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Research Article

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Comparative 2, 4 Dichlorophenoxyacetic acid (2, 4-D) Aqueous Phase Adsorption Using Natural and Synthetic Adsorbents

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ABSTRACT

Adsorption equilibrium, kinetic of 2,4-dichlorophenoxy-acetic acid (2,4-D), one of the most commonly used phenoxy acid herbicides, onto different adsorbents such as granular activated carbon (GAC) and synthetic polymeric adsorbents XAD- 7HP, XAD-1180 and XAD-4 were studied in aqueous solution in a batch system. Langmuir isotherm model was applied to experimental equilibrium data of 2,4-D adsorption depending on adsorbents used. Equilibrium data fitted very well to the Langmuir equilibrium model in the studied concentration range of 2, 4-D for all the adsorbents studied. 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, whereas in case of polymeric adsorbents 60-65 % 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: Adsorption, 2, 4-D, GAC, XAD-7HP, XAD-1180, XAD-4, Equilibrium, Kinetics, Batch adsorption.

INTRODUCTION

Water pollution caused by certain industries or agricultural activity is a source of environmental degradation. The organic and inorganic compounds that have certain toxicity are now regarded as hazardous even when exist as traces [1-4]. Among the numerous agrochemicals in use today, the herbicide 2, 4-D has been widely applied to control broad-leaved weeds in gardens and farming. 2, 4-D is commonly preferred because of its low cost and good selectivity. It is considered as moderately toxic and maximum allowable concentration is 100 ppb in drinking water [5]. On the other hand 2,4-D is a poorly biodegradable pollutant. Consequently, it has been frequently detected in water bodies in various regions of the world. The adsorption process is one of the efficient methods to remove organics from effluent [6, 7]. Activated carbon is the most widely and effectively used adsorbent used for removal of organics from water owing to its highly developed surface properties such as surface area, porosity and surface chemistry. The adsorption process has an advantage over the other methods due to the excellent adsorption efficiency of activated carbon [8]. Along with traditional adsorbents like carbon, silica gel etc., polymeric adsorbents are also more attractive alternatives because of their wide range of pore structures and physico- chemical characteristics [9, 10]. Adsorption of some pollutants on low cost, non-conventional adsorbents have been carried out which include, agriculturalsolid waste, Such as Coir pith [10], Banana pith [11],Coconut husk [12], Sawdust

[13], Peat moss [14], Paddy straw[15], Nilgiri leaves[16] and industrial solid wastes such as fly ash , coal, Red mud ,Fe (III)/ Cr (III) hydroxide andCopper ion[17].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 [18].

In the present investigation 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 (Rohm & Haas company, Pennsylvania, USA) 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 micoreticular 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 adsorbent 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

Table 3 Physico-chemical properties of adsorbate 2, 4 D

Mol. Wt.	163.1
Water solubility g/L at 30 °C	4.6
λ_{max} (nm)	284
$\in$ (cm^{-1} mol^{-1} dm^{-1})	1893

EXPERIMENTAL SECTION

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. After the temperature was reached, a calculated quantity of the stock solution was introduced into the distilled water with the help of graduated pipette.. 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.

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.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 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 spectrophotometric method using UV-Visible spectrophotometer model GBC UV-VIS 911A from GBC Scientific Equipment Pvt. Ltd., Australia. Adsorbate 2,4 D 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}).

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, 4 D with respect to all the adsorbents used in the present study are depicted in Fig.-1. 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,

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

Langmuir isotherm plot for the adsorbate-adsorbent systems using different adsorbents are depicted in Fig.-2

