COMPARATIVE AQUEOUS PHASE 2, 6-DICHLOROPHENOL (2, 6-DCP) SORPTION USING POLYMERIC ADSORBENTS

A S Ghatbandhe [1], M K N Yenkie [2]

[1]Departent of Chemistry S F S College R T M Nagpur University, Nagpur

[2]Department of Chemical Technology, Laxminarayan Institute of Technology, R T M Nagpur University, Nagpur, India

corresponding author E- mail : ajay_gbandhe@rediffmail.com

ABSTRACT

This paper provides application of non-conventional adsorbents for removal chlorophenol from wastewater. Adsorption equilibrium and kinetics of 2, 6-Dichlorophenol (2, 6-DCP) one of the chlorophenols (CPs) onto three different types of polymeric adsorbents (XAD-4 , XAD-1180 and XAD7HP) were studied in aqueous solution in a batch system. Langmuir isotherm models were applied to experimental equilibrium data of 2, 6-DCP adsorption. Equilibrium data fitted very well to the Langmuir equilibrium models of 2, 6-DCP. Adsorption is very rapid in the first hour of contact where 50 - 60 % of the adsorbate is removed in the first 40 minutes which is then followed by a slow approach to equilibrium. The order of adsorption of 2, 6-DCP on different adsorbents used in the study is found to be in following order;

XAD-4   > XAD-1180   > XAD7HP

Keywords: Adsorption equilibrium, kinetics, XAD-1180, XAD-4, XAD-7HP.

INTRODUCTION

Chlorophenols (CPs) might produce disagreeable taste and odor to drinking water at concentrations below 0.1g l^{-1} [1] and adverse effects on the environment [2]. The limiting permissible concentration of CPs in drinking water should not exceed 10 µg l^{-1} [3]. Among various physicochemical processes, adsorption is widely used for the removal of pollutants from wastewater [4, 5]. 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) [6-13]. In comparison with classical adsorbents such as silica gel, alumina and activated carbon macroporous polymeric adsorbents are also more attractive alternatives because of their wide range of pore

structures and physico- chemical characteristics [14, 15]. Because of its high stability and excellent selectivity towards aromatic solutes, Amberlite XAD-4 polymeric resin, a macroporous styrene-divinylbenzene copolymer is found to be the best polymeric adsorbent for removing phenolic compounds from aqueous streams [16].

In the present study three grades of synthetic polymeric adsorbents nam11e11ly Amberlite XAD4, XAD7HP and XAD1180 were used. The properties of polym1eric adsorbents and adsorbate 2, 6-DCP are given in table-1 and table-2 respectively

Table 1: Physico-chemical properties of adsorbent XAD Resin

Adsorbent	Moisture N2-BET	Specific gravity	Porosity	Surface area m^2/g
XAD 4	54 – 60 %	750	1.01 – 1.03	0.50
XAD 7HP	61 – 69 %	380	1.06 – 1.08	0.50
XAD 1180	61 – 67 %	500	1.015 – 1.025	0.60

Table 2: Properties of Adsorbate 2 , 6-DCP

Mol. Wt	163.1
Water solubility (mol/dm^3)	0.0201
Λ_{max}, (nm)	276
ϵ $(cm^{-1}mol^{-1})$	1672.8

Experimental

Adsorption equilibrium studies

A 500 ml round bottom flask containing 250 ml of adsorbate solution was immersed in the thermostat bath. The content were constantly stirred at 800 ± 50 RPM and allowed to attain the temperature of the bath. 0.25 ± 0.001 g of the adsorbent sample was then introduced

into the solution. The equilibrium was attained in about 3 hours, as a precautionary measure experiments were continued for four hours.

Adsorption Kinetics

For adsorption kinetics studies a 5-liter Borosil glass beaker fitted with six baffles was used. Three liters of experimental solution was prepared. 3.00 ± 0.0001 g of given adsorbent sample was introduced into the solution at a given instant of time. 5 ml of experimental solution was withdrawn at desired interval of time and concentration of adsorbate in the aqueous phase was estimated by UV analysis.

