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Research Article

Adsorption Equilibrium and Kinetics of 4-Chlorophenol: A Comparative Study

A.S.Ghatbandhe*, H. G.Jahagirdar¹ and M.K.N.Yenkie²

¹Department of Chemistry, S F S College, R.T.M Nagpur University, India

²Department of Chemical Technology, Laxminarayan Institute of Technology

R.T.M Nagpur, University, India

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ABSTRACT

Adsorption equilibrium, kinetics of 4-chlorophenol (4-CP) one of the chlorophenols (CPs) onto bituminous coal based Filtrasorb-400 grade granular activated carbon and polymeric adsorbents were studied in aqueous solution in a batch system. Langmuir isotherm models were applied to experimental equilibrium data of 4-CP adsorption. Equilibrium data fitted very well to the Langmuir equilibrium models of 4-CP. Adsorbent monolayer capacity 'Q_o' Langmuir constant b and adsorption rate constants k_a were evaluated. Adsorption using GAC is very rapid in the first hour of contact where 60 - 70 % of the adsorbate is removed by GAC followed by a slow approach to equilibrium, whereas in case of polymeric adsorbents 50-60 % of the adsorbate is removed in the first 30 min which is then followed by a slow approach to equilibrium. Comparative adsorption capacity of different adsorbents used is observed to be in following order F 400 > XAD-4 > XAD-1180 > XAD-7HP

Keywords: Batch adsorption, Equilibrium, Kinetics, 4-CP, GAC, XAD-7HP, XAD-1180, XAD-4..

INTRODUCTION

Human health has been badly affected in recent years due to increasing pollution caused by growing industries. Water pollution in this respect contributes to a greater extent. The levels of pollutants allowed in discharge waters, are directly related with the type of pollutant present in the effluent. As a result elimination of organic pollutants in aqueous solution needs one or various basic treatment techniques¹. Chlorophenols (CPs) constitute a particular group of priority toxic pollutants listed by the US EPA in the Clean Water Act² 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 concentrations³ below 0.1g l⁻¹ and adverse effects on the environment⁴. The limiting

permissible concentration of CPs in drinking water should not exceed⁵ $10 \mu\text{g l}^{-1}$. 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^{6, 7}. 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. There are many reported instances⁸⁻¹⁸ of phenol adsorption on activated carbon, in fibrous and granular form, where the carbon was subjected to various pretreatments before use. A comparative study on the performance of certain resins and activated carbon found that Filtrasorb 400 GAC is more effective in removing organics as compared to XE-340 or IRA 904^{19, 20}. Webb compared the ability of XAD grade of resins to adsorb microgram amounts of five polar organics (acids, phthlates, alcohols, and phenols), and reported the effectiveness of adsorbents in the order XAD-4 > XAD-2 > XAD-7 > XAD-8²¹.

In the present investigation, equilibrium and kinetics studies of adsorption of 4-chlorophenol (4-CP) from aqueous solution on granular activated carbon and three grades of polymeric adsorbents has been carried out. Commercially available granular activated carbon (GAC) namely Filtrasorb-400 (F-400) and three grades of synthetic polymeric adsorbents namely Amberlite XAD-4, XAD-7HP and XAD-1180 were used. Amberlite XAD-4 is a white insoluble polymeric adsorbent. It is a non-ionic cross-linked polymer, which derives its adsorptive properties from its patented macroreticular structure large surface area. Amberlite XAD-7HP and Amberlite XAD-1180 are also white insoluble polymeric adsorbent having micorecticular structure and large adsorptive surface area. The properties of GAC and polymeric adsorbents are reported in **Table-1 & 2** respectively.

Table-1: Physico-chemical properties of adsorbent Filtrasorb-400

Properties	F-400
N ₂ -BET Surface area	998 m ² /g
Particle density	0.795 g/cm ³
Pore volume	0.825 g/ cm ³
Porosity	0.65
Phenol-BET Surface area	480 m ² /g
Moisture	1.9 wt %
Ash	6.1 wt %
Volatile matter	2.7 wt %
Fixed carbon	89.3 wt %
Mineral matter	6.71 wt %

Table -2: Physico-chemical properties of XAD Resin

Adsorbent	Moisture	N ₂ -BET Surface area m ² /g	Specific gravity	Porosity
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

Pretreatment of adsorbent: In the present investigation commercially available granular activated carbon (GAC) namely Filtrasorb-400 (F-400) and three grades of polymeric adsorbents (XAD resins) were used as adsorbents. Adsorbent samples subjected to the proximate and ultimate analysis, N2-BET

surface area and scanning electron microscopy (SEM). The properties of GAC and XAD resins are reported in **Table-1 & Table-2** respectively.

