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Adsorption of 4-chlorophenol from aqueous solutions by xad-4 resin: Isotherm, kinetic, and thermodynamic analysis

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Abstract

Removal of 4-chlorophenol (4-CP) from synthetic aqueous solutions through adsorption on Amberlite XAD-4 resin, a non-ionic macroreticular resins, under batch equilibrium experimental conditions at 298, 308 and 318 K was investigated. It is necessary to propose a suitable model to a better understanding on the mechanism of 4-CP adsorption. For this purpose, Langmiur, Freundlich, Toth, and Redlich–Peterson (RP) isotherm models were compared. The two and three parameters in the adopted adsorption isotherm models were determined by the help of MATLAB package program. It was determined that best fitted adsorption isotherm models were obtained to be in the order: Redlich–Peterson > Langmuir > Toth > Freundlich isotherms. The pseudo-second-order kinetic model provided the best correlation to the experimental results. Results of the intra-particle diffusion model show that the pore diffusion is not the only rate limiting step. The lower correlation of the data to the Bangham's equation also represents that the diffusion of the adsorbate into pores of the sorbent is not the only rate-controlling step. The thermodynamic constants of adsorption phenomena; ΔG°, ΔH°, and ΔS° were found as −4.17 (at 298 K) kJ/mol, −42.01 kJ/mol, and −0.127 kJ/(mol K), respectively. The results showed that adsorption of 4-CP on Amberlite XAD-4, a nonionic polymeric resin was exothermic and spontaneous.

Keywords: Adsorption; 4-Chlorophenol; XAD-4 resin; Isotherm; Kinetic; Thermodynamic

1. Introduction

Phenolic compounds are pollutants of great concern because of the high toxicity and possible accumulation in the environment. Most of these compounds are recognized as organic contaminants in environmental systems [1,2]. Phenols occur in wastewater of a number of industries such as oil refineries, coal gasification sites, petrochemical units, paper, textile, synthetic rubber, and pharmaceutical industries [3,4]. The presence of phenolic compounds even at low concentrations can be an obstacle to the use and/or reuse of water because of the occasion of unpleasant taste and odor. Furthermore, phenols can exert negative effects on biological processes and are considered to be priority pollutants since they are known or suspected to be carcinogenic. Thus, the removal of phenols from such streams is considered to be necessary before discharging to the environment [5–8].

Toxic and recalcitrant organic pollutants such as phenolic compounds can be removed effectively by the sorption processes. A variety of adsorbents used for removal of phenols from single solute aqueous solutions include activated carbon, bentonite and perlite, rubber seed coat, hydrotalcite and its calcined product, acid-activated bituminous shale, zirconium(IV) arsenate–vanadate ion-exchanger, cross-linked polyvinylpyrrolidone, activated natural zeolites, water-insoluble cationic starch, and polymeric resins [9]. Activated carbon is the most commonly used sorbent in wastewater treatment, due to its vast surface area and affinity for many organic chemicals. However, activated carbon is costly to regenerate; the process is energy intensive and has a high attrition rate. It also tends to sorb most organic chemicals indiscriminately, making it difficult to selectively recover certain organic chemicals for reuse [10].

In recent years, there has been a growing interest in developing various adsorbents to remove phenols and other specific organic substances from water. Polymeric adsorbents have been increasingly regarded as an alternative to activated carbon for the selective removal of specific organic substances from contami-

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Nomenclature

a	Bangham constant (<1)
A, B, and D	constants of Toth isotherm
C	constant that gives idea about the thickness of the boundary layer (mg/g)
C_e	equilibrium liquid phase concentration (mg/L)
C_0	initial 4-CP concentration (mg/L)
ΔG°	Gibbs free energy of adsorption (kJ/mol)
ΔH°	enthalpy of adsorption (kJ/mol)
k_b	constant in Bangham's equation
k_F and $1/n$	constants of Freundlich isotherm
k_{id}	rate constant of intra-particle diffusion model (mg/(g min$^{0.5}$))
k_L, Q_0	constants of Langmuir isotherm
k_{RP}, p_e, and g	constants of Redlich–Peterson isotherm
k_1	rate constant of pseudo-first-order kinetic model (min^{-1})
k_2	rate constant of pseudo-second-order kinetic model (g/(mg min))
m	adsorbent mass per liter of solution (g/L)
q	solid phase concentration at time t (mg/g)
q_e	equilibrium solid phase concentration (mg/g)
R	universal gas constant (8.314 J/(mol K))
RMSE	root mean square error
R^2	regression correlation coefficient
ΔS°	entropy of adsorption (J/mol K)
SSE	sum of squares due to the errors
t	time (min)
T	temperature (K)
V	volume of solution (L)

nated water due to their wide variations in functionality, surface area, and porosity [11].

