

Studies on Sorption Isotherm Models of Ion Exchange Modified Acrylic Fibers

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ABSTRACT: The sorption behavior, favorability, shape and thermodynamic parameters of Cu(II), Ni(II), Pb(II), and Fe(III) ions sorption onto the ion exchange acrylic fiber were studied by applying Langmuir, Freundlich, Dubinin-Radushkevich and Redlich-Peterson models. Analytical studies from sorption isotherms proved that sorption process follows mono layer adsorption mechanism. Gibbs free energy was spontaneous for all interactions. The adsorption processes all exhibited endothermic

enthalpy values and were accompanied by increasing in entropy. The activation energies for the sorption of metal ions on aminated acrylic fiber were at the same order of magnitude as the activation energy of ion exchange. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 135–142, 2010

Key words: ion exchange fiber; sorption isotherm; heavy metal ions; acrylic fibers; sorption behavior

INTRODUCTION

Ion-exchange fibers have been widely used in various applications due to their high separation capacity, fast ion-exchange rate and good osmosis stability.¹ The applications of such fibers are wide ranging and include the separation and pre concentration of rare earth elements,² enrichment of uranium from seawater,³ purification of air by the removal of acidic or alkaline impurities, etc.⁴

The most appropriate method in designing the sorption systems and in assessing the performance of the sorption systems is to have an idea on sorption isotherms. In other words the adsorption isotherm is important to describe how solutes interact with adsorbent and empirical or theoretical equations is thus essential to practical operation

The adsorption isotherms of various classes of compounds on different surfaces have been classified according to their shapes. In the literature four types of isotherm have been reported⁵ i.e., (i) the Langmuir type (L) with an initial concavity to the concentration axis, (ii) the S-type with an initial convexity to the concentration axis, (iii) the H-type resulting from extremely strong adsorption and having an intercept on the ordinate and (iv) the C-type having an initial linear portion.

There are many sorption isotherms that are classified according to their parameters as follows; single parameter model, Henry's law,⁶ two parameter models, namely Freundlich,⁷ Langmuir,⁸ Dubinin-Radushkevich (DR),⁹ Temkin,¹⁰ Halsey,¹¹ and Gin,¹² three-parameter models, namely Redlich-Peterson,¹³ Sips,¹⁴ Khan,¹⁵ Radke-Prausnitzr,¹⁶ Toth,¹⁷ and Koble-Carrigan,¹⁸ and the four- and five-parameter models of Fritz and Schlunder¹⁹ isotherms in their nonlinear form.

Most of these isotherms are unfamiliar and calculation of their parameters is so difficult.

Langmuir and Freundlich models (two-parameter models) are the most commonly used isotherms to interpret equilibrium isotherm data. Simplicity and easy interpretability are some of the important reasons for extensive use of these models.

Most of the published literatures have used two or three isotherm models, mainly Freundlich, Langmuir, and DR to describe sorption process and almost many sorption processes can be fitted by one or two of these models. But in most literatures did not pay much attention to valuable parameters can be derived from these isotherms such as thermodynamic of sorption process and energy of sorption that identifying the sorption is physical, chemical or ion exchange.

Therefore, in this work first, ion sorbent acrylic fiber according to our previous works^{20,21} under optimized conditions were prepared and then most popular isotherm models include Langmuir, Freundlich, DR, and Redlich-Peterson models were applied

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to describe the distribution of metal ions between the solution and the modified acrylic fiber. The reasons for choosing these isotherms are as follows:

Langmuir and Freundlich isotherms were applied because they are most popular and simple isotherms. In Langmuir isotherm it is emphasized that the sorption is monolayer. In Redlich-Peterson isotherm it is assumed that the sorption process is not ideal monolayer.¹³ Therefore it seems that if Langmuir isotherm was fitted to experimental data, the Redlich-Peterson isotherm was applied to identify the sorption is ideal monolayer or not. Meanwhile the Henry isotherm is the special aspect of Redlich-Peterson isotherm. The energy of sorption was calculated by using DR isotherm.

In other words by applying Langmuir, Freundlich, DR, and Redlich-Peterson models in addition to describing the distribution of sorbate between the solution and the sorbent, the important parameters for identifying sorption process can be obtained. Moreover, by calculating these isotherm constants, favorability, spontaneity, energy of sorption and endothermic or exothermic of sorption process of metal ions on modified acrylic fibers were discussed. Using DR model when there is not any estimating about the rate of sorption process and therefore activation energy of sorption is more useful. If not by applying Langmuir model, obtaining constant parameters of model and calculating the rate of sorption and activation energy the nature of sorption (physical, chemical or ion exchange) can be understand.

