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## Sorption mechanism of some heavy metal ions from aqueous waste solution by polyacrylamide ferric antimonite

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### ABSTRACT

Incorporation of a polymer material into an inorganic ion exchanger provides a class of hybrid ion exchangers with a good ion exchange capacity, high stability and high selectivity for heavy metals. We can see these properties in the present study. The kinetic of Fe (III), Pb (II), Cd (II), Cu (II), and Zn (II) ions on polyacrylamide ferric antimonite has been studied by applying the Nernst-Planck equation. The rate of exchange is controlled by particle diffusion mechanism. The physical thermodynamic parameters such as activation energy and entropy of activation have been evaluated and compared with other inorganic and organic exchangers. The Langmuir and Freundlich models have been applied to the adsorption isotherm and different constants were generated. © 2011 Trade Science Inc. - INDIA

### KEYWORDS

Synthesis;  
Polyacrylamide  
ferric antimonite;  
Adsorption;  
Isotherm;  
Diffusion;  
Heavy metals.

### INTRODUCTION

The presence of heavy metal ions from the transition series, viz, Cu, Fe, Ni, Pb, etc. in the environment is of major concern due to their toxicity to many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, metal ions do not degrade into harmless end products<sup>[1]</sup>. Heavy metal contamination exists in aqueous waste stream from many industries such as metal plating, mining, tanneries, painting, car radiator manufacturing, as well as agricultural sources where fertilizers and fungicidal spray intensively used. The removal of heavy metal in an effective manner from water and wastewater is, thus, ecologically very important. There are many reported and

established technologies for the recovery of metals from wastewater, which include chemical precipitation<sup>[2]</sup>, flotation<sup>[3]</sup>, electrolytic recovery, membrane separation<sup>[4]</sup> and activated carbon adsorption<sup>[5,6]</sup>. In recent years, the search for a new class of high performance and high functional organic-inorganic composite ion-exchangers were developed by the incorporation of organic conducting polymers into inorganic precipitates<sup>[7-9]</sup>. These materials were found selective for heavy toxic metal ions and utilized for analysis of water pollution such materials have a great deal of attention because of their special mechanical and chemical stabilities<sup>[10-12]</sup>. The newly developed composite offered a high capacity and faster sorption kinetics for the metal ions such as Fe (III), Pb (II), Cd (II), Cu (II), and Zn (II) ions.

## MATERIALS AND METHODS

### Materials

All chemicals used in this work were of analytical grade and used without further purification. Distilled water was employed for all glassware and in preparing aqueous solution.

### Apparatus

Inductive Coupled plasma spectrometer (ICPS-7500) shimadzu corporation, Kyoto, japan and atomic absorption flame emission spectrophotometer (AA-6701F) shimadzu corporation, Kyoto, japan. the pH measurements were performed by pH meter and the total experimental error was about 3%.

### Procedures

#### Water washing of ion exchanger

The polyacrylamide ferric antimonate composite were washed with double distilled water to remove all fin particles. the dried material at 50°C was sieved to obtain different mesh sizes of 0.12-1.00 mm. The sieved material was used for further experimental work.

### PREPARATION OF POLYACRYLAMIDE FERRIC ANTIMONATE

#### Preparation of polyacrylamide

Polyacrylamide was prepared by mixing equal volume of 20% acrylamide prepared in distilled water with 0.1 M potassium persulfate ( $K_2S_2O_8$ ) prepared in 1 M HCl, a viscous solution was obtained by heating the mixture gently at 70±5°C with continuous stirring.

#### Preparation of ferric antimonate

Ferric antimonate prepared from 0.5 M of ferric chloride dissolved in distilled water and adding the same volume of 0.5 M antimony metal dissolved in aqua regia slowly with constant stirring using a magnetic stirrer at a temperature of 70±5°C. The resulting solution was precipitate by using ammonia solution drop by drop until the pH about 0.13. Red brown precipitate has been formed.

#### Preparation of polyacrylamide ferric antimonate

Polyacrylamide ferric antimonate formed by adding

a precipitate of ferric antimonate to polyacrylamide with stirrer by using magnetic stirrer to obtain homogenous precipitate. The precipitates were left to age in the mother liquor overnight, the precipitate washed by distilled water several times. The supernatant liquid was decanted and the gel was filtered using a centrifuge (about 10<sup>4</sup> rpm) and dried at 50±1°C. The product was crashed and sieved to obtain different mesh sizes of 0.12-1.00 mm. The weight loss of polyacrylamide ferric antimonate in the different forms such as H(I), Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions were determined by using thermal analysis technique (TG and DTA). The weight loss of polyacrylamide ferric antimonate in H(I), Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions at 1000°C are 34.9%, 17.33%, 19.81%, 21.55%, 21.22% and 21.33% w/w, respectively.

