Sorption Equilibrium and Kinetic Studies of P-Chlorophenol from Aqueous Solution Using Granular Activated Carbon and Studies on Effect of Temperature on Adsorption

[1]*A.S. Ghatbandhe*, [2]*M.K.N. Yenkie*, [1]*H.G. Jahagirdar and* [1]*S.D. Deosarkar*

[1]Dept. of Chemistry, S.F.S. College, Nagpur, 440 006, India
[2]Dept. of Chemical Technology, Laxminarayan Institute of Technology,
R.T.M. Nagpur University, Nagpur, 440 010, India

Abstract: Adsorption equilibrium, kinetics and thermodynamics of p-chlorophenol (PCP) one of the chlorophenols (CPs) onto bituminous coal based Filtrasorb-400 grade granular activated carbon were studied in aqueous solution in a batch system with respect to temperature. Langmuir isotherm models were applied to experimental equilibrium data of PCP adsorption depending on temperature. Equilibrium data fitted very well to the Langmuir equilibrium models of PCP. Adsorbent monolayer capacity 'Q°' Langmuir constant b and adsorption rate constants k_a were evaluated at different temperatures. This data was then used to calculate the energy of activation of adsorption and thermodynamic parameters, namely the free energy of adsorption. $\Delta G°$, enthalpy of adsorption $\Delta H°$ and the entropy of adsorption $\Delta S°$. The obtained results show that the monolayer capacity increases with the increase in temperatures. The adsorption rate constants increased with increase in temperature. The obtained values of thermodynamic parameters shows that adsorption of PCP on activated carbon is an endothermic process.

Key words:

INTRODUCTION

One of the most alarming phenomena today is the growing accumulation of hardly biodegradable anthropogenic substances under the saturated auto-depurative conditions. The situation worsens by the lack of adequate water treatment systems capable of diminishing the concentration of toxic substances that represent a chronic chemical risk. It can be said that badly treated wastewaters lead inevitably to a deterioration of water sources quality and consequently, of drinking water. More recently, reflecting a new environmental conscience, the European Directive 2000/60/CE [1] stresses the need to adopt measures against water pollution in order to achieve a progressive reduction of pollutants. On this way, chlorophenols (CPs) constitute a particular group of priority toxic pollutants listed by the US EPA in the Clean Water Act [2,3] and by the European Decision 2455/2001/EC [4], because most of them are toxic and hardly biodegradable and are difficult to remove from the environment. CPs might produce disagreeable taste and odor to drinking water at concentrations below $0.1 g\ l^{-1}$ [5] and adverse effects on the environment [6]. The presence of CPs has been detected in both surface and groundwaters [7]. Toxic reference value $13.0 \mu g l^{-1}$ suggested for p-chlorophenol (PCP) in surface waters and maximum average values should not exceed $0.055\ mg\ l^{-1}$ [8,9]. The limiting permissible concentration of CPs in drinking water should not exceed $10\ \mu g l^{-1}$ [10].

Adsorption is an important technique in separation and purification processes which is used in water and wastewater industry to the removal of color, odor and organic pollution [11,12]. Among many types of adsorbent materials, activated carbons which can be produced from almost any carbonaceous material, are the most widely used, because of their large adsorptive capacity and low cost [12,13]. Adsorption on activated carbon is widely employed to great advantage whenever it comes to the removal of toxic and refractory organic chemicals at tertiary levels. Sorption is not always a single process. Often a combination of interactions is responsible for the association between a particular chemical (sorbate) and solid (sorbent) [14-21]. Activated carbon, when contacted with water containing organic material, remove the compounds selectively by a

Corresponding Author: A.S. Ghatbandhe, Dept of Chemistry S.F.S. College, Nagpur, 440 006, India

combination of adsorption of the less polar molecules, filtration of the larger particles and the partial desorption of colloidal material on the exterior surface of the activated carbon. The availability of variety of GAC samples and the possibility of recovery of adsorbate has further boosted its application as an efficient and economically feasible technology for wastewater treatment [22, 23].