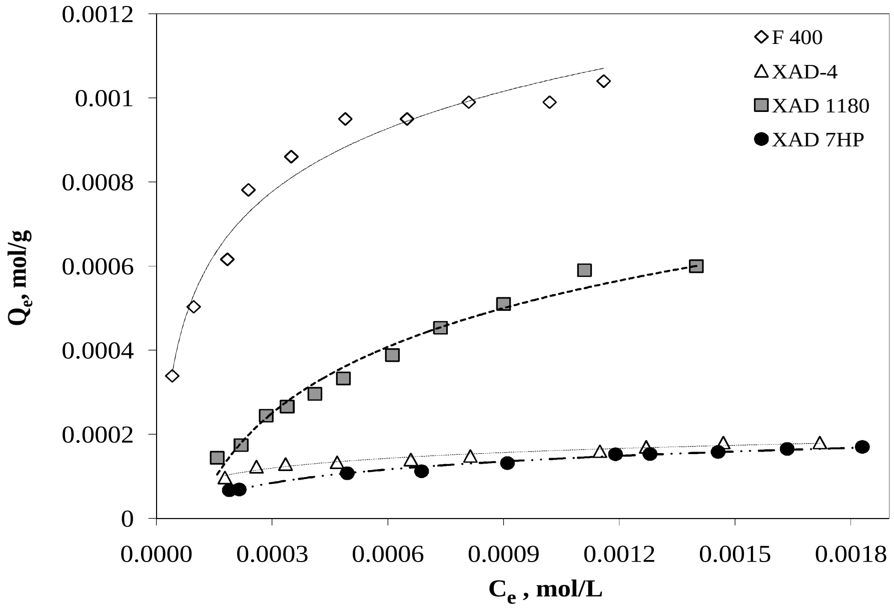


Fig 1 Comparative adsorption isotherms of 2,4 D

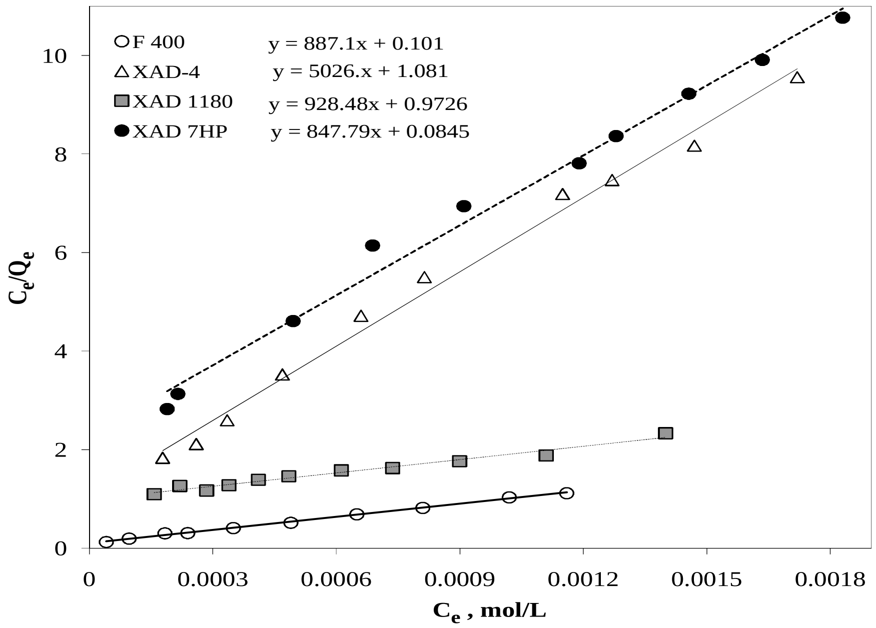


Fig 2 : Comparative Langmuir Adsorption isotherms of 2,4 D

Adsorbate 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.