MATERIALS AND METHODS

Materials

Commercial acrylic fiber with 3.3 dtex containing 93% polyacrylonitrile, 6% methyl acrylate and 1% sodium acrylamide 2-methylpropane sulfonate was supplied from Polyacryl Co. and modified with hydroxylamine hydrochloride under optimized condition obtained in our previous works.^{20,21} All chemicals consisting of Cu(II), Ni(II), Pb(II) and Fe(III) nitrate were laboratory reagent grade and supplied from Merck Co.

Equilibrium sorption isotherms

Adsorption isotherm experiments were conducted using solutions of different concentration of metal ions. All experiments were conducted by adding 2 g of modified fibers into 100 mL reagent bottles containing 50.0 mL of the metal solution under optimized pH for each metal ion which is reported by Zargaran.²¹ The mixtures in these bottles were agitated for a predetermined time in a water bath shaker at 298, 308, 318, and 328 K. Different metal

initial concentrations were used (0.5–10 mmol/L). After 2 h which equilibrium was attained,²¹ the concentration of metal ions was determined using an atomic absorption spectrophotometer. The amount of metal adsorbed by the fiber was calculated using the following equation:

$$Q_e = \frac{C_0 - C_e}{W} V \quad (1)$$

where Q_e is the amount of metal adsorbed by the modified fiber (mmol/g) at equilibrium, C_0 is the initial concentration of metal ion (mmol/L), C_e is the concentration of metal ion at equilibrium (mmol/L), V is the initial volume of metal solution (L), and W is the mass of the modified fiber (g).

RESULTS AND DISCUSSION

Determination of equilibrium model constants

Analysis of equilibrium data is important for developing an equation that can be used for designing purposes. Langmuir, Freundlich, DR and Redlich-Peterson adsorption models are examined to describe the sorption phenomena of Cu(II), Ni(II), Pb(II) and Fe(III) to aminated acrylic fiber (AAF) fiber.

Langmuir isotherm model

The Langmuir isotherm is based on the assumption that (i) maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, (ii) the surface of the fiber has the same activity for adsorption, (iii) there is no interaction between adsorbed molecules and all the adsorption occurs by the same mechanism and there is no transmigration of the adsorbate in the plane of the surface. This isotherm is represented by the following equation:

$$Q_e = \frac{Q_m b C_e}{1 + b C_e} \quad (2)$$

The Langmuir equation can be determined from the linearized form of eq. (2), represented by eq. (3).

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{1}{Q_m} C_e \quad (3)$$

where C_e is the equilibrium concentration of metal ions (mmol/L), Q_e is the amount of adsorbed metal (mmol/g). The constant b is the Langmuir constant (L/mmol). The Q_m represents the maximum adsorption capacity (mmol/g) and represents a practical limiting adsorption capacity when the surface is