A large number of equilibrium studies have been made for the adsorption of phenols on commercial or synthetic nonionic polymeric resins [1,9,11–15]. Ku and Lee [1] studied the adsorption of phenols from aqueous solutions by Amberlite XAD-4 resin under different conditions. They found that the removal of phenols by XAD-4 resin was effective at acidic conditions, while the removal efficiency decreased sharply for alkaline solutions. Juang and Shiau [15] determined that the isotherm data could not be fit by any conventional equation, where they were well fit by combined BET equation or its modified form depending on the types of solutes and the resins. They were also discussed the effect of temperature on adsorption equilibrium.

This study focuses on determination of the influence of temperature on liquid phase adsorption of 4-chlorophenol (4-CP) on Amberlite XAD-4 resin, a non-ionic polymeric resin, as an adsorbent. Batch kinetics and isotherm studies were carried out to evaluate the effect of contact time, initial concentration, and the thermodynamic constants of the adsorption process for 4-CP adsorption by XAD-4 resin. The adsorption isotherms are described by Freundlich, Langmuir, Toth, and Redlich–Peterson isotherm models. All fitted parameters were determined by the help of MATLAB package program. Four kinetic models, pseudo-first-order, pseudo-second-order, intra-particle diffusion model, and Bangham models, were used to investigate the adsorption process of 4-CP on XAD-4 resin. The kinetic parameters and the correlation coefficients were also evaluated by the help of the MATLAB program. The thermodynamics of the adsorption process was also investigated in order to evaluate the heat change of the adsorption process.

Table 1
Properties of non-ionic macroreticular XAD-4 resin

Property	Amberlite XAD-4
General description	Non-ionic macroreticular resin
Matrix	Styrene–divinylbenzene
Pore volume	0.98 mL/g
Average diameter	40 Å
Mean pore size	40 Å
Surface area	725 m^2/g
Density	1.02 g/mL (true wet) (lit.) 1.08 g/mL (skeletal) (lit.)

2. Experimental

2.1. Adsorbent

Amberlite XAD-4, a nonionic hydrophobic polyaromatic resin (Sigma–Aldrich, Germany) was used as the adsorbent for the adsorption behavior of 4-CP in aqueous solutions. Physical properties of the resin are compiled in Table 1. Amberlite XAD-4 resin has been referred as the best polymeric adsorbent for the removal of phenol from phenol-contaminated streams [12]. However, its extreme hydrophobic surface results in poor contact with aqueous solutions, and thus some activation solvents such as methanol, acetone, or acetonitrile, have to be used to enhance its surface contact with the aqueous solutions [13].

The resin was washed with deionized water several times to remove inorganic impurities like Na_2CO_3 and NaCl and then washed with acetone several times and rinsed for 12 h to remove the organic impurities. Finally the resin was dried at 325 K for 2 h prior to use [11].

2.2. Chemicals

Stock solutions of 4-CP were prepared by dissolving 1 g of analytical reagent grade (Merck, Germany) in 1 L of distilled water without pH adjustment. Some of the properties of 4-CP are given in Table 2. During adsorption the pH varied slightly between 6.8 and 6.9 for 4-CP under the concentration ranges studied. Because they were much less than pK_a (Table 2) the dissociated forms are assumed to be absent in the aqueous phase [11]. The range in concentrations of 4-CP prepared from the stock solution varied between 25 and 250 mg/L.

2.3. Experimental studies

Batch adsorption experiments were carried out by allowing an accurately weighted amount of XAD-4 resin to reach

Table 2
Physical and chemical properties of 4-chlorophenol

Property	4-Chlorophenol
Formula[a]	ClC_6H_4OH
Density[a] (318 K)	1.26 g/cm^3
Molecular weight[a]	128.56 g/mol
Solubility in water[a] (293 K)	27 g/L
Surface area[b]	3.26×10^{-19}
pK_b^a	9.41

[a] Taken from the manufacturer.
[b] Taken from Ref. [15].

