - X) - K_b (C_{R_0} + X)\end{aligned}\quad (2)$$

$$= (K_f + K_b) \left[\left(\frac{K_f C_{P_0} - K_b C_{R_0}}{K_f + K_b} \right) - X \right] \quad (3)$$

Where C_p = Phenol concentration in the liquid (mg/L);
 C_R = Phenol concentration in the adsorbent at any time (mg/g);
 C_{p_0} and C_{R_0} = Initial phenol concentration in adsorbent respectively (mg/g)

The equilibrium constant is defined as the ratio of forward to backward rate constant at equilibrium

$$K_e = \frac{K_f}{K_b} = \frac{C_{Re}}{C_{Pe}} \quad (4)$$

and

$$\frac{dC_P}{dt} = -\frac{dC_R}{dt} = \frac{dX}{dt} \quad (5)$$

From equations (2) and (5)

or,

$$0 = K_f (C_{P_0} - X_e) - K_b (C_{R_0} + X_e) \quad (6)$$

Where C_{Pe} and C_{Re} = Phenol Concentration at equilibrium in the liquid (mg/L) and
on adsorbent respectively (mg/g),

X_e = Amount of Phenol Adsorbed at equilibrium (mg/g)

From equations (3) and (6),

$$X_e = \frac{K_f C_{P_0} - K_b C_{R_0}}{K_f + K_b} \quad (7)$$

From equations (3) and (7),

$$-\frac{dX}{dt} = (K_f + K_b)(X_e - X) \quad (8)$$

Integrating the equation

$$\ln \left[\frac{X_e}{X_e - X} \right] = (K_f + K_b)t \ln[1 - U(t)] = -K't \quad (9)$$