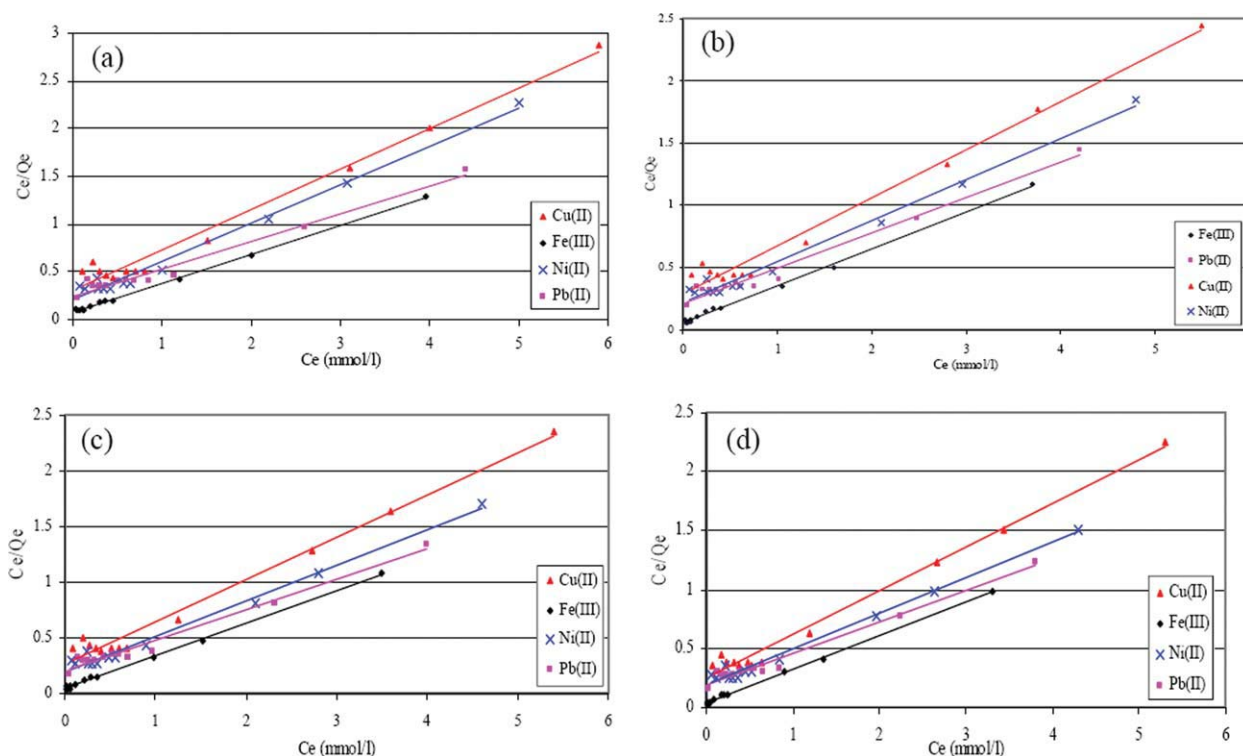


Figure 1 The plot of Langmuir isotherm at different temperatures (a) 298, (b) 308, (c) 318, (d) 328 K. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

fully covered with metal ions and assists in the comparison of adsorption performance, particularly in cases where the sorbent did not reach its full saturation during the experiments.

Therefore, the plots of C_e/Q_e versus C_e give a straight line with the slope of $1/Q_m$ and intercept of $1/Q_m b$. The linearized Langmuir model was tried to represent the experimental data of metal ion onto AAF. The Langmuir constant b is equilibrium constant²² and may be used to determine the enthalpy of the adsorption, ΔH .²³

The linearized Langmuir sorption isotherm of each metal ion obtained at the temperatures of 300, 310, 320, and 330 K are given in Figure 1. The adsorption isotherm constants were determined by using linear regression.

The constants and the correlation coefficient are given in Table I.

The results show that, the experimental data is close to the Langmuir model specially for Fe(III) ions.

Q_m represents the adsorption capacity when the surface is fully covered with metal ions. The

TABLE I
Langmuir Constants for Various Metal Ions at Different Temperatures

Metal	Temp (K)	Equation	R^2	Q_m (mmol/g)	b (L/mmol)
Cu(II)	298	$y = 0.4241x + 0.3046$	0.9819	2.3579	1.3923
	308	$y = 0.3856x + 0.2876$	0.9825	2.5933	1.3407
	318	$y = 0.3769x + 0.2704$	0.9837	2.6532	1.3939
	328	$y = 0.3722x + 0.2415$	0.9878	2.6867	1.5412
Ni(II)	298	$y = 0.4008x + 0.2087$	0.9856	2.4950	1.9204
	308	$y = 0.3291x + 0.2154$	0.9853	3.0386	1.5278
	318	$y = 0.317x + 0.2002$	0.9859	3.1546	1.5834
	328	$y = 0.3031x + 0.1871$	0.9869	3.2992	1.6199
Pb(II)	298	$y = 0.3098x + 0.1845$	0.9900	3.2280	1.6791
	308	$y = 0.3041x + 0.1581$	0.9912	3.2884	1.9235
	318	$y = 0.2981x + 0.1373$	0.9912	3.3546	2.1711
	328	$y = 0.2922x + 0.122$	0.9903	3.4223	2.3951
Fe(III)	298	$y = 0.3037x + 0.0778$	0.9979	3.2927	3.9036
	308	$y = 0.2973x + 0.0578$	0.9971	3.3636	5.1436
	318	$y = 0.2926x + 0.0452$	0.9976	3.4176	6.4734
	328	$y = 0.2886x + 0.0309$	0.9978	3.4650	9.3398