EXPERIMENTAL

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. 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. As the temperature is reached, 0.25 + 0.001 g of the adsorbent sample was then introduced into the solution with the stirring speed at 800 + 50 RPM. 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 baffles was used. Three liters of experimental solution was prepared by adding appropriate amount of stock solution into boiled and cooled distilled water. 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 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 using UV-Visible spectrophotometer. Adsorbate 4-CP has very strong absorption band in the range 270 - 300 nm to and had high molar extinction coefficient value (ϵ). 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}).

RESULT AND DISCUSSION

The equilibrium isotherms obtained for 4-CP adsorption onto different adsorbents obeyed the Langmuir equation with very high regression coefficient above 0.98 indicating a very good linear fit in all the cases. The adsorption equilibrium isotherms for 4-CP with respect to all the adsorbents used in the present study are depicted in **Fig.-1**. The Langmuir expression is given as,

$$\frac{C_e}{Q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad \text{----- 1}$$

Langmuir isotherm plots for 4-CP adsorption onto different adsorbents are depicted in **Fig.-2**

Absorbate removal rate studies: A simplified interpretation of the kinetic data based on Langmuir theory has been used for interpreting the kinetic data. The plots of removal rate of 2,4 D 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

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

$$\text{and,} \quad Q = f (C_o - C_t) \quad \text{-----3}$$

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

$$\ln \left[\frac{(C_t - C_e)}{(C_t + a)} \right] = -k_a C_t + \ln \left[\frac{(C_o - C_e)}{(C_o + a)} \right] \quad \text{-----} \quad 4$$

where, $a = \left(\frac{C_o}{b C_e} \right)$ and $b = \frac{k_a}{k_d}$

The adsorption rate constant 'ka' thus evaluated by plotting $\ln [(C_t - C_e) / (C_t + a)]$ against t. **Figs. 4** 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 'Qo' and Langmuir constant 'b' at all the five temperatures are summarized in **Table-4**.

Depending upon nature of adsorbents adsorption capacity of different adsorbents varies. Plot of % adsorption onto different adsorbents used is depicted in **Fig. 5**.