In the present investigation, equilibrium and kinetics studies of adsorption of p-chlorophenol (PCP) from aqueous solution on granular activated carbon has been carried out at five different temperatures to evaluate the effect of this process on the adsorption equilibrium capacity and adsorbate removal rate. The adsorption equilibrium data for the adsorbate-adsorbent systems studied were expressed by Langmuir isotherm model and a simplified rate expression based on Langmuir adsorption theory was used to evaluate the adsorption rate constant 'k$_a$'. This data was then used to calculate the energy of activation of adsorption Ea and the thermodynamic parameters, namely the free energy of adsorption 'ΔG°', enthalpy of adsorption 'ΔH°' and the entropy of adsorption 'ΔS°'.

Pretreatment of Adsorbent: In the present investigation commercially available granular activated carbon (GAC) namely Filtrasorb-400 (F-400) was used as adsorbent. Granular activated carbon was first sieved to get 12x16 mesh (B. S. standard) granules and was washed several times with distilled water until the leachate was free from any suspended impurities. The sample was dried in an oven at 100-110°C for 24 Hrs and stored in a desicator. Adsorbent sample was also subjected to the proximate and ultimate analysis, N$_2$-BET surface area, phenol-BET surface area measurement and scanning electron microscopy (SEM) which shows a layered, loosely packed structure with lot of cavities, cracks, irregular protrusions and widely dispersed pores (Plate 1 a,b,c,d). The properties of GAC are reported in Table 1.]

Experimental: The experimental arrangement for carrying out both the equilibrium as well as the kinetics runs varied considerably.

Adsorption Equilibrium Studies: A 500 ml round bottom flask containing 250 ml of distilled water was immersed in the thermostat bath. The content were constantly stirred at 800±50 RPM and allowed to attain the temperature of the bath. The impeller used for stirring was fabricated out of 6.0 mm glass rod of length 5.0 cm having teflon paddle of width 1.5 cm fitted to its lower end. After the

Table 1: Properties of adsorbent GAC Filtrasorb-400

N$_2$-BET Surface area	998m^2/g	Moisture	5.3 wt%
Particle density	0.795g/cm^3	Ash	5.4wt%
Pore volume	0.825g/cm^3	Volatile matter	1.7wt%
Porosity	0.65	Fixed carbon	87.6wt%
Phenol-BET Surface area	480m^2/g	Mineral matter	5.94wt%
Particle density	0.795g/cm^3	Ash	5.4wt%
Pore volume	0.825g/cm^3	Volatile matter	1.7wt%
Porosity	0.65	Fixed carbon	87.6wt%
Phenol-BET Surface area	480m^2/g	Mineral matter	5.94wt%

temperature was reached, a calculated quantity of the stock solution was introduced into the distilled water with the help of graduated pipette. The solution was allowed to mix thoroughly and the same quantity of the resulting solution was pipetted out to maintain the final volume 250 ml, which was then used for determination of initial concentration. 0.25±0.001 g of the adsorbent sample (GAC) was then introduced into the solution with the stirring speed at 800±50 RPM. The time of addition of GAC was noted. Stirring was continued till the concentration of the aqueous phase showed no detectable change in UV absorbance. The equilibrium was attained in about 4 hours. As a precautionary measure, experiments were continued for five hours.

Adsorption Kinetics: For adsorption kinetics studies a 5-liter Borosil glass beaker fitted with six baffles was used. The adsorbate-adsorbent system was stirred by a two bladed impeller having length 7.0 cm and width 1.6 cm. Three liters of experimental solution was prepared by adding appropriate amount of stock solution into boiled and cooled distilled water. 3.00±0.000 1g of given GAC sample was introduced into the solution at a given instant of time. 5 ml of experimental solution was withdrawn at desired interval of time with the help of syringe and concentration of adsorbate in the aqueous phase was estimated by UV analysis.

Analytical Method: The adsorbate concentration was determined by spectrophotometric method using UV-Visible spectrophotometer model GBC UV-VIS 911A from GBC Scientific Equipment Pvt. Ltd., Australia. The absorbance measurements were carried using 1.0 cm path length cuvette. Adsorbate PCP used had very strong absorption band in the range 270 - 300 nm to and had high molar extinction coefficient value ($\in$). This naturally served as a very simple, reliable and rapid method for analyzing the adsorbate concentration in water. To begin with substrate of known concentration was scanned in

the UV region (190-380 nm) to determine its wavelength of maximum absorbance (λ_{max}) Regression analysis of the experimental data of the concentration versus absorbance gave the values of molar extinction coefficients (ϵ).

