

Research Article

Evaluation of Thermodynamic Parameters of 2, 4-Dichlorophenoxyacetic Acid (2, 4-D) Adsorption

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Thermodynamic parameters of 2, 4-Dichlorophenoxyacetic acid (2, 4-D) adsorption were evaluated by studying the adsorption equilibrium and kinetics of 2, 4-D at different temperatures. Uptake capacity of activated carbon increases with temperature. Langmuir isotherm models were applied to experimental data of 2, 4-D adsorption. Equilibrium data fitted very well to the Langmuir equilibrium model. Adsorbent monolayer capacity Q^0 , Langmuir constant a and adsorption rate constant k_a were evaluated at different temperatures for activated carbon adsorption. The activation energy of adsorption (E_a) was determined using the Arrhenius equation. Using the thermodynamic equilibrium coefficients obtained at different temperatures, the thermodynamic constants of adsorption (ΔG^0 , ΔH^0 , and ΔS^0) were evaluated. The obtained values of thermodynamic parameters show that the adsorption of 2, 4-D is an endothermic process.

1. Introduction

Along with industrial activities, agricultural activities also contribute in water pollution to the greater extent. Hence wastewater without an efficient treatment is becoming a serious problem. 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. 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 [1, 2]. Activated carbons have also been employed to remove organic contaminants from wastewater and gaseous wastes [3–5]. Electrostatic and van der Waals forces, H-bonding, dipole-dipole interactions, ion exchange, covalent bonding, cation bridging, and water bridging can be responsible for the adsorption of organic compounds on activated carbon [6–13]. It is reported that the pore size of the activated carbons significantly influence the adsorption capacity of natural organic materials subject to their molecular sizes [14]. Several

researchers studying dye adsorption on activated carbon [15, 16] have pointed out that the presence of mesopores together with micropores in the activated carbon enhances their adsorption capacities, especially, for large adsorbates [17, 18]. These reports suggest that the pore size distributions of activated carbons decide their proper applications.

Generally an elevated temperature provides faster rate of diffusion of adsorbate molecules through the solution to the adsorbent surface and into adsorbent. Zogoroski [4, 5] obtained the adsorption isotherm for phenol at different temperatures and concluded that adsorption decreases with the increase in temperature and concluded that adsorption is an exothermic process. On the contrary Tütem et al. [19] concluded that the adsorption of chlorophenols from aqueous phase on bituminous shale was endothermic and basically of physical character. The equilibrium uptake of 2, 4-D by GAC was also affected by temperature and increases with increasing temperature [20].

In the present investigation, equilibrium and kinetics studies of adsorption of 2, 4-Dichlorophenoxyacetic acid (2,

4-D) from aqueous solution on granular activated carbon has been carried out at five different temperatures to evaluate thermodynamic parameters. 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 “ k_a ” and desorption “ k_d ” rate constants. This data was then used to calculate the energy of activation of adsorption and desorption also the thermodynamic parameters, namely, the free energy of adsorption “ ΔG^0 ”, enthalpy of adsorption “ ΔH^0 ”, and the entropy of adsorption “ ΔS^0 ”.

2. Materials and Methods

2.1. Materials. In the present investigation commercially available granular activated carbon (GAC), namely, Filtrasorb-400 (F-400) was used as adsorbent.

2.2. Methods

2.2.1. 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. 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 the determination of initial concentration. 0.25 ± 0.001 g of the adsorbate sample 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. Preliminary experiments show that the adsorbate uptake profile was independent of stirring speed above 600 rpm [21] and the equilibrium was attained in about 4 hours. As a precautionary measure, experiments were continued for five hours. Some of the experiments were carried out over a prolonged period of time where no significant difference was observed in the adsorbate concentration.

2.2.2. 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 by adding appropriate amount of stock solution into boiled and cooled distilled water. 3.00 ± 0.001 g 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 the concentration of adsorbate in the aqueous phase was estimated by UV analysis. Properties of adsorbent GAC F-400 and adsorbate used in the present study are given in Tables 1 and 2 respectively.