equilibrium with 4-CP solutions of various initial concentrations between 25 and 250 mg/L at temperatures of 298, 308 and 318 K. Known weights of XAD-4 resin (1.0 g) were added to 250 mL reaction bottles each containing 100 mL solution. The bottles were shaken in a temperature-controlled shaker (Gallenkamp Orbital Incubator) at a constant speed of 180 rpm. Preliminary experiments showed that adsorption equilibrium was reached within 120 min. At the end of the equilibrium period the contents of the bottles were filtered and the supernatant was subsequently analyzed for residual concentration of 4-CP following the direct photometric method [16]. The method based on the spectrophotometric analysis of the developed color resulting from the reaction of 4-CP with 4-aminoantipyrine. Absorbance of colored samples was measured at 500 nm after 15 min. of reaction by UV/vis Spectrophotometer (Jenway 6105 UV/vis Spectrophotometer).

The effect of temperature on the adsorption characteristics was investigated by determining the adsorption isotherms at 298, 308, and 318 K. Thermodynamic parameters of adsorption have been determined using classical thermodynamic equations.

3. Results and discussion

3.1. Contact time and optimum dosage

The effect of the adsorbent dosage on the adsorption of 4-CP on XAD-4 resin is shown in Fig. 1. XAD-4 dosage was varied between 1 and 20 g/L and equilibrated for 120 min. It can

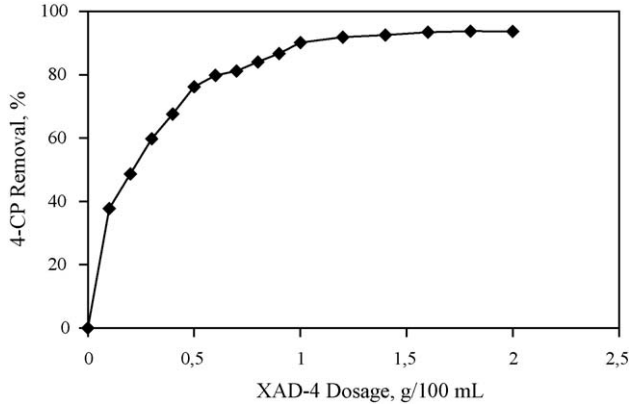

Fig. 1. Effect of XAD-4 dosage on 4-CP removal (T = 298 K; contact time = 120 min; C_0 = 100 mg/L).

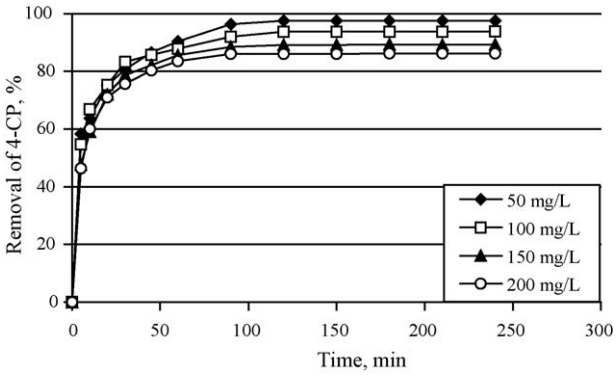

Fig. 2. Removal of 4-CP vs. contact time (XAD-4 dosage = 1 g/100 mL; C_0 = 100 mg/L).

be revealed from Fig. 1 that the removal of 4-CP increase with increase in XAD-4 dosage. The 4-CP removal efficiency of the XAD-4 resin was 90% at the adsorbent concentration of 10 g/L, while it is varied from 90% to 93% at adsorbent concentrations of 12–20 g/L. The removal of 4-CP at XAD-4 dosage greater than 10 g/L remains almost constant. Thus, the equilibrium concentration is considered to be 10 g/L (90% removal) for XAD-4 resin.

The preliminary experiments showed that the adsorption of 4-CP is fast at the initial stages and becomes slower near the equilibrium. Fig. 2 presents the plot of 4-CP removal versus contact time for XAD-4 resin at initial concentrations between 50 and 200 mg/L at 298 K with a contact time of 240 min. The rate of 4-CP removal is very rapid during the initial 30 min and decreases thereafter, as can be seen from Fig. 2. It is revealed that there was no considerable change for 4-CP removal after 120 min of contact time for different initial concentrations.

