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Modeling of Adsorption of Bi(III) from Nitrate Medium by Impregnated Resin D2EHPA/XAD-1180

Nasr-Eddine Belkhouche*, Nacera Benyahia

Laboratory of Separation and Purification Technologies, Department of Chemistry-Faculty of Sciences, Tlemcen University, Algeria.
Email: nbelkhouche@yahoo.fr

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ABSTRACT

Di(2-*ethylhexyl*)*phosphoric acid* (*D2EHPA*) *in acetone was supported on the Amberlite XAD*-1180 *polystyrene divinylbenzene copolymer resin. The use of XAD*-1180 *impregnated with D2EHPA for the extraction of bismuth*(*III*) *from nitrate medium was carried out using batch technique. Various parameters affecting the uptake of this metal ion were described in the previous paper Reference* [1] *and the capacity of the impregnated resin for bismuth(III) was found to be* 490.7 *mg/g of resin. Effect of temperature on the values of distribution equilibrium was studied to evaluate the changes in standard thermodynamic quantities. A comparison of Langmuir forms I, II and Freundlich sorption isotherms was realized and the kinetic models applied to the adsorption rate data were evaluated for Lagergren first order, the pseudo second order and Morris–Weber models. From the results, the adsorption of Bi*(*III*) *onto D2EHPA/XAD*-1180 *resin shown the exothermic character and followed the Langmuir form II isotherm. Thus, the capacity of monolayer adsorption of Bi*(*III*) *was equal to* 769.23 *mg/g of resin. Both the Lagergren pseudo first order and film-diffusion models were found to best describe the experimental rate data.*

Keywords*: *Bismuth, XAD*-1180 *Resin, D2EHPA, Sorption Isotherms, Kinetic Models

1. Introduction

The previous paper [1] was devoted to study the kinetics of bismuth(III) extraction from nitrate medium by solvent impregnated resin technique (SIR) using the Amberlite XAD-1180 resin as support for di(2-ethylhexyl) phosphoric acid (D2EHPA) as organophosphorus extractant, in order to know the best operating conditions of later selective extraction from other metals such as lead, copper and tin. The bismuth(III) was fixed at 490.7 mg/g of XAD-1180 resin, at 295 K. The extractant impregnated resin (EIR) of bismuth(III) was studied in function of the experimental parameters such as: Amberlite XAD-1180 impregnation, D2EHPA/XAD-1180 ratio, Contact time and stirring speed, pH of Bi(III) solution, Concentration of Bi(III), Aqueous phase volume, NaCl electrolyte and elution of Bi(III) from loaded EIR. The results were used to determine the constants of polynomial model which described the experimental data of bismuth (III) extraction process.

In this present paper we are interested to study the thermodynamic parameters of the distribution equilibrium of Bi(III) sorption process for evaluated the changes in standard thermodynamic quantities. The sorption isotherms such as: Langmuir forms I, II and Freundlich were tested for experimental data of Bi(III) sorption onto D2EHPA/XAD-1180 resin. Also, the kinetics models as the Lagergren first order, the pseudo second order and Morris–Weber were applied for modeling the adsorption rate data.

2. Results and Discussion

2.1. Effect of the Temperature

The study of the temperature effect on the bismuth(III) sorption from nitrate medium onto 15 mmol of D2HPA/g of XAD-1180 resin was carried out by using 250 ppm of the concentration of metal ion at pH 3.6 with v/m ratio equal to 50 ml/g.

The distribution coefficient (K_d) of metal ion between the aqueous bulk phase and the resin phase was calculated from the Equation (1):

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$$K_d = \frac{C_0 - C_e}{C_e} x \frac{V}{M} \quad (1)$$

Figure 1 shows the variation of the distribution coefficient (K_d) of bismuth(III) sorption in function of different temperatures. From where, an increasing of the temperature from 22 to 60˚C decreased the adsorption of the bismuth(III). The van't Hoff relation [2] given by Equation (2) can be used to calculate the enthalpy changes associated with the adsorption process of the bismuth(III).

$$\log K_d = -\frac{\Delta H^0}{2.303R} \times \frac{1}{T} + C \quad (2)$$

From the plots of K_d vs. $1/T$ (**Figure 1**), a straight line was observed, from which ΔH^0 (the enthalpy variation) can be deduced according to the Equation (3):

$$\Delta H^0 = -2,303R \times Slope \quad (3)$$

The free energy variation ΔG^0 was also calculated based on the logarithmic value of the distribution ratio $LogK_d$ at 22˚C according to the Equation (4):

$$\Delta G^0 = -2.303RTLogK_d \quad (4)$$

Also, the entropy variation ΔS^0 was obtained from ΔG^0 and ΔH^0 with the Equation (5):

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (5)$$

The thermodynamic parameters of the sorption of bismuth (III) were given in **Table 1**. The negative sign of the enthalpy variation value showed the exothermic character of the liquid-solid extraction and sorption process. This result is similar to the previous paper [3]. While the negative sign of the free energy variation value indicated the spontaneous phenomenon of bismuth(III) sorption and the value sign of the entropy variation suggested that the system exhibit a disorder.