or

$$\ln[1 - U(t)] = -K't \quad (10)$$

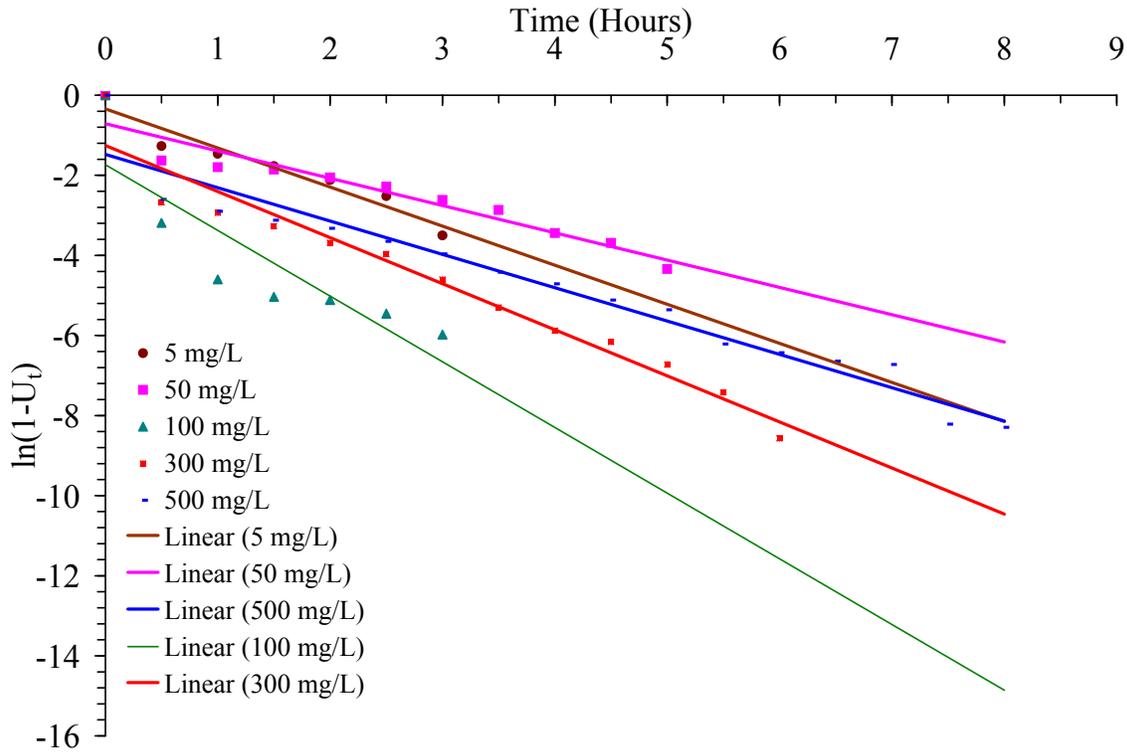


Figure 5 : Evaluation of Rate Constant

Where Equation (8) has been used to draw the relationship between $\ln[1-U(t)]$ and time (Figure 5) that gives the overall rate constant.

Activated carbon, a porous solid involves mass transport steps mainly film diffusion and pore diffusion. The rate-controlling step is the slower of the two steps [13]. By assuming a spherical geometry for the sorbent particles, the half time equations as follows are evaluated [14].

$$t_{1/2} = \frac{0.03r^2}{\bar{D}} \tag{9}$$

$$t_{1/2} = 0.23r\left(\frac{\sigma}{D}\right)\left(\frac{\bar{C}}{C}\right) \tag{10}$$

Where r = radius of the adsorbent (cm),

\bar{D} and D = Pore and Film Diffusion Coefficients respectively

σ = Film Thickness = 0.001 cm (Assumed)

$t_{1/2}$ = Time required to obtain half the Initial Concentration (hours)

C and \bar{C} = Concentration of phenol in the solution and at equilibrium respectively (mg/g)

Asher et al [15] suggested that rate limiting step can also be obtained from equation (11) as below and the values of K' , \bar{D} and D calculated from the equation are shown in Table-3.

$$t_{1/2} = -\ln\left(\frac{0.5}{K'}\right) \tag{11}$$

Where D is the film diffusion coefficient and \bar{D} is the pore diffusion coefficient.

If the value of D ranges between (10^{-6} to 10^{-8}) cm^2/s , then film diffusion is considered to be the rate limiting step and if \bar{D} ranges between (10^{-11} to 10^{-13}) cm^2/s then pore diffusion is said to be the rate limiting step. The illustrated data in Table-3 indicates pore diffusion to be the rate limiting step.

The increase in diffusion coefficient with the increase in initial phenol concentration also confirms the pore diffusion to be the rate controlling step (Table-3).

Table 2 : Rate limits for the phenol reduction by activated carbon

| Phenol concentration (mg/l) | Overall-rate constant K (h ⁻¹) |
|-----------------------------|--|
| 100 | 0.506 |
| 200 | 0.464 |
| 300 | 0.469 |
| 400 | 0.450 |
| 500 | 0.406 |

Table 3 : Evaluation of Pore Diffusion and Film Diffusion Coefficients

| Initial phenol concentration (mg/l) | \bar{D} | D |
|-------------------------------------|---------------------------|---------------------------|
| 200 | 0.00113*10 ⁻¹¹ | 0.00216*10 ⁻¹³ |
| 300 | 0.00119*10 ⁻¹¹ | 0.00227*10 ⁻¹³ |
| 400 | 0.00134*10 ⁻¹¹ | 0.00186*10 ⁻¹³ |

Conclusion

The adsorbent activated carbon prepared from withered leaf litter (*Shorea robusta*) is a waste material that has a potential to remove phenol from the solution. The adsorption conforms to the Freundlich isotherm. The rate of adsorption was affected by pH of solution, initial phenol concentration and adsorbent dosage. It has maximum adsorption capacity in the pH range 6-8. The carbon dose of 30 mg/L has a maximum potential to adsorb 87% phenol from its solution initially at 200 mg/l. The adsorption capacity is 0.216 mg/g(L/mg)ⁿ and intensity of adsorption is 0.99 in the particle size 50 - 70 mesh. A simple first order reversible kinetic model is developed. The reaction kinetics suggests pore diffusion as the rate limiting step.