TABLE II
 R_L Values for Various Concentrations of Metal Ions

Conc. R_L	0.5 (mmol/g)	1 (mmol/g)	1.5 (mmol/g)	2 (mmol/g)	2.5 (mmol/g)	3 (mmol/g)	3.5 (mmol/g)	4 (mmol/g)	5 (mmol/g)	7 (mmol/g)	8 (mmol/g)	10 (mmol/g)
Cu^{2+}	0.59	0.42	0.32	0.26	0.22	0.19	0.17	0.15	0.13	0.09	0.08	0.07
Ni^{2+}	0.51	0.34	0.26	0.21	0.17	0.15	0.13	0.11	0.09	0.07	0.06	0.05
Pb^{2+}	0.54	0.37	0.28	0.23	0.19	0.16	0.14	0.13	0.11	0.09	0.07	0.06
Fe^{3+}	0.34	0.20	0.15	0.11	0.09	0.08	0.07	0.06	0.05	0.03	0.03	0.02

adsorption capacity of AAF increased with increasing the temperature and the maximum adsorption capacity, Q_m , of metal ions onto AAF is between 2.35 and 3.46 mmol/g against negligible value for native acrylic fiber. The maximum Q_m values were determined as 2.68, 3.30, 3.42, and 3.46 mmol/g at 328 K for Cu(II), Ni(II), Pb(II), and Fe(III) ions, respectively. The value of correlation coefficient, R^2 is over 0.98 indicates that the adsorption of metal ions onto AAF is fitted well on the Langmuir isotherm (obey Langmuir isotherm).

A high b value indicates the affinity for binding of metal ions. The highest value of b was found at 330 K for each metal ion.

The essential features of Langmuir adsorption isotherm can be expressed in terms of dimensionless constant called separation factor or equilibrium parameter (R_L). To confirm the favorability of the metal sorption process, the separation factor was calculated by the following equation²⁴:

$$R_L = 1/(1 + bC_0) \quad (4)$$

where " R_L " is a dimensionless separation factor indicating the shape of the isotherm, b is the Langmuir constant and C_0 is the initial adsorbate concentration. The isotherm is (i) unfavorable when $R_L > 1$, (ii) linear when $R_L = 1$, (iii) favorable when $R_L < 1$, and (iv) irreversible when $R_L = 0$.

The values of R_L for different concentrations of metal ions onto AAF are given in Table II. It is clear from Table II that the values of R_L lie between 0.059 and 0.07 for Cu(II), 0.51 and 0.05 for Ni(II), 0.54 and 0.06 for Pb(II) and 0.34 and 0.02 for Fe(III) ions onto AAF indicating a favorable adsorption of metal ions onto AAF.

Freundlich isotherm model

Freundlich equation was also applied for sorption of metals onto AAF. The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface. It is often useful as a means for data description. The Freundlich equation is commonly represented as:

$$Q_e = K_F C_e^{1/n} \quad (5)$$

and the eq. (5) may be linearized by taking logarithms as follows:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (6)$$

where Q_e is the amount of adsorbate adsorbed on the surface of adsorbent (mmol/g), C_e is the equilibrium concentration of the adsorbate (mmol/L) and

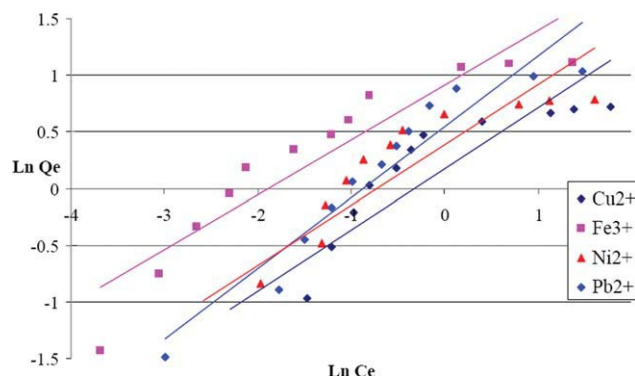


Figure 2 The plot of Freundlich equation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

K_F and n are Freundlich constants related to adsorption capacity and favorability of adsorption, respectively. In general, as the K_F value increases, the adsorption capacity of the adsorption for metal increases. Values of n between 1 and 10 show favorable of sorption on adsorbent.²⁵ The plots of $\ln Q_e$ against $\ln C_e$ give a straight line with the slope and intercept of which corresponds to $1/n$ and $\ln K_F$, respectively.