RESULT AND DISCUSSION

The equilibrium isotherms obtained for all the adsorbate-adsorbent systems in the studied concentration range and at various temperatures had type I favorable isotherm characteristics, which is desirable for scavenging solute from its aqueous solution. These isotherms obeyed the Langmuir equation with very high regression coefficient above 0.98 indicating a very good linear fit in all the cases. The Langmuir expression is given as,

$$\frac{C_e}{Q_e} = \frac{1}{Q^0{}_b} + \frac{C_e}{Q^0} \qquad (1)$$

Langmuir isotherm plot for the adsorbate-adsorbent systems at different temperatures are depicted in Fig. 1.

Adsorbate Removal Rate Studies: A simplified interpretation of the kinetic data based on Langmuir theory has been used for interpreting the kinetic data. Adsorbate removal rate is expressed as a function of directly measurable fluid phase adsorbate concentration. Langmuir theory assumes that the rate of adsorption is proportional to the product of adsorbate concentration in fluid phase and the fraction of the vacant adsorbent surfaces. The fraction of the surface covered by the adsorbate, Q, will be proportional to the decrease in fluid phase adsorbate concentration, thus

$$\frac{dq}{dt} = k_a C_t (1-Q) - k_d Q \qquad (2)$$

$$Q = f(C_0 - C_t) \qquad (3)$$

Where, k_a and k_d are adsorption and desorption rate constants. C_o, C_t and C_e are the fluid phase adsorbate concentrations at zero, time t and at equilibrium respectively and f is proportionality constant. Substituting Eqn. (3) in Eqn. (2) and solving the resultant equation by applying the concept of steady state gives the final expression

$$\ln[(C_t - C_e)/(C_t + a)] = -k_a C_e t + \ln[(C_o - C_e)/(C_o + a)] \qquad (4)$$

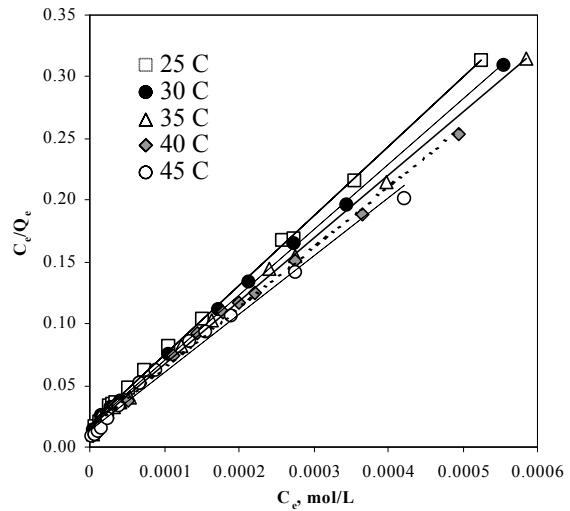Where, $a = (C_o / bC_e)$ and $b = k_a / k_d$

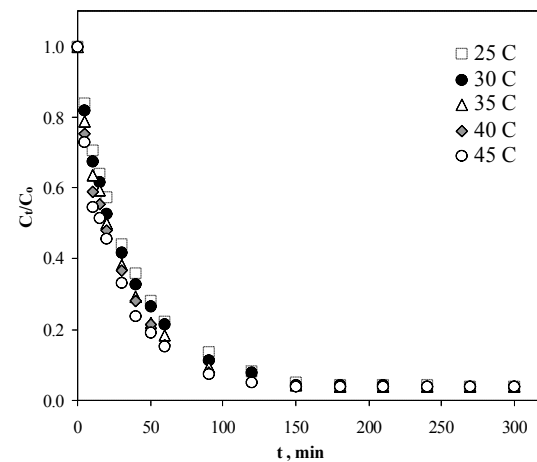Fig. 1: Langmuir adsorption isotherms of [PCP-F-400] system at different temperatures