Temperature has a pronounced effect on the adsorption capacities of the adsorbents. Fig. 3 shows the plots of adsorption isotherms, q_e versus C_e, for 4-CP adsorption by XAD-4 resin at different temperatures of 298, 308, and 318 K. It was indicated that 4-CP adsorption capacity decreased with increasing temperature. The decrease in the adsorption capacity at increased temperature indicated the exothermic nature of the adsorption process of 4-CP onto XAD-4 resin. Similar results were

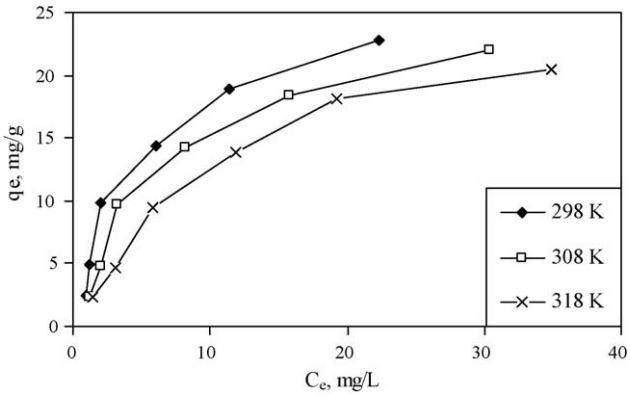

Fig. 3. Equilibrium adsorption isotherms at different temperatures (XAD-4 dosage = 10 g/L).

observed in the literature for 4-CP adsorption by macroreticular resins [11]. The increase in the temperature from 298 to 318 K decreases the adsorption capacity from 22.8 to 20.5 mg/g confirming the exothermic nature of the adsorption process.

3.2. Adsorption isotherms

An adsorption isotherm describes the relationship between the amount of adsorbate that is adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. Several two or three parameter models have been published in the literature to describe experimental data of adsorption isotherms. The Langmuir and Freundlich models are the most frequently used models. The Langmuir model is obtained under the ideal assumption of a totally homogenous adsorption surface, whereas the Freundlich isotherm is suitable for a highly heterogenous surface. The Redlich–Peterson equation is a combination of Langmuir and Freundlich models. The Toth isotherm model also combines the characteristics of the Langmuir and Freundlich isotherms [17].

In this study, the adsorption of 4-CP on Amberlite XAD-4 resin at different temperatures is evaluated and compared with popular two and three parameter single solute isotherm models given in Table 3.

The two parameters in the Langmuir and Freundlich equations can be determined graphically by linear regression. However, Redlich–Peterson, and Toth equations could not be solved graphically. Thus, the constants of these three parameter equations can be determined by using non-linear regression. The batch isothermal data fitted to the four models used in this study

Table 3
Isotherm models adopted in this work and their parameters

Isotherm	Model
Freundlich	$q_e = k_F \cdot C_e^{1/n}$
Langmiur	$q_e = \frac{Q_0 \cdot k_L \cdot C_e}{1+k_L \cdot C_e}$
Redlich–Peterson	$q_e = \frac{k_{RP} \cdot C_e}{1+p_e \cdot C_e^g}$
Toth	$q_e = \frac{A \cdot C_e}{(B+C_e^D)^{1/D}}$

solved by using the curve fitting toolbox of MATLAB program. The sum of squares due to the errors (SSE), the residual degrees of freedom (R^2), and the root mean square errors (RMSE) of the obtained models are calculated so as to evaluate the goodness of fit. The adsorption isotherms of 4-CP for different temperatures are shown in Fig. 4. The fitted parameter values are listed in Table 4. As can be seen from Fig. 4 and Table 4, the experimental data can be fitted well except for the Freundlich model.

The fit of the data to Freundlich isotherm indicates the heterogeneity of the sorbent surface. It has been stated by [18] that magnitude of the exponent $1/n$ gives an indication of the favorability and capacity of the adsorbent/adsorbate system. Values $n > 1$ represent favorable adsorption conditions. In most cases, the exponent between $1 < n < 10$ shows beneficial adsorption.

It is indicated that the three-parameter models resulted in better fittings than the two-parameter models. In this study, three parameter model, Redlich–Peterson, fitted the experimental data a little better than the Langmuir and the Toth models. Although all the evaluated equilibrium models, except Freundlich model, fitted well to the experimental data, the Redlich–Peterson model is the best model describing the adsorption of 4-CP on the XAD-