Result and Discussion

Adsorption Equilibrium

The equilibrium isotherms obtained for all the adsorbate-adsorbent systems in the studied concentration range and at various adsorbents had type I favorable isotherm characteristics, which is desirable for scavenging solute from its aqueous solution. The adsorption equilibrium isotherms for 2,6-DCP with respect to all the adsorbents used in the present study is as given in Fig.-1.
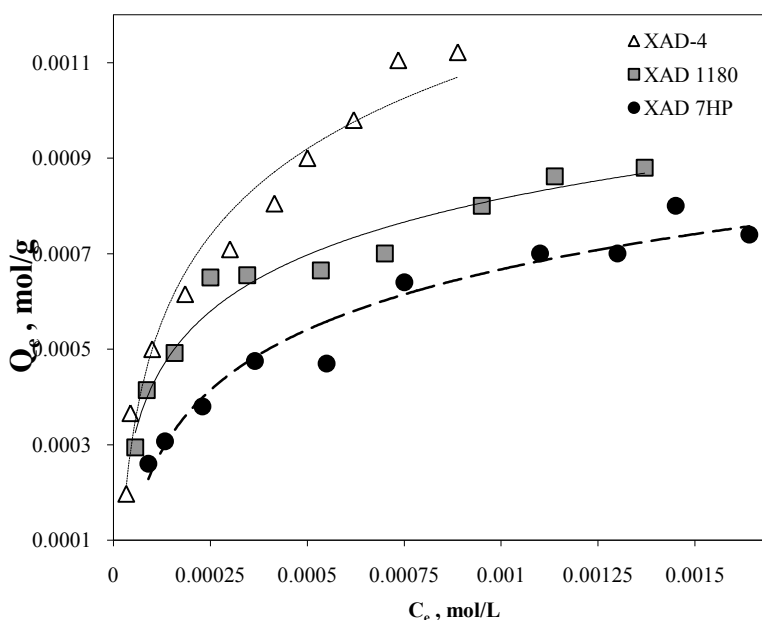

Fig 1 : Comparative 2,6-DCP Adsorption Isotherms

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,

$$\frac{Ce}{Qe} = \frac{1}{Q^0 b} + \frac{Ce}{Q^0} \qquad \text{-------- 1}$$

Langmuir isotherm plot for the adsorbate-adsorbent systems using different adsorbents is as given in Fig.-2
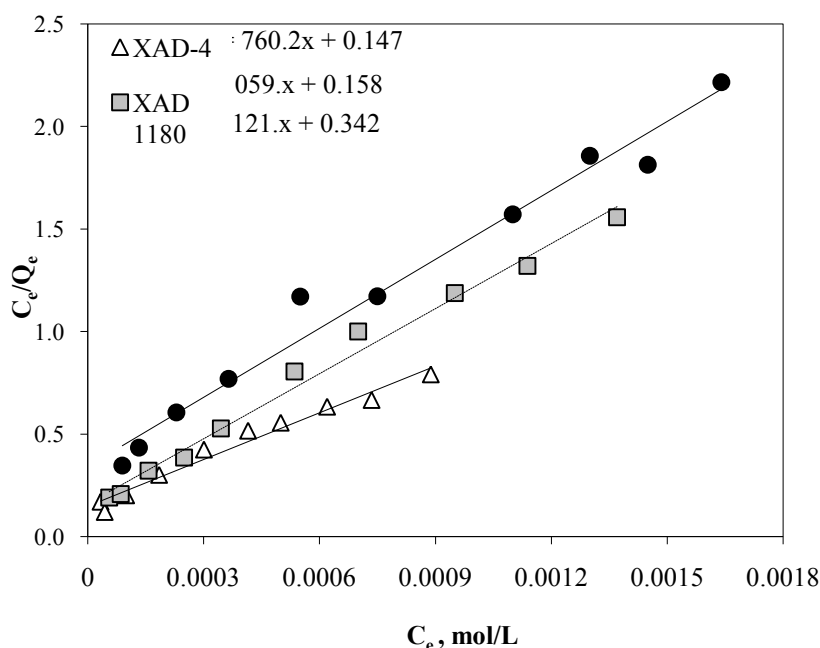

Fig 2: Comparative 2,6-DCP Langmuir adsorption isotherms

Adsorbate removal rate studies

The plots of removal rate of 2,6-DCP using different adsorbents with respect to time are depicted in Fig-3. 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

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

$$\text{and,} \qquad Q = (Co - Ct) \qquad -------3$$

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

$$\ln\left[\frac{(C_t - C_e)}{(C_t + ı)}\right] = ka\ C_t + n\left[\frac{(C_o - C_e)}{(C_o + ı)}\right] \qquad -------\ 4$$

$$\text{where,} \qquad a = \frac{C_o}{b\,C_e}) \qquad \text{and} \qquad b = \frac{ık_a}{k_d}$$

The adsorption rate constant 'ka' thus evaluated by plotting ln [(Ct-Ce) / (Ct+a)] against t, Fig. 4. The plot also show the rate expressions obtained by linear regression analysis of the kinetic data.