Acknowledgements

The author gratefully acknowledges IIT Kharagpur, India for the research felicity and NIT, Rourkela, India for sanctioning the leave to pursue the research work.

References

- Haghseresht, F. and Lu, G.Q. (1998) "Adsorption Characteristics of phenolic compounds onto coal-reject derived adsorbents", *Energy and Fuels*, **12**, 1100-1107
- Huang, Jianhan., Huang, Kelong., Liu, Suqin, Luo, Qiong., and Shi, Shuyun. (2008) "Synthesis, characterization, and adsorption behavior of aniline modified polystyrene resin for phenol in hexane and aqueous solution", *Journal of Colloidal and Interface Science*, **317**, 434-441.
- Fan, M., Marshall, W., Daugard, D., Brown, R.C. (2004) "Steam activation chars produced from oat hulls and corn stover", *Bioresource Technology*, **93**, 103-107.
- Lu GQ, Low JCF, Liu CY, Lua AC. (1995) "Surface area development of sewage sludge during pyrolysis", *Fuel*, **29**, 344-348
- Mishra, S. and Bhattacharya, J.B. (2003) "Development of Porosity in Activated Carbon obtained from Shorea Robusta Leaf Litter under Chemical Activation with ZnCl₂", in *CHEMCON-2003, IE (India), RRL, Bhubaneswar*, **19-22**.
- Clesceri, L.S., Greenberg, A.E. and Trussel, R.R. (1989) "Standard methods for the determination of water and wastewater", *American Public Health Association, Washington, DC*, **2005**, 5.48-5.53
- Banat, F., Al-Asheh, S., Makhadmeh, L.A.I. (2004) "Utilization of Raw and activated date Pits for the removal of Phenol from aqueous solution", *Chemical engineering Technology*, **27**, 80-86.
- Goud, V.V., Mohanty, K., Rao, M.S., and Jayakumar, N.S. (2005) "Phenol from aqueous solution using tamarind Nut Shell activated

- carbon: batch and Column study”, *Chemical engineering Technology*, **28**, 814-821.
9. Singh, D.K. and Srivastava, B. (1999) “Removal of Basic Dyes from aqueous solution by chemically treated *Psidium* Guava Leaves”, *Indian Journal of Environmental Health*, **41** (4), 333-345
 10. Rengaraj, S., Seung-Hyeon Moon, Sivabalav, R., Arobindo, B., Murugesan, V. (2002), “Agricultural solid waste for the removal of organics: Adsorption of phenol from water and wastewater by palm seed coat activated carbon”, *Waste Management*, **22**, 543-548.
 11. Banat F.A., B. Al-Bashir, S. Al-Asheh, and O. Hayajneh (2000). “Adsorption of phenol by Bentonite”, *Environmental Pollution Control*, **107**, 391-398.
 12. Ioannidou, O. and Zabaniotou, A. (2007) “Agricultural residues as precursors for activated carbon production-A review”, *Renewable and Sustainable Energy Reviews*, **11**, 1966-2005.
 13. Benefield, Larry D., Judkins, Joseph F., and Weand, Barron L. (1982) "Process Chemistry for Water and Wastewater Treatment", *Prentice Hall, Englewood Cliffs, New Jersey*.
 14. Helfferich, F. (1962) “Ion Exchange”, *McGraw Hill, N.Y.*, **72-74**.
 15. Asher, B.T., Spark, D.L., Pesek, J.D. and Fergenbaum, S. (1990) “Analysis of Adsorption Kinetics using a stirred-flow chamber: I. Theory and Critical Tests”, *Soil Sci. Soc. Amer. J.*, **54**, 1273-1278.
 16. ISI (1989) Activated Carbon, powdered and granular –methods of sampling and Tests (Bureau of Indian Standards, New Delhi), IS **877**.
-