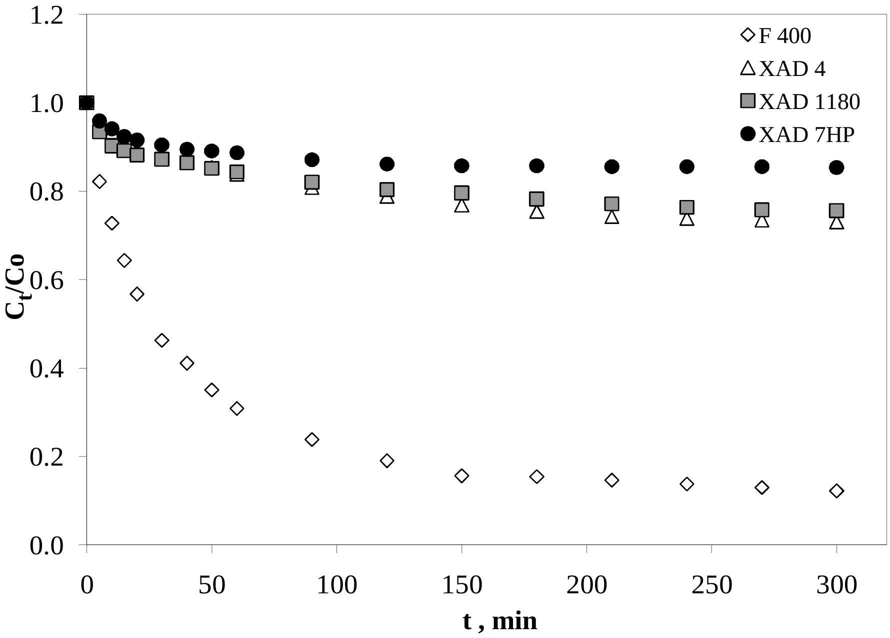


Fig 3 Comparative adsorption kinetics of 2,4 D

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

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

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

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

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

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

The adsorption rate constant 'ka' thus evaluated by plotting ln [(Ct-Ce) / (Ct+a)] against t. Fig. 4 depicts these plots for the adsorbate-adsorbent systems for all the adsorbents studied in the present work. The plot also show the rate expressions obtained by linear regression analysis of the kinetic data. The experimentally determined values of adsorbent monolayer capacity 'Q^o', Langmuir constant 'b' and the adsorption-desorption rate constant for all thje adsorbents used are summarized in Table-4.