From the above study it is clear that depending upon the nature of adsorbent, the adsorbing capacity of every adsorbent varies. The % adsorption of 2,6-DCP for different adsorbents used in present study is mentioned in the form of plot in Fig-5
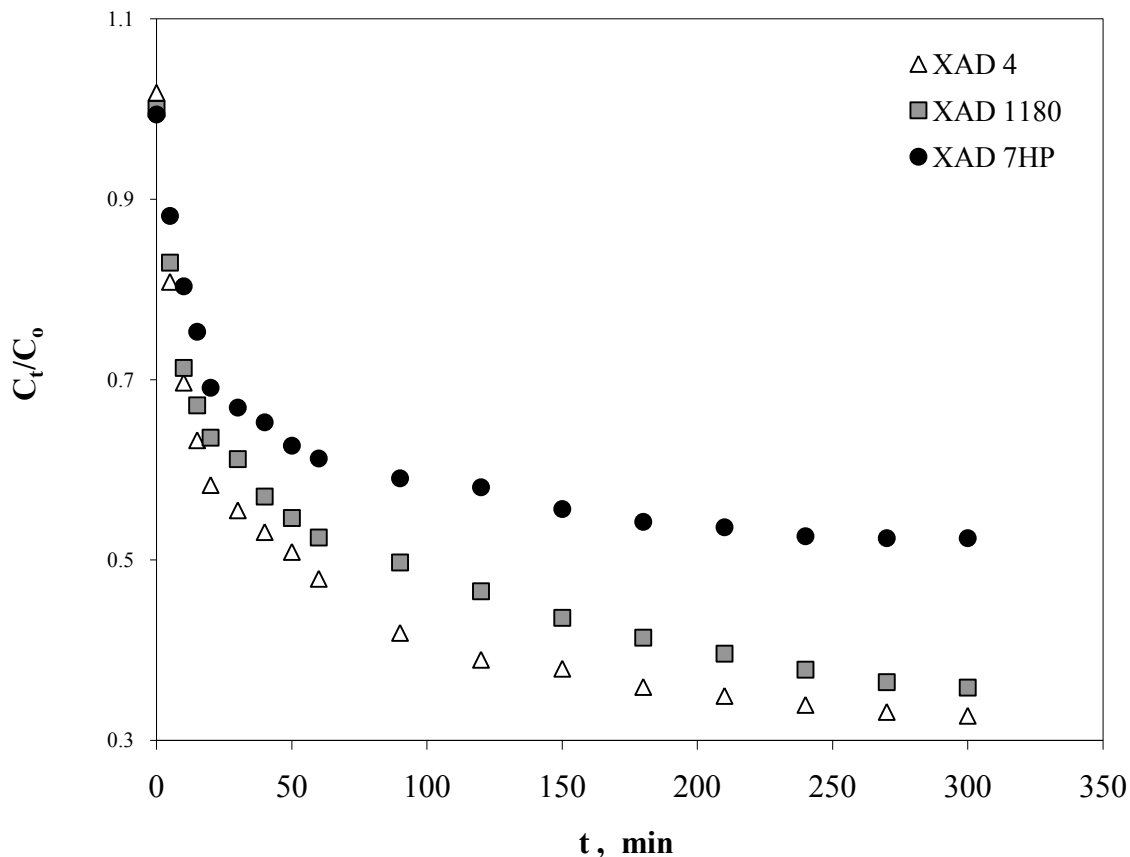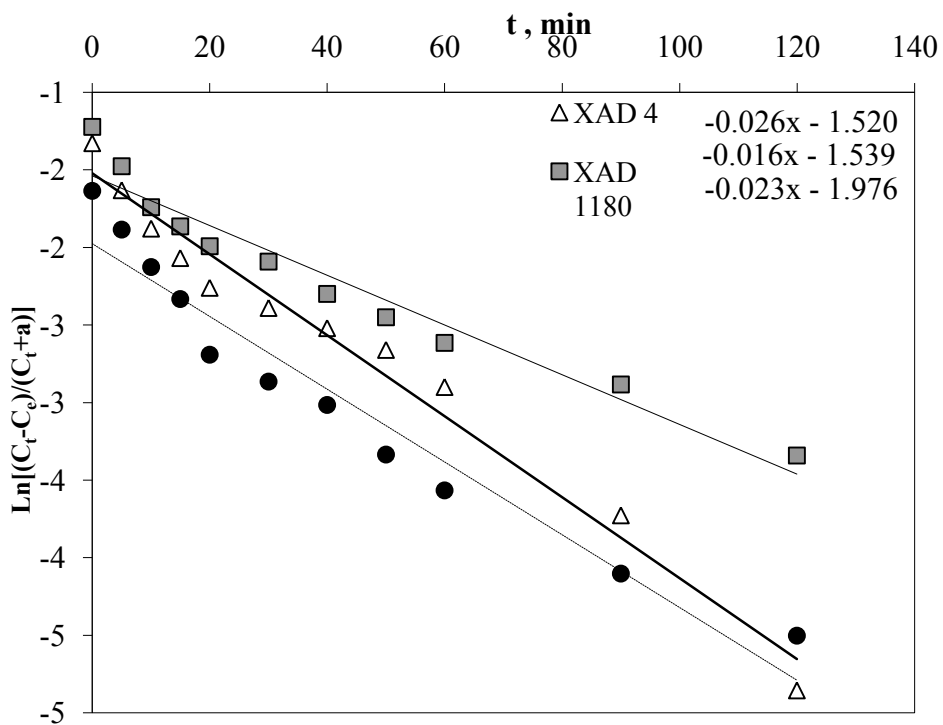
Fig 3: Comparative 2,6-DCP Adsorpton Kinetics