Fig. 2: Adsorption kinetics of [PCP F-400] system at different temperatures
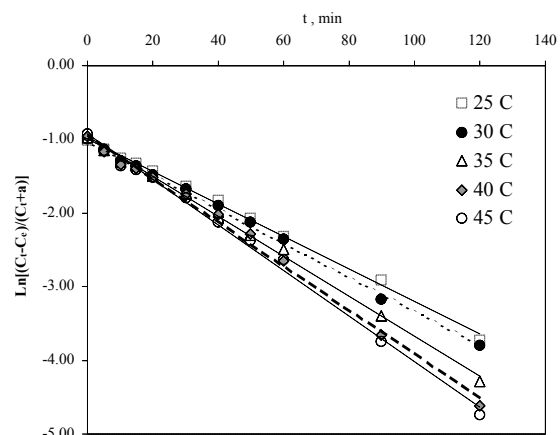

Fig. 3: Adsorbate removal rate of [PCP F-400] system at different temperatures

The adsorption rate constant 'ka' thus evaluated by plotting ln [(Ct-Ce) / (Ct+a)] against t. Fig. 2 and 3 depicts these plots for the adsorbate-adsorbent systems for all the studied temperatures in the present work. The plots also show the rate expressions obtained by linear regression analysis of the kinetic data. The experimentally determined values of adsorbent monolayer capacity 'Q°'and Langmuir constant 'b' at all the five temperatures are summarized in Table 2.

Effect of Temperature on Adsorption Capacity and Adsorption Rate: The results obtained in the present investigation are very informative. The equilibrium uptake of PCP by GAC is affected by temperature and increases with the rise in temperature. The adsorption rate was found to increase with the rise in temperature. PCP adsorption is exothermic thus the extent of adsorption is increased with the increasing temperature. This could also be due to the enhanced mobility of PCP ions from the bulk solution towards the adsorbent surface and extent of penetration within GAC structure overcoming the activation energy barrier and enhancing the rate of intraparticle diffusion [14,15,16]. Adsorption rate removal plots are given in (Fig. 2 and 3).

Thermodynamic Parameters: From the variation of b (thermodynamic distribution coefficient or Langmuir constant) with temperature, thermodynamic parameters $\Delta G°$, $\Delta H°$and $\Delta S°$ namely the standard free energy change, standard free enthalpy change and standard free entropy change respectively were calculated using following equations;

$$\Delta G^0 = -RT \ln b \qquad (6)$$

and Vant' Hoff equation,

$$\ln b = (\Delta G^0 / R) - (\Delta H^0 / RT) \qquad (7)$$

The Vant' Hoff plot of ln b against 1/T was plotted (Fig. 4) which shows an excellent linearity. $\Delta H°$and $\Delta S°$ are obtained from slope and intercept of the plot. The values of $\Delta G°$ for all the studied temperatures are given in Table 3. The negative values of free energy are the indicative of spontaneous process with a high affinity of the adsorbate to the surface of adsorbent. The positive value of enthalpy change points the endothermic nature of adsorption process.

Table 2: Effect of temperature on adsorption capacity and Langmuir constant

T°C	T K	b	Q° x 10⁴ mol/g
25	298	31488.27	17.74
30	303	31806.59	18.83
35	308	32998.71	19.55
40	313	34434.27	20.31
45	318	35300.00	21.30

Table 3: Thermodynamic parameters for the adsorption of PCP on GAC F-400

T, K	$\Delta G°$ kJ mol⁻¹	$\Delta H°$kJ mol⁻¹	$\Delta S°$ Jmol⁻¹
298	-25.66	4.84	102.27
303	-26.12		
308	-26.64		
313	-27.19		
318	-27.69		