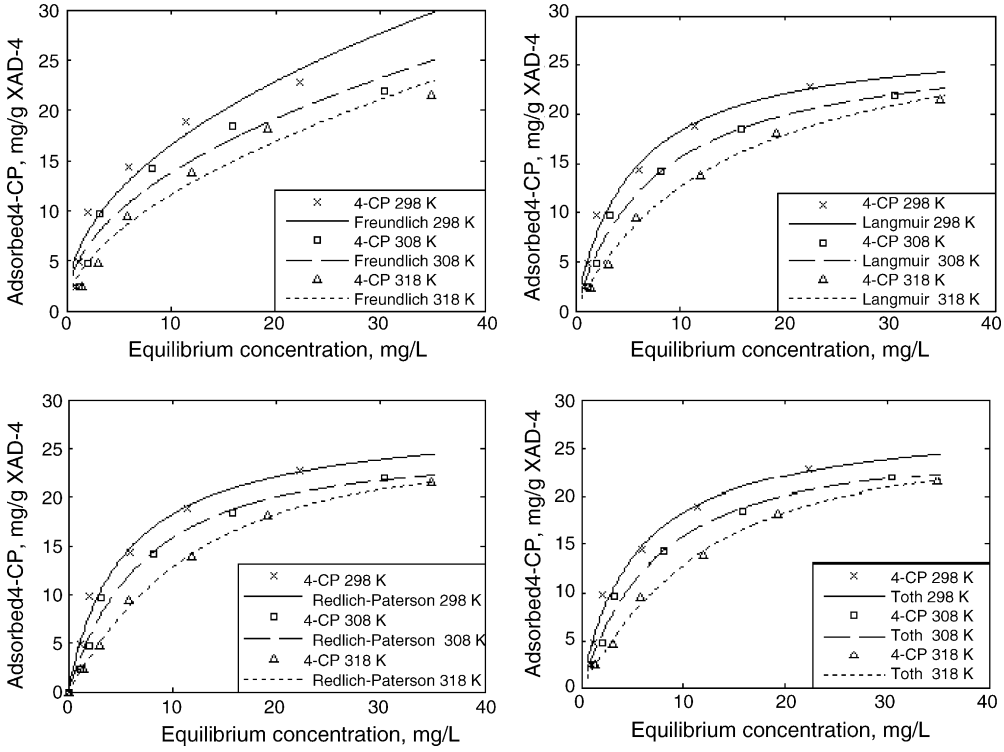

Fig. 4. Comparison of different isotherm models for 4-CP adsorption on XAD-4 resin.

Table 4
Isotherm parameters for 4-CP adsorption on XAD-4 resin at different temperatures

Isotherm model	Temperature (K)	Model parameters
Freundlich	298	$k_F = 5.630$; $n = 2.137$; $R^2 = 0.9551$; SSE = 19.91; RMSE = 1.996
	308	$k_F = 4.620$; $n = 2.108$; $R^2 = 0.9551$; SSE = 18.69; RMSE = 1.934
	318	$k_F = 3.305$; $n = 1.836$; $R^2 = 0.9735$; SSE = 10.56; RMSE = 1.453
Langmuir	298	$k_L = 0.1897$; $Q_0 = 27.91$; $R^2 = 0.9825$; SSE = 7.753; RMSE = 1.245
	308	$k_L = 0.1293$; $Q_0 = 27.59$; $R^2 = 0.9879$; SSE = 5.029; RMSE = 1.003
	318	$k_L = 0.0689$; $Q_0 = 30.89$; $R^2 = 0.9968$; $SSE = 1.279$; $RMSE = 0.506$
Redlich–Peterson	298	$k_{RP} = 5.385$; $p_e = 0.2019$; $g = 0.9858$; $R^2 = 0.9825$; SSE = 7.744; RMSE = 1.391
	308	$k_{RP} = 3.315$; $p_e = 0.0934$; $g = 1.072$; $R^2 = 0.9884$; SSE = 4.846; RMSE = 1.101
	318	$k_{RP} = 1.851$; $p_e = 0.0287$; $g = 1.194$; $R^2 = 0.9979$; SSE = 0.826; RMSE = 0.454
Toth	298	$A = 27.05$; $B = 4.951$; $D = 0.9858$; $R^2 = 0.9755$; SSE = 7.744; RMSE = 1.607
	308	$A = 33.13$; $B = 10.71$; $D = 1.072$; $R^2 = 0.9836$; SSE = 4.846; RMSE = 1.271
	318	$A = 53.94$; $B = 34.81$; $D = 1.194$; $R^2 = 0.9971$; SSE = 0.8256; RMSE = 0.525

4 resin, as it has the maximum R^2 values at all temperatures. According to the results of the study best isotherm models fitted to 4-CP adsorption on XAD-4 resin were determined in the order of Redlich–Peterson > Langmuir > Toth > Freundlich isotherms.