### CHEMICAL STABILITY

Chemical stability of polyacrylamide ferric antimonate ion exchangers were studied in water, nitric and hydrochloric acid [1,2,3,4,5 and 6M], as well as in potassium and sodium hydroxide (0.1, 1M) by mixing 50mg of ion exchanger samples and 50 ml of the desired solution with intermittent shaking for three weeks at 25 ±1°C.

### CAPACITIES OF POLYACRYLAMIDE FERRIC ANTIMONATE FOR $Pb^{2+}$ , $Fe^{3+}$ , $Cd^{2+}$ , $Zn^{2+}$ AND $Cu^{2+}$ IONS

Capacities were determined by repeated batch equilibration of 0.1M metal chloride solution solutions ( $Pb^{2+}$ ,  $Fe^{3+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$  and  $Cu^{2+}$ ) with the solid material in V/m ratio 50ml/g was carried out for the capacity evaluation. The mixture was shaken in a shaker thermostat at 25±1°C. After over night standing the solid was separated and the concentration of the metal ions was measured by using Inductive Coupled plasma spectrometer (ICPS-7500) and atomic absorption flame emission spectrophotometer (AA- 6701F). The procedure was repeated until no further absorption of cations occurred. The capacities were calculated from the following equation:

$$\text{Capacity in meg / g} = \frac{\% \text{ uptake}}{100} \times C_0 \times \frac{V}{m} \times Z \quad (1)$$

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where  $C_0$  is the initial concentration of the ion in solution,  $V$  is the solution volume,  $m$  is the weight of the exchanger,  $Z$  is the valence of the exchanged ions.

### KINETIC STUDIES

The kinetic analysis of the adsorption process for Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions on polyacrylamide ferric antimonate was carried out by mixing of the exchanger with metal ions solution (pH equal to 4.55, 4.06, 4.32, 4.11 and 4.3 for Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions, respectively) with a  $V/m$  ratio of 100 ml/g in a shaker thermostat at  $25 \pm 1^\circ\text{C}$ . the solution was separated at different time intervals and analyzed to determine the metal ion concentration in solution by using ICPS-7500 for Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions. the extent of sorption was determined. All the experiments were carried out at 25, 45 and  $65 \pm 1^\circ\text{C}$  and the results agreed to  $\pm 3\%$  for all reaction times.

$$\text{Sorption \%} = [(A_i - A_f)/A_i] \times 100 \quad (2)$$

Where  $A_i$  and  $A_f$  are the initial and final concentration of the metal ions in solution.

### ADSORPTION ISOTHERM

The equilibrium adsorption isotherms are one of the promising data to understand the mechanism of the adsorption. Various isotherm equations are well known and two different isotherms are selected in this study, which are the Langmuir and Freundlich isotherms. The sorption isotherm is done by the gradual increase of the concentration of the sorbate in solution and measuring the amount sorbed at each equilibrium concentration. The degree of sorption should be a function of the concentration of the sorbate only. The sorption isotherms for Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions were determined at the concentration range ( $5 \times 10^{-3}$  - 0.1M) at pH = 4 and at a  $V/m$  ratio of 100 ml/g. The experiments were carried out at 25, 45 and  $65 \pm 1^\circ\text{C}$  in a shaker thermostat.

#### Analysis

Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions were measured using ICPS-7500 and atomic absorption flame emission spectrophotometer (AA- 6701F).

## RESULTS AND DISCUSSION

In this work we attempt to synthesize a high chemical stable composite material with high selectivity for some heavy metals.

The ion exchange capacity of polyacrylamide ferric antimonate for Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions were investigated and the data are represented in TABLE 1. TABLE 1 indicated that the affinity sequence for all cations is  $\text{pb}^{2+} > \text{Fe}^{3+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$ . This trend may be due to the stronger electrostatic interaction reducing its mobility in the exchanger. The electronegativity of  $\text{pb}^{2+} > \text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  and may be due to the ionic radii of  $\text{Fe}^{3+} < \text{Cu}^{2+} < \text{Cd}^{2+} < \text{Zn}^{2+}$ . Also, may be owing to the hydrated radius according to the fact that on increasing atomic number decreasing the hydrated ionic radii<sup>[13]</sup>.