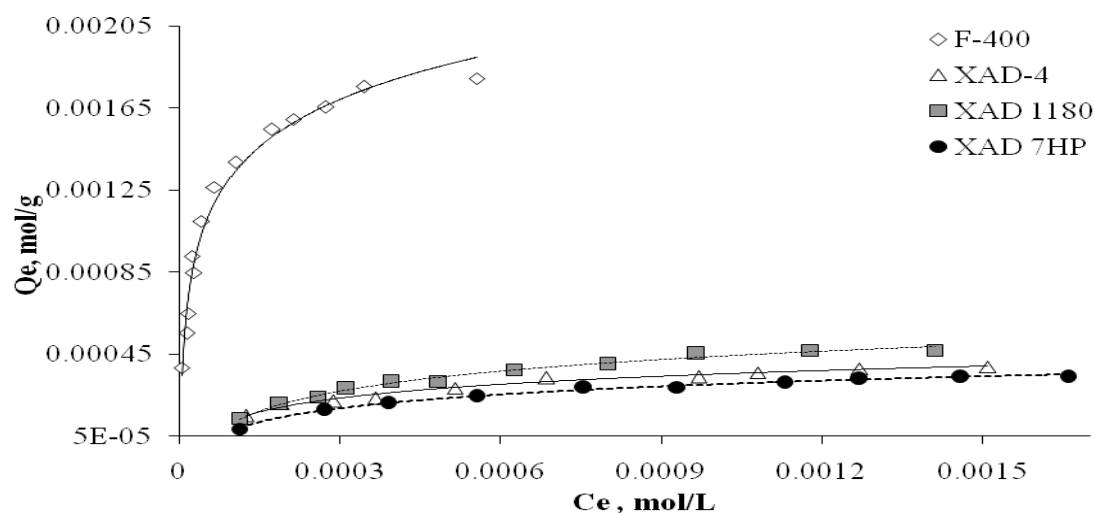


Fig 1 : Comparative Adsorption isotherms of 4-CP

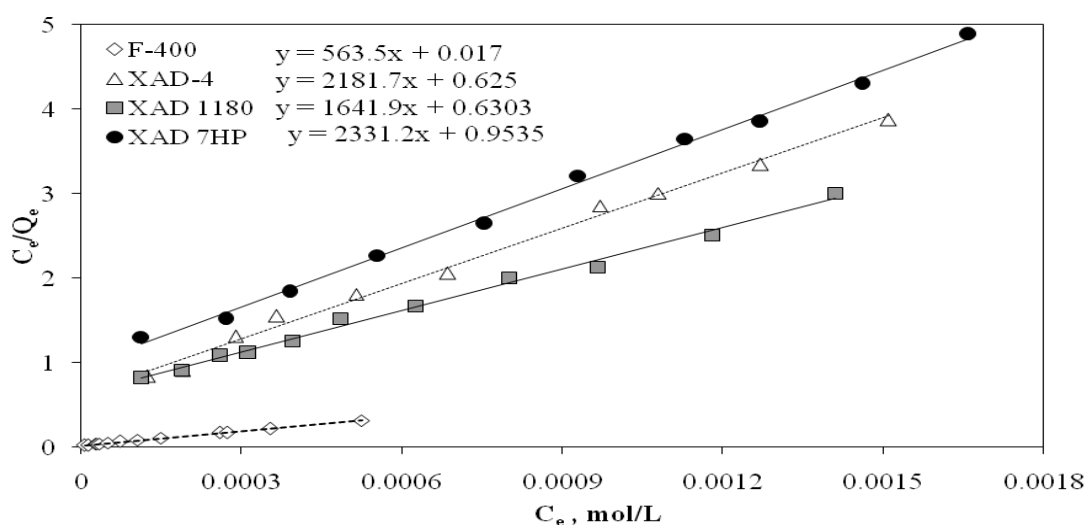


Fig 2 : Comparative Langmuir adsorption isotherms of 4-CP

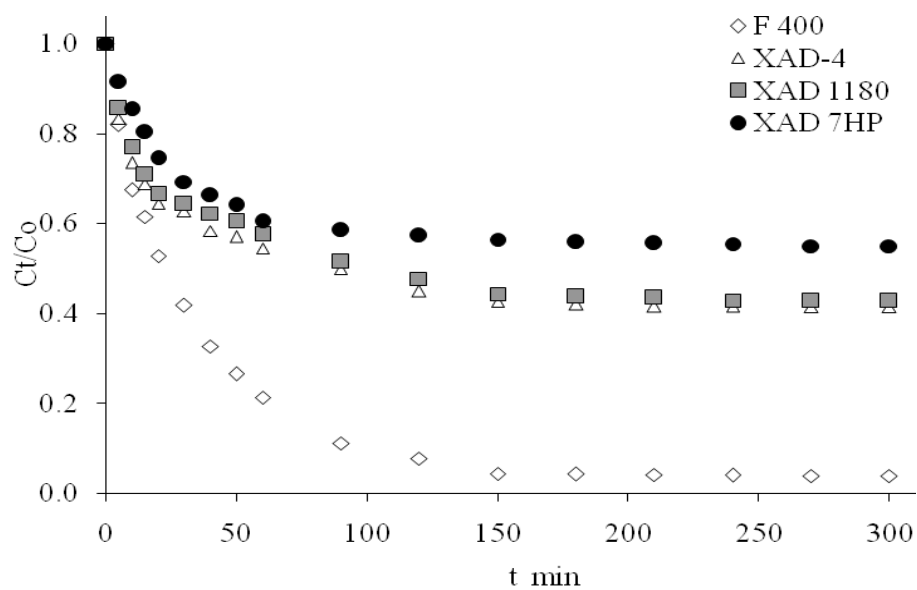


Fig 3 : Comparative Adsorption kinetics of 4-CP

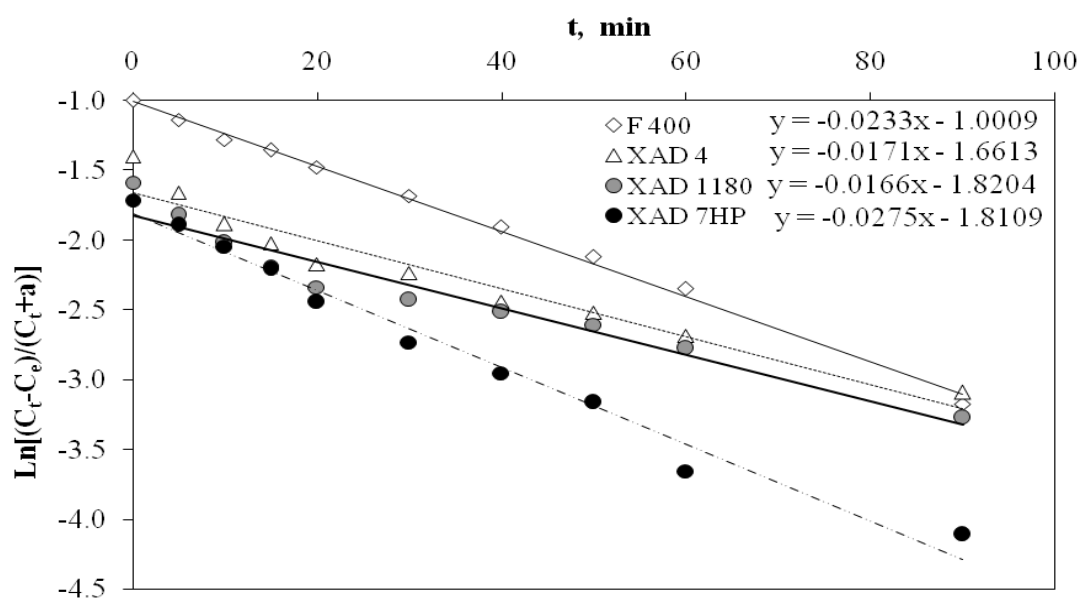


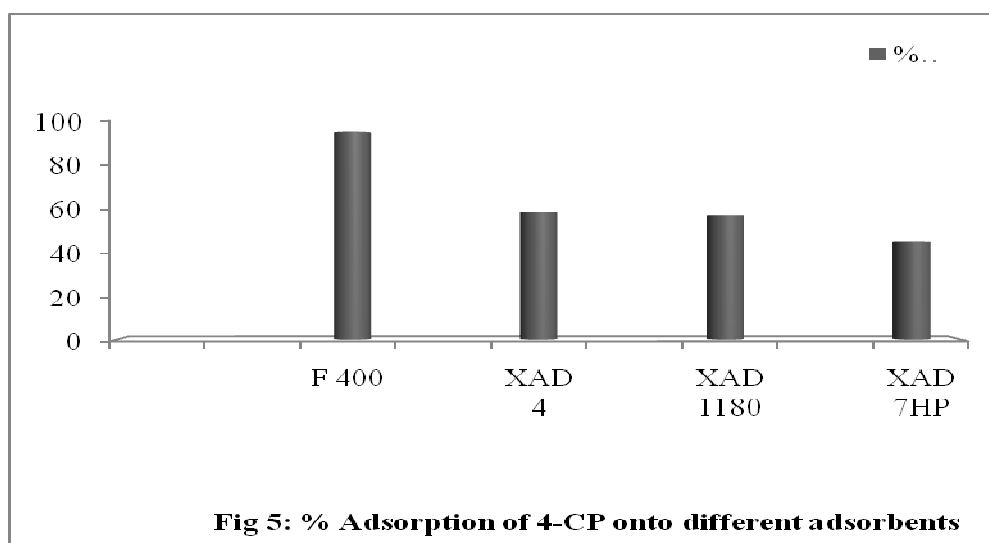
Fig 4: Comparative Adsorbate removal rate of 4-CP

Table -3: Physico-chemical properties of 4-CP

Mol. Wt.	128.56
Water solubility mol/L at 30 °C	0.2107
λ_{\max} (nm)	279
ϵ ($\text{cm}^{-1} \text{mol}^{-1} \text{dm}^{-1}$)	1463.3

Table 4: Comparative adsorbent monolayer capacity and Langmuir constant for 4-CP

No.	Adsorbent	Slope	Intercept	$Q^o \times 10^4$ mol/g	$C_e \times 10^4$ mol/L	b
1	F 400	563.54	0.0179	17.74	0.0673-5.25	31482.68
2	XAD 4	2181.7	0.625	4.58	1.25-15.1	3490.72
3	XAD 1180	1641.9	0.6303	6.09	1.12-14.1	2604.95
4	XAD 7HP	2331.2	0.9535	4.29	1.13-16.6	2444.88