3.3. Adsorption kinetics

Kinetic models are used to determine the rate of the adsorption process. Four kinetic models pseudo-first-order, pseudo-second-order, intra-particle diffusion, and Bangham models were used to investigate the adsorption process of 4-CP on XAD-4 resin.

A series of contact time experiments were carried out with constant initial 4-CP concentration of 100 mg/L and constant XAD-4 resin dosage of 10 g/L at 298, 308, and 318 K. The linearized forms of the pseudo-first and pseudo-second-order models with the other two models, intra-particle diffusion, and Bangham, used in this study are given in Table 5. Kinetic equations solved by the help of MATLAB program and the parameters of the models were determined.

The plots of $\log(q_e - q)$ against t for the pseudo-first-order equation give a linear relationship and k_1 and q_e values can be determined from the slope and the intercept of this equation, respectively. Fig. 5(a) shows the plots of the linearized form

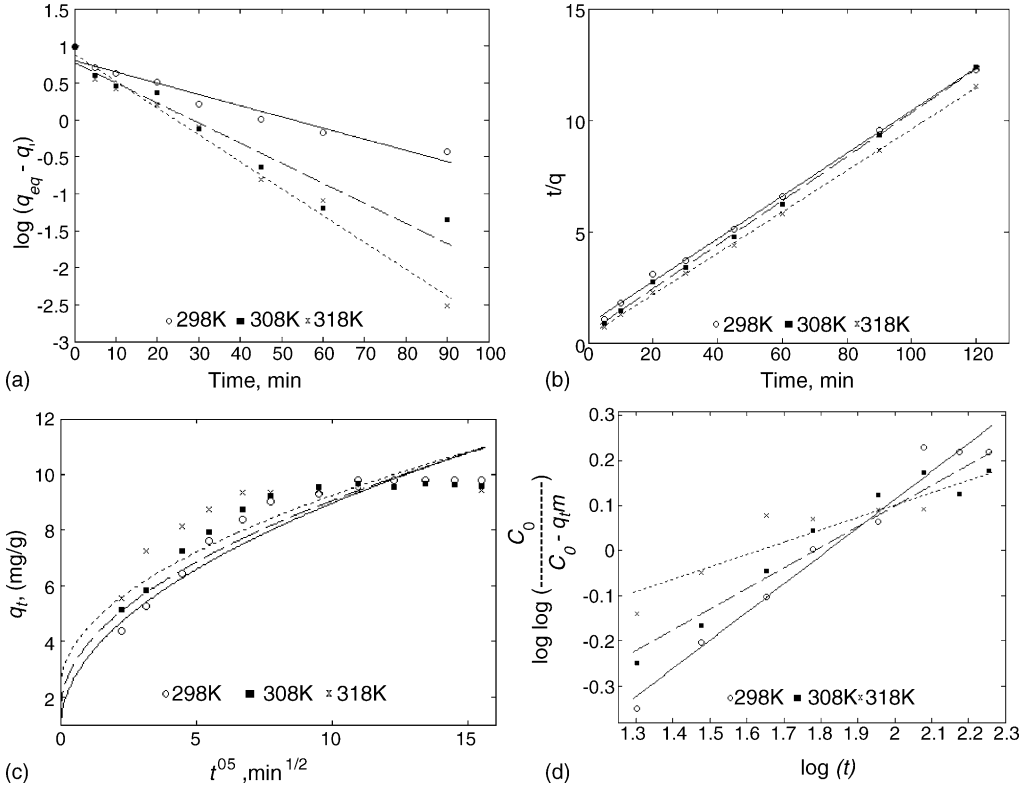

Fig. 5. Adsorption kinetics of 4-CP at different temperatures ($C_0 = 100$ mg/L; XAD-4 dosage = 10 g/L; (a) pseudo-first-order; (b) pseudo-second-order); (c) intra-particle diffusion model; (d) Bangham's model.