TABLE 1 : Capacities of polyacrylamide ferric antimonite for  $\text{pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions on

Metals	$\text{Pb}^{2+}$	$\text{Fe}^{3+}$	$\text{Cu}^{2+}$	$\text{Cd}^{2+}$	$\text{Zn}^{2+}$
Capacity of meq/g	5.33	4.31	3.12	2.51	2.35

The rate of ion exchange reaction is governed by the slowest step which may be diffusion in the liquid surrounding the particle of the exchanger (film diffusion control) or diffusion inside the exchanger particles (particle diffusion mechanism) and or the ion exchange process when the exchanging ions form strong complexes with the functional groups of the exchanger (chemical control)<sup>[14]</sup>. The experimental conditions of the present work were set to study the particle diffusion mechanism only as a limited batch technique. Beside, stirring and mechanical shaking did not enhance the rate of exchange. The equation used for evaluating the kinetic parameters is developed by *Boyd*<sup>[15]</sup> as follows:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 \pi^2 D_i / r^2} \quad (3)$$

Where  $F$ : is the fractional attainment of equilibrium,  $n$ : is an integer number,  $D_i$ : is the effective diffusion coefficient of the exchanging inside the particles,  $r$ : is the particle radius.

This equation was improved by *Reichenberg*<sup>[16]</sup> and can be used if the rate determining step is diffusion through the exchanger particles. Thus, equation (3) may be written in the following form:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp^{-n^2 Bt} \quad (4)$$

$$B = \pi^2 D_i / r^2$$

Where  $Bt$  is a mathematical function of  $F$ . Reichenberg has tabulated the values of  $Bt$ . Corresponding to each value of fractional attain of equilibrium from equation (4). For a particle diffusion mechanism, the relation between  $Bt$  vs.  $t$  should be giving a straight line. When  $F(t)$  is less than 0.4, equation (4) is approximated to the simple form<sup>[15]</sup>.

$$F(t) = 6/r(D_i/\pi)^{1/2} \quad (5)$$

Which hold to a good approximation. Therefore, a plot of  $F(t)$  against the square root of the contact time must give a straight line passing through the origin in the range in which  $F(t)$  is less than 0.4.

The effect of concentration on the rate of exchange of the metal ion on polyacrylamide ferric antimonate at  $25 \pm 1^\circ\text{C}$  demonstrates that the initial rate of exchange is independent of concentration. From the relation between the fractional attainment of equilibrium ( $F$ ) and time for  $\text{Pb(II)}$ ,  $\text{Fe(III)}$ ,  $\text{Cd(II)}$ ,  $\text{Cu(II)}$  and  $\text{Zn(II)}$  ions, it is evident that the rate of exchange is independent on the metal ion concentration. These results agreed with that reported for tin antimonate and hydrous titanium dioxide<sup>[17]</sup>.

The effect of particle sizes on the rate of exchange of  $\text{Pb(II)}$ ,  $\text{Fe(III)}$ ,  $\text{Cd(II)}$ ,  $\text{Cu(II)}$  and  $\text{Zn(II)}$  ions on polyacrylamide ferric antimonate was studied at  $25 \pm 1^\circ\text{C}$ . Straight lines passing through the origin are obtained, which had taken as indication of a particle diffusion mechanism as shown in (Figure 1, we took the results and figures of lead as example for the sake of brevity), a relation between  $F$  and  $Bt$  against time. Similar trend was observed by (El-Naggar et al., 2007; Abou-Mesalam and El-Naggar, 2003)<sup>[18,13]</sup>. This figure shows that the exchange rate of  $\text{Pb(II)}$ ,  $\text{Fe(III)}$ ,  $\text{Cd(II)}$ ,  $\text{Cu(II)}$  and  $\text{Zn(II)}$  ions increases with decreasing the particle sizes which is agreement with the conditions of particle diffusion mechanism. Detailed results and figures of the other metal ions are not given here for the sake of brevity.

A plot of  $B$  against  $1/r^2$  Figure 2 for all metal  $\text{Pb(II)}$ ,  $\text{Fe(III)}$ ,  $\text{Cd(II)}$ ,  $\text{Cu(II)}$  and  $\text{Zn(II)}$  ions studied are a straight line, indicating that the rate of exchange is inversely proportional to the square of the particle

radius, which is another proof of particle diffusion control<sup>[19]</sup>. Data in TABLE 2 shown that,  $D_i$  values are generally slightly increased with increasing the particle sizes. The small increase of  $D_i$  with increase of par-