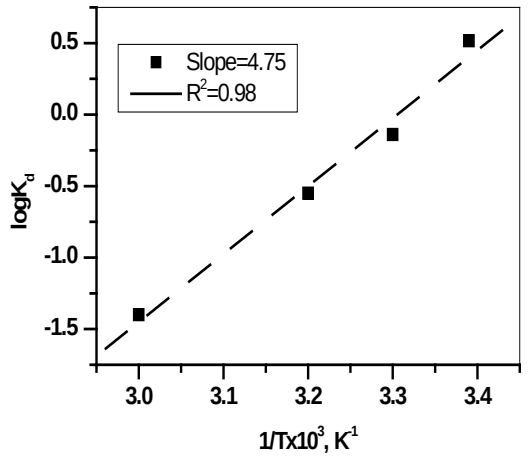

Figure 1. Variation of log K_d with $1/T$ for the sorption of Bi (III) ion from nitrate medium by D2EHPA/XAD-1180 resin.

Table 1. Thermodynamic parameters for the adsorption of bismuth (III) from nitrate medium by D2EHPA/XAD-1180 resin.

Metal ion	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)	ΔS^0 (J/mol·K)
Values (KJ/mol)	−91.01	−2.91	−298.64

As reported in literature [4], the process of solvent impregnated resin (SIR) can be evaluated as film-diffusion controlled when E_a < 16.7 kJ/mol, particle diffusion controlled when E_a > 42 kJ/mol and reaction controlled when E_a = 50.2 kJ/mol. The activation energy (E_a) of sorption reaction of bismuth(III) by the XAD-1180 resin impregnated with D2EHPA was calculated by applying the Arrhenius relation where E_a was be found to 1.14 kJ/mol which confirmed that the sorption was governed by the film-diffusion.

2.2. Sorption Isotherm

The experimental results obtained for the adsorption of bismuth(III) by D2EHPA impregnated onto XAD-4 resin at temperature equal to 295 K under the optimum conditions [1] were tested for Langmuir form I, II and Freundlich adsorption isotherms. The Langmuir isotherm can be written under the Equation (6) and Equation (7), form I and II respectively as:

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \quad \text{(Form I)} \quad (6)$$

$$\frac{1}{q_e} = \frac{1}{bQ_0C_e} + \frac{1}{Q_0} \quad \text{(Form II)} \quad (7)$$

where

$$q_e = (C_0 - C_e) x \frac{V}{M} \quad (8)$$

The Langmuir isotherms Form I and II for sorption of bismuth (III) ions on the impregnated resin were presented in **Figure 2** and **Figure 3** respectively.

The representation of Langmuir isotherm form II for experimental data of bismuth(III) sorption by D2EHPA impregnated in XAD-1180 resin (**Figure 3**) showed a good linear fitting (R^2 = 0.99) compared with that given in **Figure 2**. From where the fit of experimental data using Langmuir isotherm form I was equal to 0.92. Thus, the sorption of Bi(III) onto D2EHPA impregnated in XAD-1180 was expected as a monolayer adsorption and that all active sites are similar and have the same energy [5]. Parameters of Langmuir model form II are given in **Table 2**.

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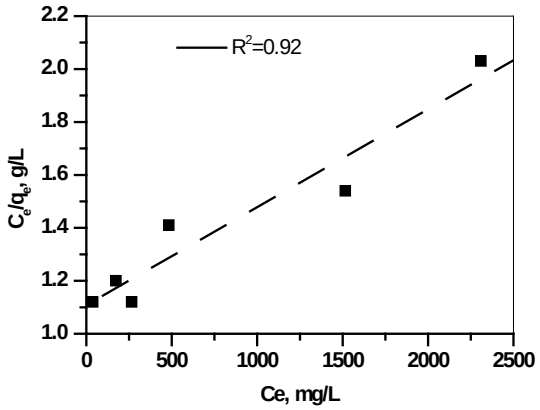

Figure 2. Langmuir isotherm (Form I) for sorption of Bi(III) onto impregnated D2EHPA/XAD-1180 resin.