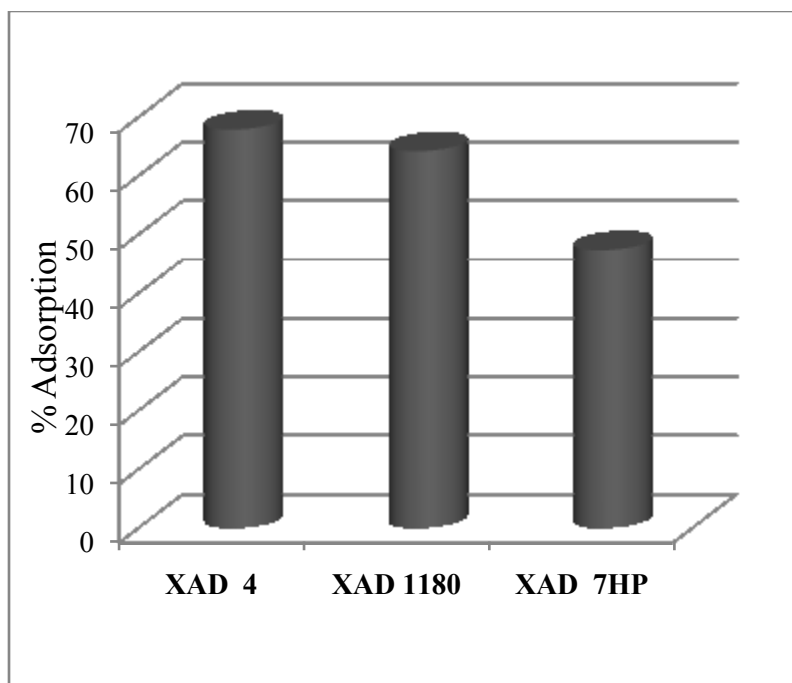**Fig 4 : Comparative Adsorbate Removal Rate**

Fig 5: % Adsorption of 2, 6-DCP onto different adsorbents

Conclusions

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

1. In case of polymeric adsorbents 50-60 % of the adsorbate is removed in the first 40 min of contact time which is then followed by a slow approach towards equilibrium.

2. The adsorption of 2, 6-DCP from aqueous solution on to polymeric adsorbents confirms to a Langmuir equation based on a monomolecular layer adsorption.

3. The order of adsorptive capacity of 2,6-DCP on different adsorbents used in the study is found to be in following order:

   XAD-4 > XAD-1180 > XAD7HP

NOMENCLATURE

R   = universal gas constant (JK^{-1} mol^{-1})

T   = temperature of the system (K)

 b   = Langmuir constant

k_a = adsorption rate constant (min^{-1})

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)

Q^o = adsorbent monolayer capacity (mol/g)

Q_e = adsorbent phase concentration at equilibrium   (mol/g)

REFERENCES

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

J. Folke, 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.

G.B. Shul'pin, 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.

 A. A. M. Daifullah and B. S. Girgis, (1998). *Water Res.,* 32, 1169.

5. P. K. Asthana and S. Bhatia, *Ind. J. Environ. Protection.*, 14 (1994) 490.

A. Fabra, R. Duffard, A. and Evangelista de Duffard, (1997). Bull. Environ. Contam. Toxicol. 59, 645.

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

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

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

S. Susarla, G.V. Bhaskar, and S.M. Bhamidimarri, (1993). Environ. Technol. 14, 159.

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

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

P. Benoit, E. Barriuso, and R. Calvet, (1998). Chemosphere 37.

Z.Y. Xu, Q.X. Zhang, C.L. Wu, and L.S. Wang, (1997). Adsorption of naphthalene derivative on different macroporous polymeric adsorbents, Chemosphere 35 (10) 2269-2276.

Z.Y. Xu, Q.X. Zhang, C.L. Wu, L.S. Wang, and G.K. Anderson, (1999). Adsorption of naphthalene derivative on hypercrosslinked polymeric adsorbents, Chemosphere 38 (9) 2003-2011.

B.L. He, and W.Q. Huang, (1992). Ion exchange and adsorption resin, 1st Edition. The science and education press of Shanghai, Shanghai, China, 439-466.