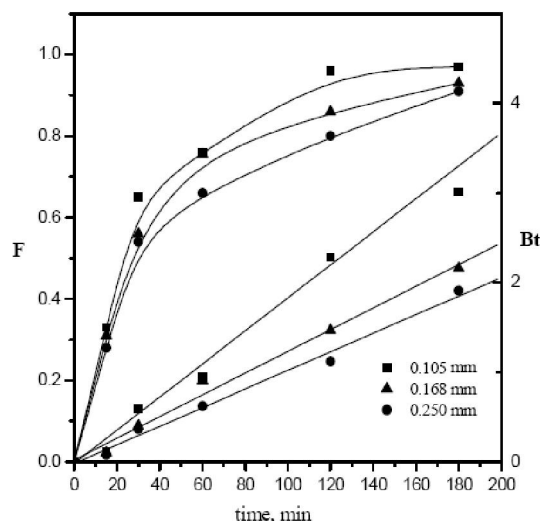


Figure 1 : Plots of  $F$  and  $Bt$  against time for exchange of  $\text{Pb(II)}$  on polyacrylamid ferric antimonate at different particale diameters.

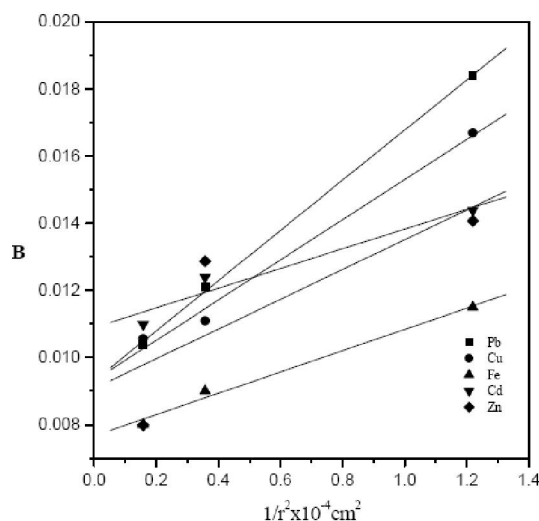


Figure 2 : Plots of  $B$  against  $1/r^2$  for adsorption of  $\text{Fe(III)}$ ,  $\text{Pb(II)}$ ,  $\text{Cd(II)}$ ,  $\text{Cu(II)}$ , and  $\text{Zn(II)}$  ions on polyacrylamide ferric antimonate.

TABLE 2 : Values of diffusion coefficient of  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$  on polyacrylamide ferric antimonate, at different particle diameters at  $25 \pm 1^\circ\text{C}$ .

Particle diameter ( $\pm 0.02$ mm)	$D_i, \text{cm}^2 \text{s}^{-1} \times 10^8$				
	Pb(II)	Fe(III)	Cd(II)	Cu(II)	Zn(II)
0.11	0.26	0.16	0.198.	0.189	0.195
0.17	0.57	0.44	0.59	0.81	0.59
0.25	1.10	0.85	1.17	1.17	0.85

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ticle size may be attributed to the large particles are less compact<sup>[18]</sup>.

The plots of  $Bt$  and  $F$  against  $t$  for the exchange of Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions at different reaction temperatures (25, 45 and 65 ± 1°C) on polyacrylamid ferric antimonate are presented in (Figure 3, we took the results and figures of lead as example for the sake of brevity). It was found that straight lines passing through the origin. This confirms that the phenomenon is particle diffusion controlled, and the rate of exchange increases by increasing the reaction temperatures from 25 to 65 ± 1°C. Figure 4 shows that, the value of  $D_i$  increases with increasing the heat-

ing temperatures from 25 to 65°C for all metal ions studied, as illustrated in TABLE 3. The values of effective diffusion coefficient ( $D_i$ ) have been calculated and summarize in TABLE 3.

TABLE 3 shows that the appreciable increase of diffusion coefficient of  $Fe^{3+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$  ions with an increase in reaction temperature. When  $\log D_i$  is plotted against  $1/T$  for exchange of Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions Figure 4, straight lines are obtained for the above five heavy metals ions, enabling the calculation of energy of activation ( $E_a$ ) and the self diffusion coefficient ( $D_o$ ) from Arrhenius equation as follows.

$$D_i = D_o \exp(-E_a/RT) \quad (6)$$

However, the entropy of activation ( $\Delta S^*$ ) can be calculated from  $D_o$  by substituting in the equation proposed by Barrer<sup>[20]</sup>.