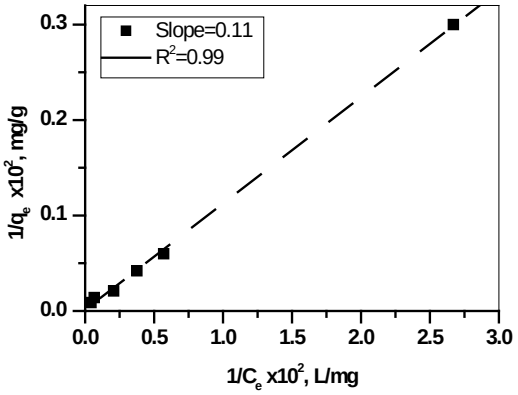

Figure 3. Langmuir isotherm (Form II) for sorption of Bi(III) onto impregnated D2EHPA/XAD-1180 resin.

Table 2. Parameters of Langmuir isotherm for sorption of Bismuth(III) by D2EHPA/XAD-1180 resin.

Metal ion	Parameters of Langmuir model form II	
	Q_0 (mg/g)	b(L/g)
Bi(III)	769.23	0.011

In fact, the fit of data using the equation of Freundlich isotherm was carried out. From the fitting factor (R^2 = 0.97) which was lower than that the Langmuir isotherm, we suggests that, the sorption process was restricted to one specific class of sites and assumes surface homogeneity.

2.3. Kinetic Modeling

Several kinetic models were tested to select the model that describes our experimental data for established to the appropriate mechanism of sorption of Bi^{3+} by D2EHPA impregnated onto XAD-1180 resin. The batch sorption process of bismuth(III) was analyzed using Lagergren first order and the pseudo second order kinetics model [6,7]. The equation of Lagergren was widely used in liquid-solid extraction for sorption of solute from aqueous or organic solution [3]. The Legergren first order model was given by the Equation (9):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (9)$$

From the results shown in **Figure 4**, linear fit was observed for the metal ion, during the first 30 min of shaking time, the first order rate constant (k_1) was found to be approximately 0.10 min^{-1}. In fact, the experimental data were analyzed using the Legergren pseudo second order model but the data fitting was not better than the Legergren pseudo first order which confirm that it's appropriate to use this last model to predict the sorption kinetics of bismuth(III) ions onto D2EHPA impregnated in XAD-1180 resin.

The diffusion of the particles from the bulk solution into the sorbent pores can constitute a limiting step in the process of bismuth(III) sorption by D2EHPA impregnated in XAD-1180 resin. For this, the experimental data were used to study intraparticle diffusion. The equation of Morris–Weber model is given as Equation (10):

$$q_t = K_{ad}\sqrt{t} \quad (10)$$

As shown in **Figure 5**, multi-linearity correlation of experimental data was obtained by plotting a graph of q_t vs. $t^{0.5}$. From theory [8,9], the preliminary conclusions indicated that the intraparticule diffusion cannot be involved in the sorption process (linear plot, R^2 = 0.95) and was not the rate controlling step because the fit line no pass through the origin.

In the way to verify the conclusions brought on the rate controlling step of bismuth(III) sorption, the graphs: [–Ln(1 – F)] = kt and [3-3(1 – F)$^{2/3}$– 2F] = kt plotted in

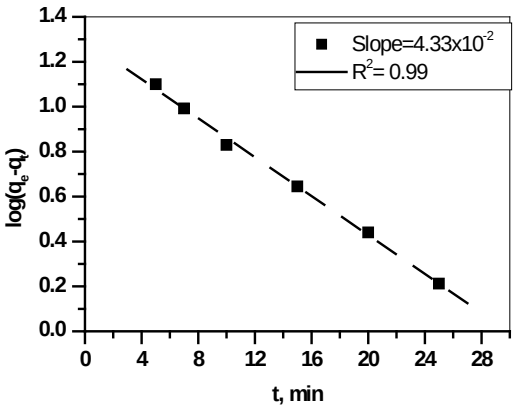

Figure 4. Legergren pseudo first order plot for the removal of Bi(III) ion from nitrate solution by D2EHPA/XAD-1180.

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the cases of film-diffusion controlled and chemical reaction controlled respectively [10,11].

From the results shown in **Figure 6** and **Figure 7**, the linear correlation of experimental data was better (R^2 = 0.99) when plotting [–Ln(1 – F)] vs. time where the correlation factor was equal to 0.95 in the case of the plotting $[3 - 3(1 - F)^{2/3} - 2F]$ vs. time. Thus, the film-diffusion was the rate controlling step of bismuth(III) sorption by impregnated resin D2EHPA/XAD-1180. This result was similar to that found by the activation energy explanation.