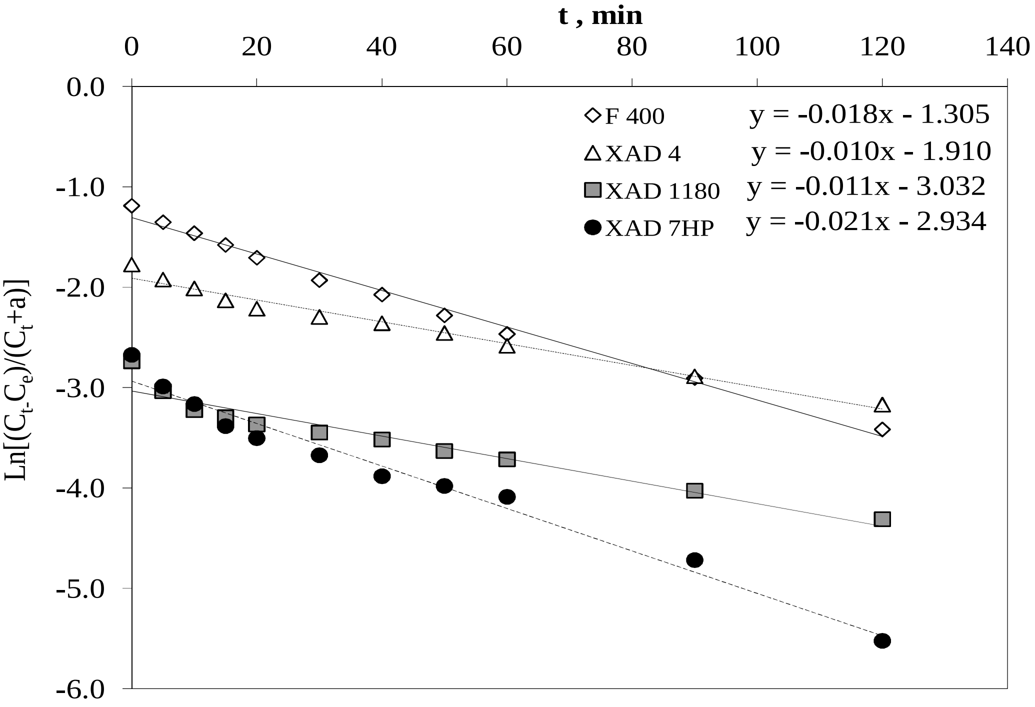
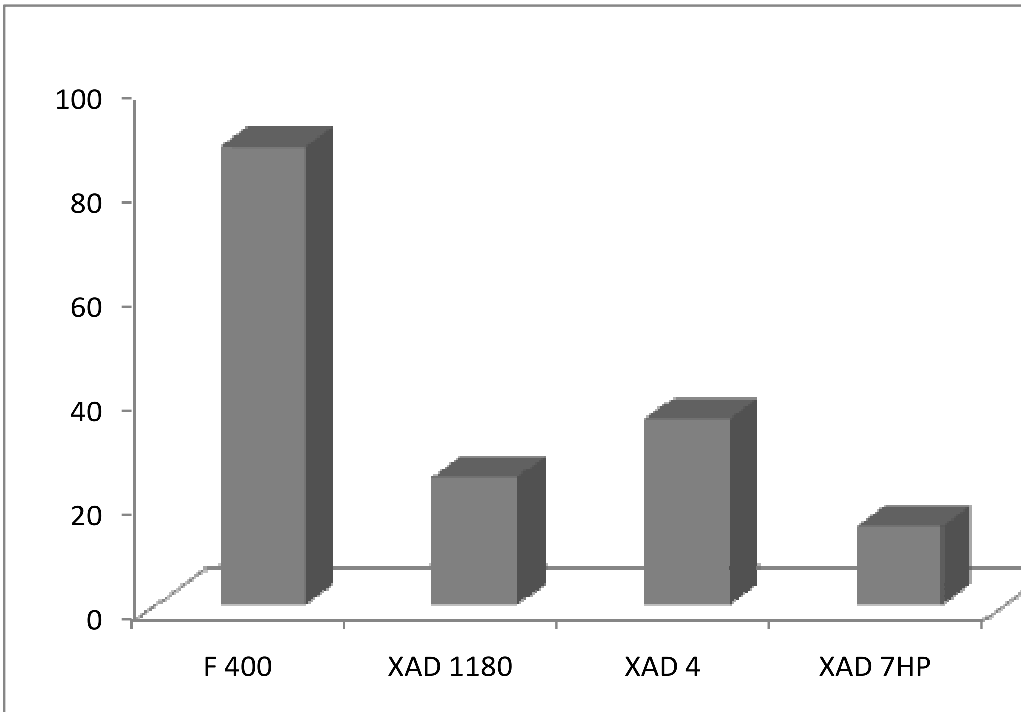


Fig 4 : Comparative adsorbate removal rate of 2,4 D

Table 4:Comparative adsorbent monolayer capacity and Langmuir constant for 2,4 D

No.	Adsorbent	Slope	Intercept	Q^o x 10^4	C_e x 10^4	b
				mol/g	mol/L	
1	F 400	887.12	0.102	11.27	0.41-11.6	8705.79
2	XAD 4	5026.9	1.081	1.99	1.78-17.2	4648.94
3	XAD 1180	928.48	0.973	10.77	1.58-14.1	954.64
4	XAD 7HP	847.79	0.085	11.80	1.89-18.3	10033.02

From the above study it is clear that depending upon the make of individual adsorbent, the overall adsorbing capacity of every adsorbent varies. The % adsorption of 2,4 D for different adsorbents used in present study is mentioned in the form of plot in Fig-5



CONCLUSION

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

- 2, 4 D adsorption using GAC F-400 is rapid in the first hour of contact where 65 - 75 % of the adsorbate is removed by GAC F-400 followed by a slow approach towards equilibrium.
- In case of polymeric adsorbents 55-65 % 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 2, 4 D 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 2, 4 D on different adsorbents used in the study is found to be in following order F-400> XAD-1180>XAD-4> XAD7HP

Application of adsorption of 2,4 D by the GAC and polymeric adsorbents in purification of wastewater for can be suitable for of wastewater treatment by using these kinetic parameters.

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)

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