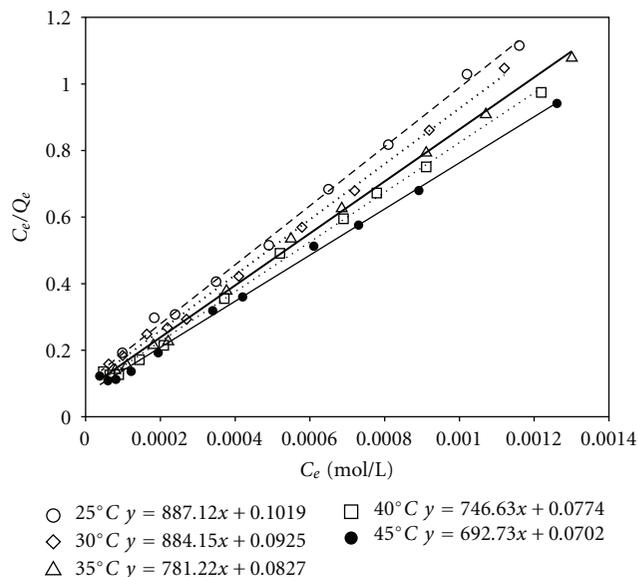


FIGURE 1: Langmuir adsorption isotherms at different temperatures.

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%

3. Result and Discussion

The adsorption isotherms obeyed the Langmuir equation with a very high regression coefficient above 0.98 indicating a very good linear fit in all the cases. The Langmuir adsorption isotherm is represented by the following equation [21]:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (1)$$

Langmuir isotherm plot at different temperatures is depicted in Figure 1. The plot also shows the Langmuir equation obtained by linear regression of the data.

The Langmuir isotherm characteristics can be expressed in terms of dimensionless constant separation factor R_L [22] represented as

$$R_L = \frac{1}{(1 + bC_0)}, \quad (2)$$

where b is the Langmuir constant and C_0 initial adsorbate concentration; R_L values are given in Table 3 and indicate the

TABLE 2: Physico-chemical properties of adsorbate 2, 4-Dichlorophenoxyacetic acid (2, 4-D).

Mol. wt.	221.0
Water solubility mol/L at 30°C	0.00452
λ_{\max} (nm)	282
ϵ (dm ³ mol ⁻¹ cm ⁻¹)	2057.1

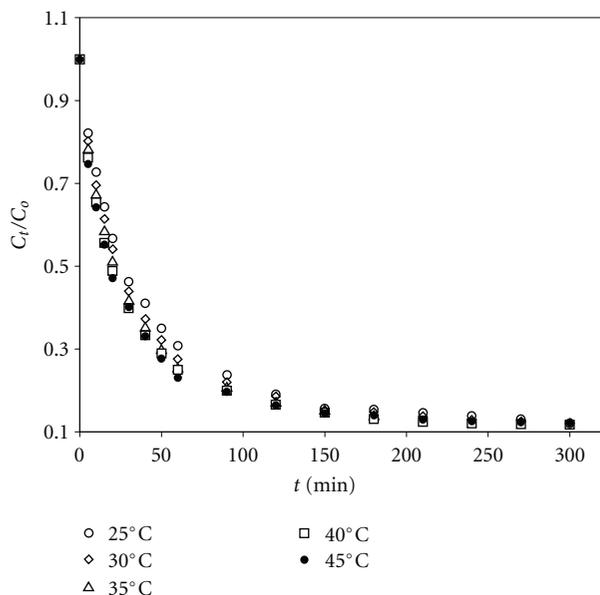


FIGURE 2: Adsorption kinetics of 2, 4-D at different temperatures.

type of isotherm. R_L values between zero and one indicate favorable adsorption for 2, 4-D in the studied concentration range.

3.1. Adsorbate Removal Rate Studies. 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

$$\frac{dq}{dt} = k_a C_t (1 - Q) - k_d Q, \quad (3)$$

$$Q = f(C_0 - C_t), \quad (4)$$

where, k_a and k_d are adsorption and desorption rate constants. C_0 , C_t and C_e , are the fluid phase adsorbate concentrations at time zero t and at equilibrium, respectively; f is proportionality constant. Substituting (4) in (3) and solving the resultant equation by applying the concept of steady state gives the final expression

$$\ln \left[\frac{(C_t - C_e)}{(C_t + a)} \right] = -k_a C_e t + \ln \left[\frac{(C_0 - C_e)}{(C_0 + a)} \right], \quad (5)$$

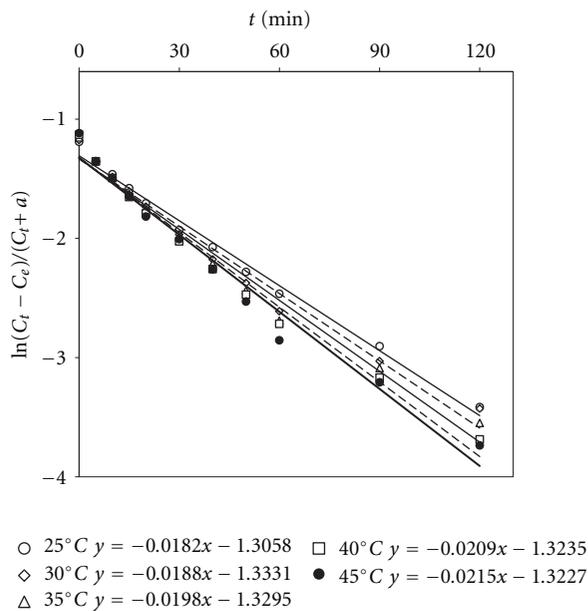


FIGURE 3: Adsorbate removal rate of 2, 4-D at different temperatures.