Table 4: Effect of temperature on adsorption rate constants

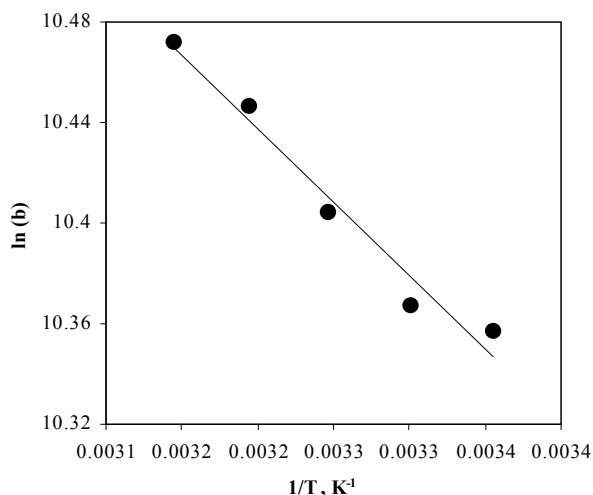| T K	K_a kJ min⁻¹	E_a kJ mol⁻¹	% Increase in K_a
298	1153.85	15.27	-
303	1207.25		4.63
308	1404.15		21.69
313	1573.68		36.39
318	1640.21		42.15

Fig. 4: Vant Hoff plot for [PCP F-400] system atdifferent temperatures

Energy of Activation of Adsorption: The activation energy of adsorption was determined using Arrhenius equation

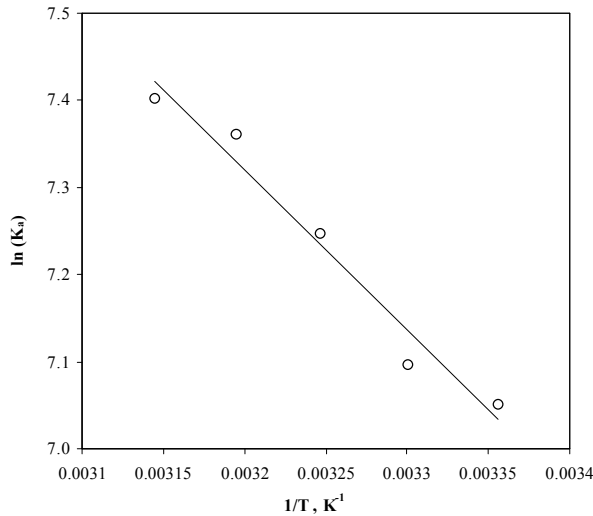$$\ln k_a = -(E_a / RT) + \ln(a) \qquad (8)$$

Fig. 5: Plot of energy of activation of adsorption [PCP F-400] system

The plot of ln k_a versus 1/T was plotted (Fig. 5) and the linear regression analysis gave a linear regression coefficient above 0.9651. The values adsorption rate constants K_a and the energy of activation of adsorption E_a obtained for the PCP – GAC system are given in Table 4.

CONCLUSIONS

The present work has led to some important conclusions as stated below:

- PCP adsorption using GAC is very rapid in the first hour of contact where 70-80 % of the adsorbate is removed by GAC followed by a slow approach to equilibrium.
- The adsorption of p-chlorophenol from aqueous solution on to granular activated carbon confirms to a Langmuir equation based on a monomolecular layer.
- The Langmuir constant (b), related to energy of adsorption increased with temperature for all the adsorbate studied probably due to enhanced solute-sorbent interactions of dipolar nature. Also increase in the value of 'ln b' indicate that the rate of adsorption is much higher than the rate of desorption.
- Adsorption is endothermic as enthalpy change (?H°) values are positive. Since ΔH° is relatively small in magnitude; the forces of uptake are weak.
- The positive values of ΔS° indicate increase in disorder of PCP adsorption on GAC.

- For adsorbate-adsorbent system studied, free energy change ΔG° values were negative indicating the spontaneity of the process and high affinity of the adsorbate to the surface of adsorbent.
- Energy of activation of adsorption indicates the physical nature of the process.
- The relative affinity of the chlorophenolic compound toward the surface of the activated carbon was related to the electron donor-acceptor complexes formed between the basic sites on the carbon surface (basic surface oxygen complexes and/or electron-rich regions at the basal planes) and the aromatic ring of the chlorophenol.

We believe that application of adsorption by the GAC in purification of wastewater for the removal of PCP from industrial wastewaters can be suitable for the fabrication and designing of wastewater treatment plants by using these kinetic parameters.