Freundlich plots for metal ions onto AAF are shown in Figure 2. The values of Freundlich constants are listed in Table III. It is clear from Table III that the values of n over 1.70 for metal ions (i.e. $0 < n < 10$) showing that the adsorption of metal ions onto AAF is favorable. The correlation coefficient, R^2 value (Table III) of metal ions was in the range 0.8–0.9 indicating that the adsorption of metal ions onto AAF is not fitted well on Freundlich equation rather than Langmuir model.

Redlich–Peterson isotherm model

The three-parameter Redlich–Peterson equation has been proposed to improve the fit by the Langmuir or Freundlich equation and is given by eq. (7):

$$Q_e = \frac{K_R C_e}{1 + a_R C_e^\beta} \quad (7)$$

where K_{RP} , a_{RP} , and β are the Redlich–Peterson parameters. β lies between 0 and 1.²⁶ For $\beta = 1$, eq. (7) converts to the Langmuir form and for $\beta = 0$, eq. (7) converts to the Henry form ($(Q_e = \frac{K_R}{1+a_R} C_e)$). The

TABLE III
The Freundlich Parameters for Different Metal Ions

Metal ions	Equation	R^2	K_f	n
Cu(II)	$y = 0.5377x + 0.1723$	0.8044	1.188	1.86
Ni(II)	$y = 0.5297x + 0.386$	0.8106	1.471	1.89
Pb(II)	$y = 0.5831x + 0.5392$	0.9143	1.7146	1.71
Fe(III)	$y = 0.4827x + 0.9093$	0.8730	2.6990	2.07

TABLE IV
The DR Isotherm Parameters

Metal ion	K_1 (initial guess)	K	R^2	β	a
Cu(II)	3.2	21	0.7524	0.49	16.46
Ni(II)	4.8	4.8	0.7819	0.72	1.89
Pb(II)	5.41	11.8	0.8670	0.56	5.78
Fe(III)	12.8	12.8	0.9265	0.87	3.60

adsorption model constants were obtained by linear regression analysis method.

$$\ln \left[\left(\frac{K_j C_e}{Q_e} \right) - 1 \right] = \ln a_j + \beta \ln C_e \quad (8)$$

For lead ion the initial guess for K , obtained from Langmuir model ($K = bQ_m$),²⁶ is 5.41. But with this value, the parameter $\ln \left[\left(\frac{K_j C_e}{Q_e} \right) - 1 \right]$ will be uncertain. By other guesses of K , the values of R^2 were obtained. By selecting $K = 11.8$ the R^2 value reach to maximum point. The R^2 values and final K obtained from error and effort and DR isotherm parameters for different metal ions were listed in Table IV.

The results show that this isotherm could not fit to experimental data. In other words the distribution of metal ions between the solution and sorbent fibers is closer to ideal monolayer (Langmuir) model than RP model.

Determination of thermodynamic constants of sorption

The thermodynamic parameters, such as the standard free energy (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) have been estimated to evaluate the feasibility and exothermic nature of the sorption process. The Gibbs free energy change of the process is the fundamental criterion of spontaneity of a process and related to the equilibrium constant (b) by the following equation²⁶:

$$\Delta G^0 = -RT \ln b \quad (9)$$

where R is the universal gas constant (8.314 J mol⁻¹ K⁻¹) and T is the absolute temperature (K) and b is Langmuir constant. According to thermodynamics, the equilibrium constant is also related to enthalpy change and entropy change at constant temperature by the following Van't Hoff equation²⁶ [eq. (10)]:

$$\ln b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (10)$$

where R is the universal gas constant (8.314 J mol⁻¹ K⁻¹) and T is the absolute temperature (K) and b is Langmuir constant. The values of ΔH^0 and ΔS^0 are calculated from the slope and intercept of the plots of $\ln b$ versus $1/T$.