Table 5
Kinetic models and their equations used in this study

Model	Equation
Pseudo-first-order	$\log(q_e - q) = \log(q_e) - \frac{k_1}{2.303}t$
Pseudo-second-order	$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$
Intra-particle diffusion	$q = k_{id}t^{1/2} + C$
Bangham	$\log\log\left(\frac{C_0}{C_0 - q\times m}\right) = \log\left(\frac{k_b \times m}{2.303 \times V}\right) + a\log(t)$

of the pseudo-first-order equation. Kinetic parameters along with correlation coefficients of the kinetic models are shown in Table 6. As can be seen from Fig. 5 and Table 6, despite the correlation coefficients for the first-order kinetic model obtained at 298, 308, and 318 K are quite high (>0.90), the calculated q_e values do not give reasonable values, so the adsorption of 4-CP on XAD-4 resin do not fit this equation.

The q_e and k_2 values of the pseudo-second-order kinetic model can be determined from the slope and the intercept of the plots of t/q versus t, respectively. Fig. 5(b) gives the results of the linearized form of the pseudo-second-order kinetic model. The calculated q_e values are closer to the experimental data than the calculated values of pseudo-first-order model. Therefore, the adsorption of 4-CP can be approximated more favorably by the pseudo-second-order model. Error functions as shown in Table 6 are also considerably less and the correlation coefficients are very high for pseudo-second-order kinetic model reinforcing the applicability of this model.

The adsorbate transport from the solution phase to the surface of the adsorbent particles occurs in several steps. The overall adsorption process may be controlled by one or more steps, such as film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or a combination of more than one step. The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model [19]. The intra-particle diffusion model equation is given in Table 5. The value C (mg/g) in this equation is a constant that gives idea about the thickness of the boundary layer, larger the value the greater is the boundary effect [19]. If the plot of q versus $t^{0.5}$ gives a straight line, than the adsorption process is controlled by intra-particle diffusion only. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process.

The plots of q versus $t^{0.5}$ are given in Fig. 5(c) for the adsorption of 4-CP onto XAD-4 resin at different temperatures. It can be seen from the figure that the adsorption data could be fitted by two straight lines, but do not fit to the existing model. Thus the experimental data do not fit the intra-particle model data. The deviation of the straight line indicates that the pore diffusion is not the only rate limiting step. The error functions and the kinetic parameters given in Table 6 are representing that the intra-particle diffusion model shows lower representation of the data than the pseudo-first-order kinetic model.

Kinetic data can further be used to check whether pore-diffusion is the only rate-controlling step or not in the adsorption system using Bangham's equation given in Table 5. If the experimental data represented by this equation then the adsorption kinetics are limited by the pore diffusion. However, the experimental data do not give a good fit to the model data as expressed in Fig. 5(d). This situation represents that the diffusion of adsorbate into pores of the sorbent is not the only rate-controlling step. Kinetic parameters and the correlation coefficients obtained by the Bangham's equation are given in Table 6 and the data are exploring poorer fit of the model.

3.4. Determination of thermodynamic parameters

The Gibbs free energy change ΔG°, indicates the degree of the spontaneity of the adsorption process. For significant adsorption to occur, the free energy changes of adsorption, ΔG°, must be negative. The Gibbs free energy change of adsorption is defined as;

$$\Delta G^\circ = -RT\ln K \tag{1}$$

The effect of temperature on the equilibrium constant is determined as follows:

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{2}$$

After integration and rearrangements Eq. (2) gives;

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{3}$$

Table 6
Kinetic parameters for the adsorption of 4-CP onto XAD-4 resin at different temperatures

Kinetic model	Temperature	Kinetic parameters
Pseudo-first-order	298	$k_1 = 0.03496$; $q_e = 6.294$; SSE = 0.09039; $R^2 = 0.9447$; RMSE = 0.1227
	308	$k_1 = 0.06252$; $q_e = 5.893$; SSE = 0.3283; $R^2 = 0.9376$; RMSE = 0.2339
	318	$k_1 = 0.08366$; $q_e = 7.68$; SSE = 0.1165; $R^2 = 0.987$; RMSE = 0.1394
Pseudo-second-order	298	$k_2 = 0.01106$; $q_e = 10.42$; SSE = 0.1878; $R^2 = 0.9982$; RMSE = 0.1769
	308	$k_2 = 0.02142$; $q_e = 10.13$; SSE = 0.02838; $R^2 = 0.9988$; RMSE = 0.151
	318	$k_2 = 0.02838$; $q_e = 10.76$; SSE = 0.03487; $R^2 = 0.9996$; RMSE = 0.07624
Intra-particle diffusion	298	$k_{id} = 2.569$; $C = 0.8416$; SSE = 6.076; $R^2 = 0.9417$; RMSE = 0.7432
	308	$k_{id} = 2.397$; $C = 1.489$; SSE = 9.251; $R^2 = 0.9023$; RMSE = 0.917
	318	$k_{id} = 2.202$; $C = 2.286$; SSE = 16.36; $R^2 = 0.8151$; RMSE = 1.22
Bangham's equation	298	$k_b = 0.007409$; $a = 0.6235$; SSE = 0.009194; $R^2 = 0.9671$; RMSE = 0.03915
	308	$k_b = 0.01018$; $a = 0.274$; SSE = 0.0121; $R^2 = 0.9228$; RMSE = 0.04491
	318	$k_b = 0.01473$; $a = -0.45$; SSE = 0.01002; $R^2 = 0.8361$; RMSE = 0.04087