CONCLUSIONS

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

4-CP adsorption using GAC F-400 is rapid in the first hour of contact where 60 - 70 % of the adsorbate is removed by GAC F-400 followed by a slow approach towards equilibrium. In case of polymeric adsorbents 50-60 % of the adsorbate is removed in the first 30 min of contact time which is then followed by a slow approach to equilibrium. The adsorption of 4-CP from aqueous solution on to granular activated carbon and polymeric adsorbents confirms to a Langmuir equation based on a monomolecular layer. Comparative adsorbent monolayer capacity of GAC F-400 is greater than all the three polymeric adsorbents used. The order of adsorptive capacity of 4-CP on different adsorbents used in the study is found to be in following order F-400 > XAD-4 > XAD-1180 > XAD7HP

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);

k_a = adsorption rate constant (min⁻¹); Q_o = 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. T. Chuang, S. Cheng and S. Tong "Removal and destruction of benzene, toluene and xylene from wastewater by air stripping and catalytic oxidation", *Ind. Eng. Chem. Res.*, 1992, **31**: 2466.
2. K. Hayward, Drinking water contaminant hit-list for US EPA, Water 21, September October, 19984.
3. H.K. Veschuereen, Handbook of Environmental Data on Organic Chemicals, VNR, New York, 1983.
4. J. Folke, J. Birklund, Danish coastal levels of 2,3,4,6-tetrachlorophenol, pentachlorophenol, and total organohalogens in blue mussels (*Mytilus edulis*), *Chemosphere* 1986, **15**, 895.
5. P.H. Howard, Handbook of Environmental Fate and Exposure Data for Organic Chemical, vol. I, Large Production and Priority Pollutants, Lewis Publishers, Chelsea, MI, USA, (1989).
6. W.A. Abbasi, M. Streat, *Sep. Sci. Technol.* 1994, **29**, 1217.
7. Kirk-Othmer, Encyclopedia of Chemical Technology, vol. 24, fourth ed., Wiley-Interscience, USA, 1997.
8. C. Brasquet, J. Roussy, E. Subrenat, P. le Cloirec, *Env. Tech.*, 1996, **17**, 1245.
9. A. R Khan, T. A. Al-Bahri, A. Al-Haddad, *Water Res.* 1997, **31**, 2102.
10. B. M. Vliet, W. J. Weber. Jr., and H. Hozumi, *Water Res.*, 1980, **14**, 1719.
11. H. S. Kim and H. C. Choi, *Water Sci. Tech*, 1998, **38**, 95.
12. A. Seidel, E. Tzscheuschler, K.-H. Radeke, and D. Gelbin, *Chem. Eng. Sci.*, 1985, **40**, 215.
13. G. Calleja, J. Serna, and J. Rodriguez, *Carbon*, 1993, **31**, 691.
14. A. A. M. Daifullah, and B. S. Girgis, *Water Res.* 1998, **32**, 1169.
15. Kh. A. Halhouli, N. A. Darwish and N. M. Al Dhoun, *Sep. Sci. Technol.*, 1995, 3313.
16. C. Moreno-Castilla, J. Rivera-Utrilla, M. V. López-Ramón and F. Carrasco-Mar, *Carbon*, 1995, **33**, 845.
17. R. S. Juang, R. L. Tseng, F. C. Wu, and S. H. Lee, *Sep. Sci. Technol.* 1996, **31**, 1915.
18. D. M. Nevskaya, A. Santianes, V. Muñoz, and A., *Carbon* 1999, **37**, 1065.
19. P. Wood and J. Demarco; "Activated Carbon Adsorption of organics of the Aqueous Phase", Vol II, Chapter -5, Eds.: McGuire, M.J. and Suffet, I.H., Ann Arbor Science, Ann Arbor, Michigan, 1980.

20. R. Kurin, and I.H. Suffet, "Activated Carbon Adsorption of organics of the Aqueous Phase", Vol II, Chapter -18, Eds: McGuire, M.J. and Suffet, I.H., Ann Arbor Science, Ann Arbor, Michigan, 1980.
21. P .Van Rossum, and R.G. Webb. *J. Chromatogr.* 1978, **150**:381.

***Correspondence Author: A.S.Ghatbandhe**, Department of Chemistry, S F S College,
R.T.M Nagpur University, Indi E mail: ajay_gbandhe@rediff