TABLE V
Gibbs Free Energy Changes for the Sorption Process of Metal Ions at Different Temperatures

Metal ion	Temp (K)	<i>b</i> (L/mmol)	ΔG (kJ/mol)
Cu(II)	298	1.3923	-0.8255
	308	1.3407	-0.7556
	318	1.3939	-0.8835
	328	1.5412	-1.1867
Ni(II)	298	1.9204	-1.6275
	308	1.5278	-1.0923
	318	1.5834	-1.2227
	328	1.6199	-1.3234
Pb(II)	298	1.6791	-1.2840
	308	1.9235	-1.6751
	318	2.1711	-2.0496
	328	2.3951	-2.3818
Fe(III)	298	3.9036	-3.3968
	308	5.1436	-4.2210
	318	6.4734	-4.9690
	328	9.3398	-6.1300

The Gibbs free energy changes for the sorption process were calculated by using the equilibrium constants obtained from Langmuir model and tabulated in Table V. As can be seen from the Table V, all the Gibbs free energy changes values are negative. A negative value of ΔG^0 indicates the feasibility of the process and spontaneous nature of the metal sorption on AAF.

The standard enthalpy and entropy changes of sorption were determined from the $\ln b$ versus $1/T$

TABLE VI
Thermodynamic Constants of Different Metal Ions

Metal ion	Equation	ΔH (kJ/mol)	ΔS (J/mol K)	R^2
Cu(II)	$y = -1010.6x + 4.6005$	8.4021	38.2436	0.9222
Ni(II)	$y = -467.54x + 3.0459$	3.8871	25.3236	0.9898
Pb(II)	$y = -784.8x + 3.8436$	19.5287	79.3505	0.9998
Fe(III)	$y = -17184x + 61.099$	142.8678	507.9771	0.9412

plot (Fig. 3). The values of these thermodynamic parameters and correlation coefficients are given in Table VI. The ΔH values are found to be positive indicating that the adsorption of metal ions by AAF is endothermic.

Evaluation of adsorption energy

For evaluating the adsorption energy, Dubinin-Radushkevick equation was analyzed according to eq. (11)²⁷:

$$Q_e = Q_m \exp(-B\varepsilon^2) \quad (11)$$

The eq. (11) may be linearized by taking logarithms as follows:

$$\ln Q_e = \ln Q_m - B\varepsilon^2 \quad (12)$$

in which:

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (13)$$

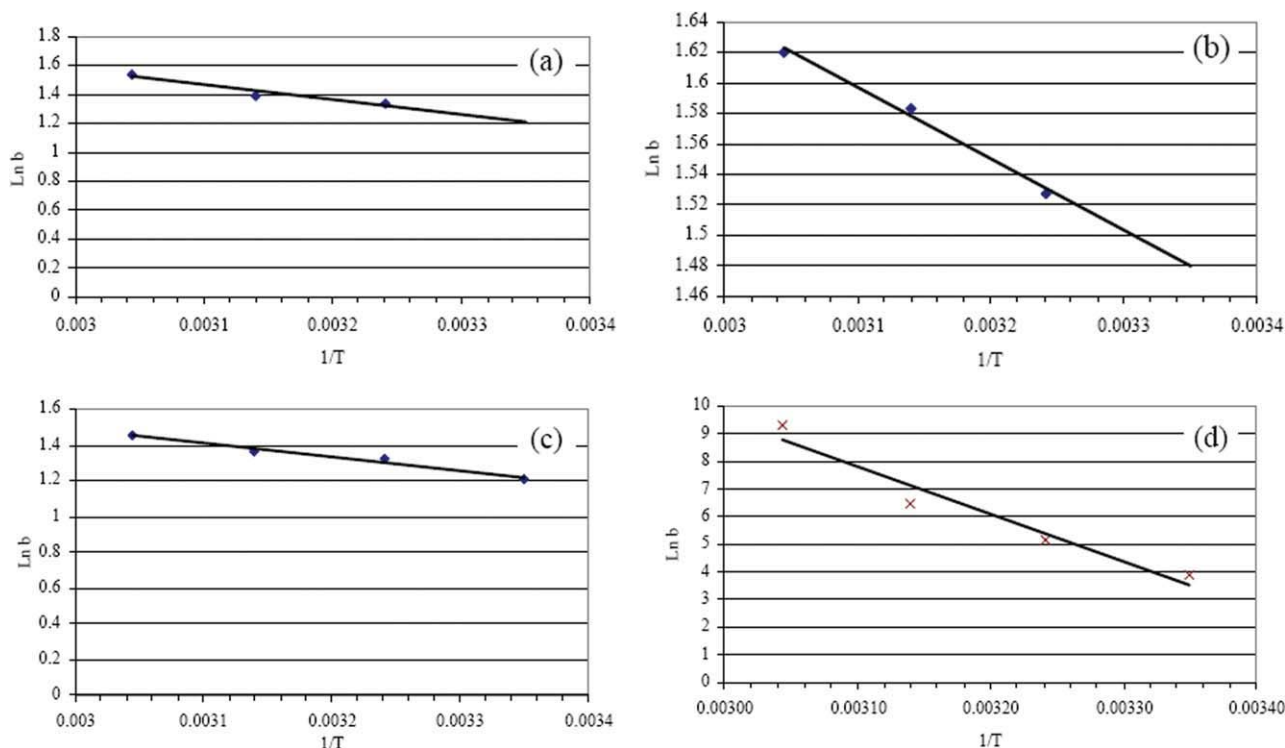


Figure 3 The plot of $\ln b$ versus $1/T$ from linear regression of DR isotherm for (a) Cu(II), (b) Ni(II), (c) Pb(II), and (d) Fe(III) ions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

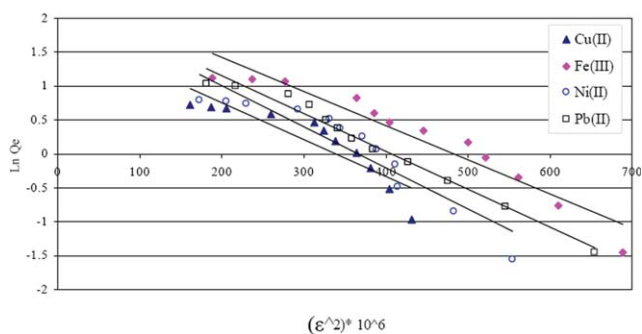


Figure 4 The plot of $\ln Q_e$ versus ε^2 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

where ε is the Polanyi potential (kJ/mol) [eq. (13)], Q_m is the monolayer capacity (mmol/g), and B is a constant related to adsorption energy (mol^2/kJ^2). The Q_m and B parameters have been evaluated from the intercepts and slopes of the plots of $\ln Q_e$ versus ε^2 (Fig. 4). The mean free energy of adsorption (E) is the free energy change when one mole of ion is transferred to the surface of the adsorbent from infinity in the solution,²⁷ and that has been calculated by eq. (14).

$$E = 1/(2B)^{0.5} \quad (14)$$

The evaluated Dubinin–Radushkevick parameters and mean free energies are given in Table VII. The magnitude of E_{DR} is useful for estimating the type of

TABLE VII
Calculation of E from DR Isotherm Constant for Different Metal Ions

Metal ion	Equation	R^2	β	E (kJ/mol)
Cu(II)	$y = -5E-09x + 1.8509$	0.81	5×10^{-9}	10
Ni(II)	$y = -6E-09x + 2.2299$	0.87	6×10^{-9}	9.13
Pb(II)	$y = -7E-09x + 2.5733$	0.98	6×10^{-9}	9.13
Fe(III)	$y = -5E-09x + 2.425$	0.93	5×10^{-9}	10

adsorption reaction, and if it ranged between 8 kJ/mol^{-1} and 16 kJ/mol^{-1} , the adsorption should be taken place by ion exchange reaction.^{27,28} In the present case, E_{DR} values obtained in the range of 8 kJ/mol^{-1} to 16 kJ/mol^{-1} indicate the adsorption of Cu(II), Ni(II), Pb(II), and Fe(III) on AAF takes place by ion exchange mechanism.

Figure 5 shows the application of all sorption models in the nonlinear form. It can be observed that comparing all the isotherm models, the predicted Langmuir model has the best fit to experimental data with a high correlation coefficient.