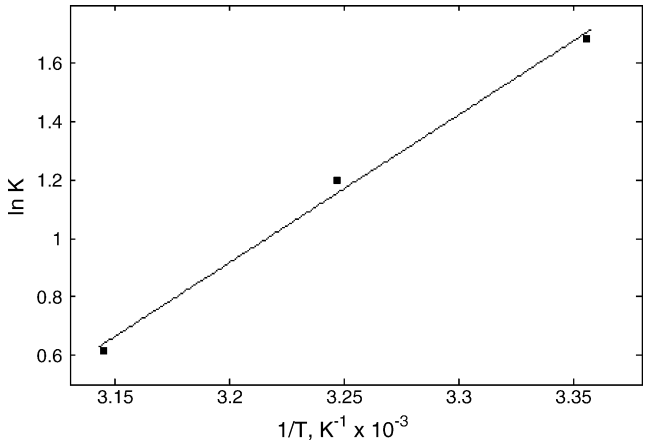

Fig. 6. $\ln K$ vs. $1/T$ plot of adsorption equilibrium constant k_{RP}, using Redlich–Peterson isotherm.

Table 7
ΔG° values for the adsorption of 4-CP on XAD-4 resin at different temperatures

T (K)	k_{RP} (L/g)	ΔG° (kJ/mol)
298	5.385	−4.17
308	3.315	−3.07
318	1.851	−1.63

and

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \quad (4)$$

ΔH° and ΔS° can be determined from the slope and the intercept of the linear plot of $\ln K$ versus $1/T$.

The equilibrium constants obtained from the best fitted model (Redlich–Peterson, k_{RP}) at 298, 308, and 318 K were used to determine the Gibbs free energy changes by the help of MATLAB program in Fig. 6. Table 7 gives the free energy values for the adsorption process. The values of the standard enthalpy and the entropy changes were determined as −42.01 kJ/mol and −0.127 kJ/(mol K) from Fig. 6 ($R^2 = 0.995$), respectively. The negative value of ΔH° suggests the exothermic nature of the adsorption. ΔH° derived from the k_{RP} with XAD-4 is less than 45 kJ/mol, which is comparable to those reported for adsorption of phenols on non-ionic polymeric resins [15]. Based on the apparent enthalpy changes of adsorption (<45 kJ/mol), the uptake of 4-CP on non-ionic polymeric XAD-4 resin is a type of transition between physical and chemical adsorption [15].

ΔG° values were negative indicating that the sorption process led to a decrease in Gibbs free energy. Negative ΔG° values indicate the feasibility and spontaneity of the adsorption process.

4. Conclusions

The isotherms for the adsorption of 4-CP from aqueous solutions by Amberlite XAD-4 macroreticular polymeric resin have been analyzed. Optimum adsorbent dose observed as 10 g/L of solution for 4-CP concentrations higher than 50 mg/L. The equilibrium between 4-CP and the XAD-4 resin was achieved in approximately 120 min with 90% removal of 4-CP. According to the comparison of the two-parameter models, the Langmuir model was found to give a better fitting than the Freundlich model. However, the other two three-parameter isotherm models Redlich–Peterson and Toth, were both in better agreement with the experimental data. Although all the evaluated equilibrium models, except Freundlich model, fitted well to the experimental data, the Redlich–Peterson model is the best model describing the adsorption of 4-CP on the XAD-4 resin, as it has the maximum R^2 values. Adsorption kinetics was found to follow the pseudo-second-order model expression. The negative value of ΔG° indicates the feasibility and spontaneity of the adsorption process. The negative value of ΔH° suggests the exothermic nature of the adsorption. The present results on temperature effect show the uptake of 4-CP on XAD-4 resin to be a type of transition between physical and chemical adsorption.

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