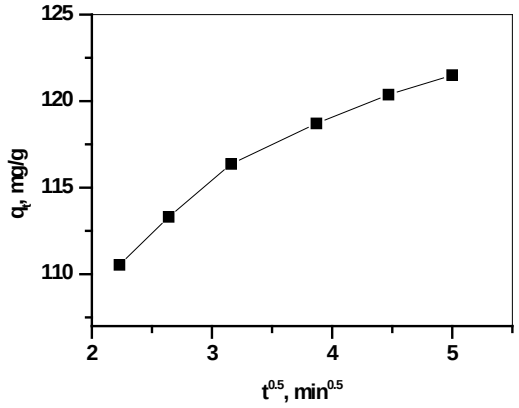

Figure 5. Morris–Weber plot for the adsorption of Bi(III) ion from nitrate solution by D2EHPA/XAD-1180 resin.

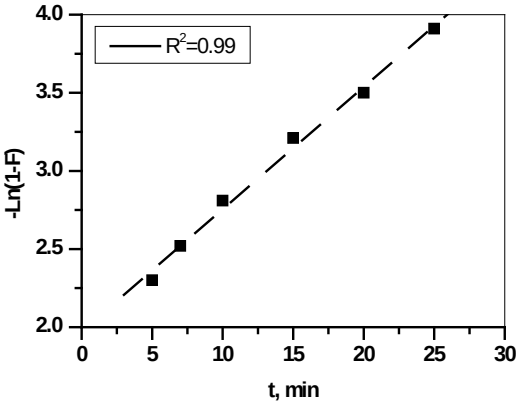

Figure 6. Plot [–Ln(1 – F)] vs. time for the adsorption of Bi(III) ion from nitrate solution by D2EHPA/XAD-1180 resin.

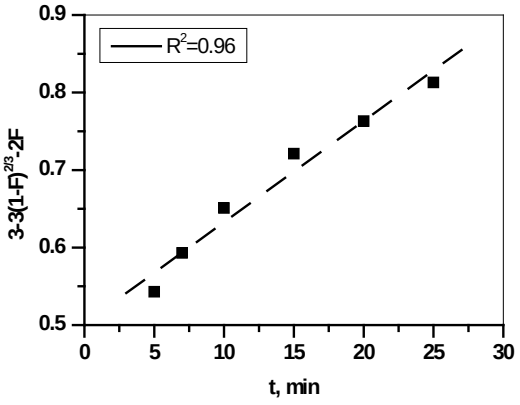

Figure 7. Plot $[3-3(1 - F)^{2/3} - 2F]$ vs. time for the adsorption of Bi(III) ion from nitrate solution by D2EHPA/XAD-1180 resin.

The calculation of the diffusion coefficient (D_r) was given by the Equation (11) [10]:

$$D_r = k\frac{r_0^2}{\pi^2} \tag{11}$$

where, the diffusion coefficient was equal to $5.84 \cdot 10^{-6}$ $cm^2 \cdot min^{-1}$.

3. Conclusions

The physical impregnation of D2EHPA in Amberlite XAD-1180 resin for the Bi(III) sorption from aqueous nitrate medium was carried in batch system. The thermodynamics values of extraction reaction of Bi(III) shown the exothermic process where the activation energy was be found to 1.14 kJ/mol. The equilibrium isotherms for sorption of the investigated metal ion were modeled successfully using the Langmuir isotherm (Form II) where the sorption capacity of monolayer was found equal to 769.23 mg/g of impregnated resin.

Also, the experimental data were tested for different kinetic model expressions and the data were successfully modeled using the Legergren pseudo first order where the first order rate constant was found to be approximately 0.1 min^{-1}. Besides, the pushed studies on the mechanism of the Bi(III) sorption showed that the rate controlling step was the fim-diffusion and the coefficient of diffusion was $5.84 \cdot 10^{-6}$ $cm^2 \cdot min^{-1}$.

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Symbols

b: Constant related to the free energy of adsorption, b ∞ exp($-\Delta G/RT$)
C: Constant
C_0: Initial concentration of metal ion in solution, mg/L
C_e: Equilibrium concentration of metal ion in solution, mg/L
$F = q_t/q_e$
k: Rate constant, min^{-1}
k_1: Pseudo first order rate constant, min^{-1}
K_{ad}: Rate constant of intraparticle transport, mg/g $min^{0.5}$
M: Weight of the adsorbent, g
Q_0: Monolayer adsorption capacity, mg/g
q_e: Amount of solute sorbed per unit weight of adsorbent at equilibrium, mg/g
q_t: Concentration of ion in the adsorbent at time t, mg/g
R: Universal gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$)
r_0: radius of particles of resin (0.024 cm)
T: Absolute temperature, Kelvin
V: Volume of bulk solution, L

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