Nomenclature

b = Langmuir constant
C = Concentration of the adsorbate in liquid phase (mol/L)
C_o = Initial concentration of the adsorbate (mol/L)
C_e = Equilibrium concentration of the adsorbate (mol/L)
E_a = Energy of activation (kJ/mol)
ΔG° = Standard free energy of adsorption (kJ/mol)
ΔH° = Standard enthalpy of adsorption (kJ/mol)
ΔS° = Standard entropy change of adsorption (JK^{-1} mol^{-1})
k_a = Adsorption rate constant (min^{-1})
Q° = Adsorbent monolayer capacity (mol/g)
Q_e = Adsorbent phase concentration at equilibrium (mol/g)
R = Universal gas constant (JK^{-1} mol^{-1})
T = Temperature of the system (K)

REFERENCES

1. EC Directive, 2000/60/EC of the European Parliament and of the Council of October 23, 2000 establishing a framework for community action in the field of water policy (L 327 of 22-12-2000).
2. EPA, July 2002. http://www.scorecard.org.
3. Hayward, K., 1998. Drinking water contaminant hit-list for US EPA, Water 21, September October, 4.

4. EC Decision, 2455/2001/EC of the European Parliament and of the Council of November 20, 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC (L 331 of 15-12-2001).

5. Veschueren, H.K., 1983. Handbook of Environmental Data on Organic Chemicals, VNR, New York.

6. Folke, J. and J. Birklund, 1986. Danish coastal levels of 2,3,4,6- tetrachlorophenol, pentachlorophenol and total organohalogens in blue mussels (Mytrulus edulis), Chemosphere, 15: 895-900.

7. Howard, P.H., 1989. Handbook of Environmental Fate and Exposure Data for Organic Chemical, vol. I, Large Production and Priority Pollutants, Lewis Publishers, Chelsea, MI, USA.

8. EPA, 1992. National Recommended Water Quality Criteria, Federal Register, 57-60848.

9. Jones, A.P. and R.J. Watts, 1997. Dry phase dioxide-mediated photocatalysis: basis for in situ surface destruction of hazardous chemicals, J. Environ. Eng., 123(10): 974-981.

10. Shul'pin, G.B., M.M. Bochkova, G.V. Nizova and N.B. Kozlova, 1997. Aerobic photodegradation of phenols in aqueous solutions promoted by metal compounds, Appl. Catal., B 12: 1-19.

11. Abbasi, W.A. and M. Streat, 1994. Sep. Sci. Technol., 29: 1217.

12. Kirk-Othmer, 1997. Encyclopedia of Chemical Technology, Vol. 24, fourth ed., Wiley-Interscience, USA.

13. Zhonghua, H., M.P. Srinisavan and N. Yaming, 2001. Carbon, 39: 877.

14. Fabra, A., R. Duffard, A. Evangelista de Duffard, 1997. Bull. Environ. Contam. Toxicol., 59: 645.

15. Celis, R., M.C. Hermosin, L. Cox and J. Cornejo, 1999. Environ. Sci. Technol., 33: 1200.

16. Bekbölet, M., O. Yenigün and I. Yücel, 1999. Water Air Soil Pollut., 111: 75.

17. Mahramanlioglu, M., I. Kizilcikli, I.O. Biçer and M. Tunçay, 2000. J. Environ. Sci. Health, B 35: 187.

18. Susarla, S., G.V. Bhaskar and S.M. Bhamidimarri, 1993. Environ. Technol., 14: 159.

19. Sotelo, J.L., G. Ovejero, A. Delgado and I. Martinez, 2001. Water Res., 36: 599

20. Belmouden, M., A. Assabbane and Y.A. Ichou, 2001. Ann. Chim. Sci. Materiaux, 26: 79.

21. Benoit, P., E. Barriuso and R. Calvet, 1998. Chemosphere, pp: 37.

22. Borowko M. and M. Jaroniek, 1983. Adv. Colloid Interface Sci., 19: 137.

23. Chatzopoulos, D., A. Varma and R.L. Irvine, 1993. AIChE J, pp: 39(12).