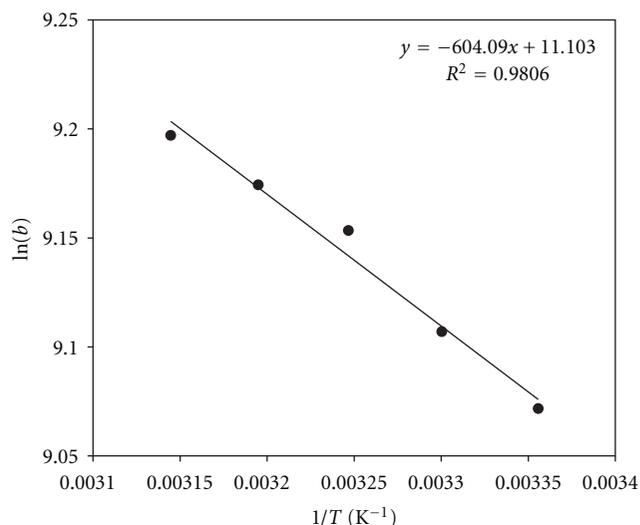


FIGURE 4: Vant Hoff plot for 2, 4-D adsorption at different temperatures.

where,

$$a = \left(\frac{C_0}{bC_e} \right), \quad b = \frac{k_a}{k_d}. \quad (6)$$

The adsorption " k_a " and desorption " k_d " rate constants were thus evaluated by plotting $\ln[(C_t - C_e)/(C_t + a)]$ against t . Figures 2 and 3 depict these plots for the adsorbate-adsorbent 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^0 ", Langmuir constant " b " for the adsorbate-adsorbent systems at all the five temperatures are

TABLE 3: Effect of temperature on adsorption capacity and Langmuir constant.

T, K	Slope	Intercept	$Q^{\circ} \times 10^4$, mol/g	$C_e \times 10^4$, mol/L	b	R_L
298	887.12	0.1019	11.27	0.41–11.6	8705.79	0.187
303	834.15	0.0925	11.99	0.62–11.2	9017.84	0.182
308	781.22	0.0827	12.80	0.48–13.0	9446.43	0.174
313	746.63	0.0774	13.39	0.49–12.2	9646.38	0.170
318	692.73	0.0702	14.44	0.38–12.6	9867.95	0.169

TABLE 4: Adsorption desorption rate constants and thermodynamic parameters of 2, 4-D adsorption.

T, K	K_a , min ⁻¹	K_d , min ⁻¹	ΔG^0 , kJ mol ⁻¹	ΔH^0 , kJ mol ⁻¹	ΔS^0 , JK ⁻¹
298	298.36	0.0343	-22.48		
303	313.33	0.0347	-22.56		
308	335.59	0.0355	-22.68	5.02	92.31
313	348.33	0.0361	-22.73		
318	358.33	0.0363	-22.79		

summarized in Table 3. The adsorption and desorption rate constants obtained are given in Table 4.

3.2. Effect of Temperature. The results obtained in the present investigation are very informative. The equilibrium uptake of 2, 4-D by GAC is affected by temperature and increases with the rise in temperature. The adsorption desorption rate were found to decrease with the rise in temperature. The increase in the adsorption capacity with rise in temperature illustrates that 2, 4-D adsorption on to GAC F-400 is an endothermic process. The increase in the adsorption capacity of activated carbon at higher temperature may be attributed to the enlargement of pore size or activation of the adsorbent surface or creation of some new active sites on the surface of adsorbent due to bond rupture. This could also be due to the enhanced mobility of 2, 4-D 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 [6, 23, 24].