CONCLUSIONS

The equilibrium of sorption process for Cu(II), Ni(II), Pb(II), and Fe(III) ions onto the modified acrylic fiber was tested using Langmuir, Freundlich,

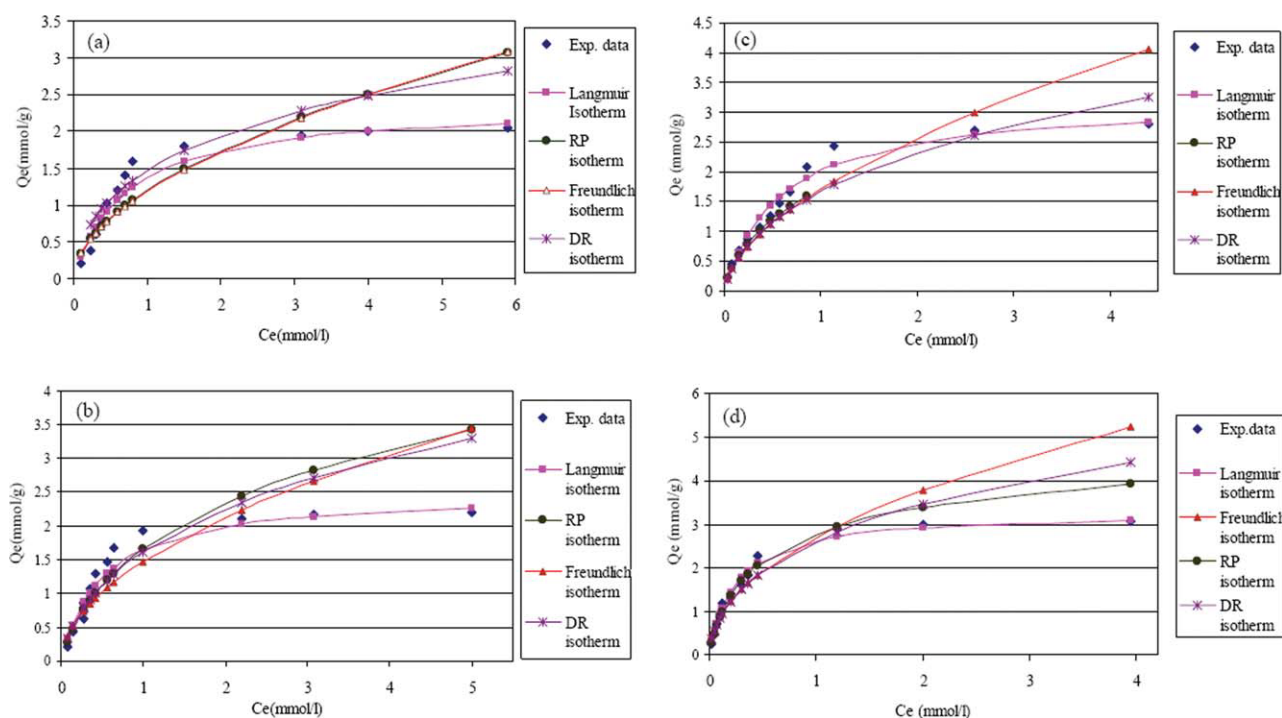


Figure 5 Comparison of sorption models to experimental data obtained from sorption of different metal ions on to AAF (a) Cu(II), (b) Ni(II), (c) Pb(II), (d) Fe(III) ions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

DR and Redlich–Peterson models. Although all the adsorption models applied seemed to agree well with the experimental data, the Langmuir equation was the best model that represented the experimental data. The models parameters obtained in this work can be used to estimate reactor volume, required sorption quantity for desired separation, purification degree, etc.

The activation energies for the sorption of metal ions on AAF were determined to be of the same order of magnitude as the activation energy of ion exchange. Thermodynamic constants were also evaluated using equilibrium constants changing with temperature. The negative value of ΔG^0 indicated the spontaneity of the process. The positive values of ΔH^0 and ΔS^0 showed the endothermic nature of metal ions sorption.

Consequently, each sorption process may be recognized by applying four isotherm models; Langmuir, Freundlich, DR and Redlich–Peterson. In any sorption process the following steps can be performed: In first step, Langmuir and Freundlich isotherms because of their simplicity can be applied for interpreting equilibrium isotherm data. Then if the Langmuir isotherm can be fitted to experimental data, in second step, the Redlich–Peterson model may be used to ensure that the sorption process is ideal monolayer or not. If the dominant isotherm was Langmuir model, in the third step, by calculating and using suitable equations, the valuable parameters can be derived from Langmuir model which can describe the favorability, tendency of sorbate to sorbent, endothermic or exothermic and spontaneity of sorption process. Meanwhile the physical, chemical or ion exchangeable process can be distinct by calculating the energy or sorption derived from DR model.

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