3.3. Thermodynamic Parameters. From the variation of b (thermodynamic distribution coefficient or Langmuir constant) with temperature, thermodynamic parameters ΔG^0 , ΔH^0 , and ΔS^0 namely, the standard free energy change, standard free enthalpy change, and standard free entropy change, respectively, were calculated using the following equations,

$$\Delta G^0 = -RT \ln b \quad (7)$$

and Vant' Hoff equation,

$$\ln b = \left(\frac{\Delta S^0}{R} \right) - \left(\frac{\Delta H^0}{RT} \right). \quad (8)$$

The Vant' Hoff plot of $\ln b$ against $1/T$ was plotted (Figure 4) which shows an excellent linearity. ΔH^0 and ΔS^0 are

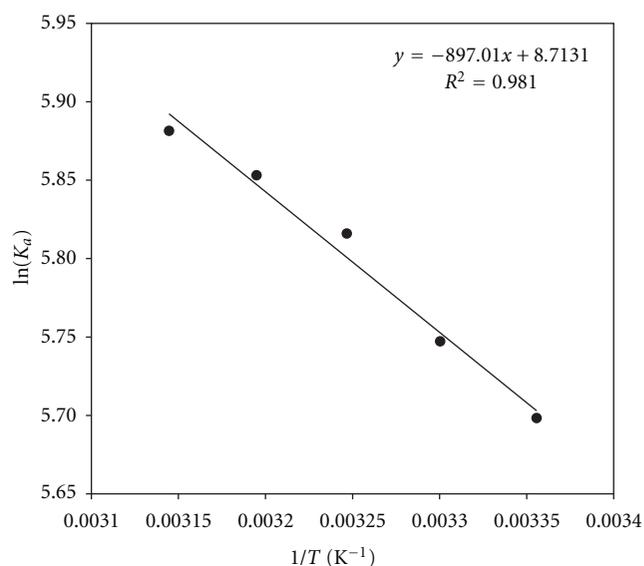


FIGURE 5: Plot of energy of activation of 2, 4-D adsorption.

obtained from slope and intercept of the plot and are given in Table 4. The values of ΔG^0 for all the studied temperatures are found to be negative. The negative values of free energy are indicative of a spontaneous process with a high affinity of the adsorbate to the surface of the adsorbent. The positive value of enthalpy change points to the endothermic nature of the adsorption process.

3.4. Energy of Activation of Adsorption. The activation energy of adsorption was determined using the Arrhenius equation

$$\ln k_a = - \left(\frac{E_a}{RT} \right) + \ln A. \quad (9)$$

The plot of $\ln k_a$ versus $1/T$ was plotted (Figure 5), and the linear regression analysis gave a linear regression coefficient above 0.980. E_a value for the 2, 4-D-GAC system is given in Table 5.

4. Conclusion

- (i) 2, 4-D adsorption using GAC is very rapid in the first hour of contact where 70% of the adsorbate is removed by GAC followed by a slow approach to equilibrium.
- (ii) The Langmuir constant (b), related to the energy of adsorption, increased with temperature for all the

TABLE 5: Effect of temperature on adsorption rate constants.

T, K	k_a , min ⁻¹	E_a , kJ mol ⁻¹	% increase in k_a
298	298.36		
303	313.33		5.02
308	335.59	7.46	12.48
313	348.33		16.75
318	358.33		20.10

adsorbate studied probably due to enhanced solute-sorbent interactions of dipolar nature.

- (iii) Increase in the value of “ln b ” indicate that the rate of adsorption is much higher than the rate of desorption.
- (iv) The 2, 4-D adsorption by GAC is a complex and is probably a combination of external mass transfer, intraparticle diffusion, and sorption process. Thermodynamic constants were also evaluated using equilibrium constants changing with temperature.
- (v) The negative value of ΔG^0 indicated the spontaneity and the positive values of ΔH^0 and ΔS^0 showed the endothermic nature and increase in disorder of 2, 4-D adsorption, respectively.
- (vi) Energy of activation of adsorption indicates the physical nature of the process.
- (vii) The kinetics of adsorption is an activation process that is as the temperature of system increases the rate of the removal of adsorbate increases whereas adsorption capacity decreases.
- (viii) Thus as the temperature of the system increases, the rate of adsorption increases.

Nomenclature

- b : Langmuir constant
- C : concentration of the adsorbate in liquid phase (mol/L)
- C_0 : Initial concentration of the adsorbate (mol/L)
- C_e : Equilibrium concentration of the adsorbate (mol/L)
- E_a : Energy of activation (kJ/mol)
- ΔG^0 : Standard free energy of adsorption (kJ/mol)
- ΔH^0 : Standard enthalpy of adsorption (kJ/mol)
- ΔS^0 : Standard entropy change of adsorption (JK⁻¹ mol⁻¹)
- k_a : Adsorption rate constant (min⁻¹)
- k_d : Desorption rate constant (min⁻¹)
- Q_0 : 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).

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