$$D_o = 2.72 (KTd^2/h) \exp(\Delta S^*/R) \quad (7)$$

Where,  $K$  is the Boltzmann constant,  $T$  is the absolute temperature;  $d$  is the average distance between two successive positions in the process of diffusion and it taken as equal to 5 Å,  $h$  is Plank constant and  $R$  is the gas constant. It is interesting to compare the values of activation energies for all metal ions studied reported herein TABLE 3 with other values of activation energies which have been observed for the exchange of other metal ions on polypyrrole/polyantimonic acid and acrylamid cerium(IV) phosphate, where as the activation energy values for Mg(II), Ca(II), Sr(II), Ba(II), Cu(II), Ni(II), Zn(II) and Mn(II) to be 4.11, 5.14, 5.16, 5.12, 9.23, 8.47, 8.72 and 6.44  $KJmol^{-1}$  respectively, the activation energy for Mg(II), Ca(II), Sr(II) and Ba(II) on acrylamid cerium(IV) phosphate to be 9.95, 9.15, 8.89 and 6.03  $KJmol^{-1}$  respectively<sup>[7]</sup>, the values of activation energy observed on acrylonitrile based cerium(IV) phosphate for Mg(II), Ca(II), Sr(II), Ba(II), Mn(II), Co(II), Cu(II) and Zn(II) were found to be 14.88, 11.76, 10.32, 8.62, 13.85, 9.93, 9.53 and 11.36  $kJ mol^{-1}$  respectively, the values of activation energy for Zn(II), Cd(II), Hg(II), La(III) and Th(III) on ferric antimonate were found to be 17.2, 21.1, 23.0, 15.3 and 13.5  $kJ mol^{-1}$  respectively<sup>[21]</sup> and the values of activation energy for the cobalt on tin antimonate to be 19.15  $kJmol^{-1}$  respectively<sup>[22]</sup>. The activation energy for Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions stud-

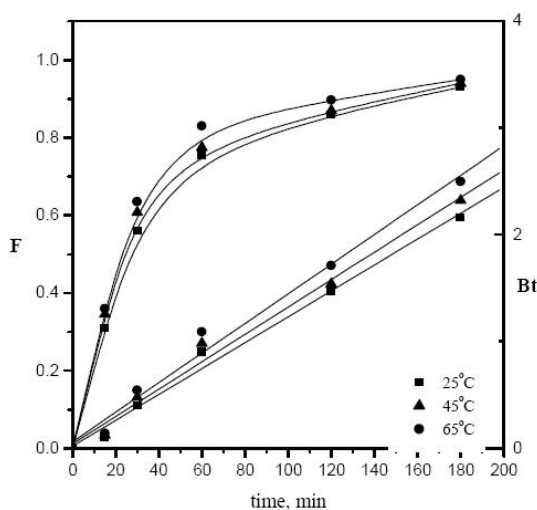


Figure 3 : Plots of  $F$  and  $Bt$  against time for exchange of Pb(II) on polyacrylamid ferric antimonate at different reaction temperatures.

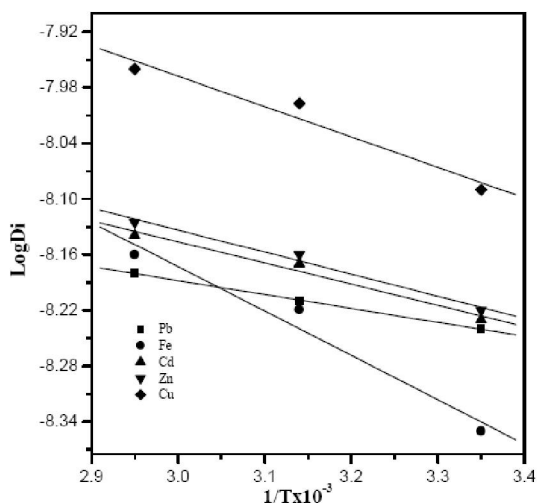


Figure 4 : Arrhenius Plots ( $\log D_i$ ) against  $1/T$  for the exchange Fe(III), Pb(II), Cd(II), Cu(II), and Zn(II) ions on polyacrylamid ferric antimonate at different reaction temperatures.

ied on polyacrylamide ferric antimonate takes the order: Fe(III) (9.14) > Cu(II) (5.77) > Zn(II) (4.56) > Cd(II) (4.37) > Pb(II) (2.86)

The relatively small activation energy values ( $E_a$ ) obtained in TABLE 3, for Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions, indicated that the rate of exchange is particle diffusion mechanism<sup>[23]</sup>. On other word, these values of activation energy are relatively small compared to that reported for other composite, organic and inorganic exchangers which confirm the particle diffusion mechanism.

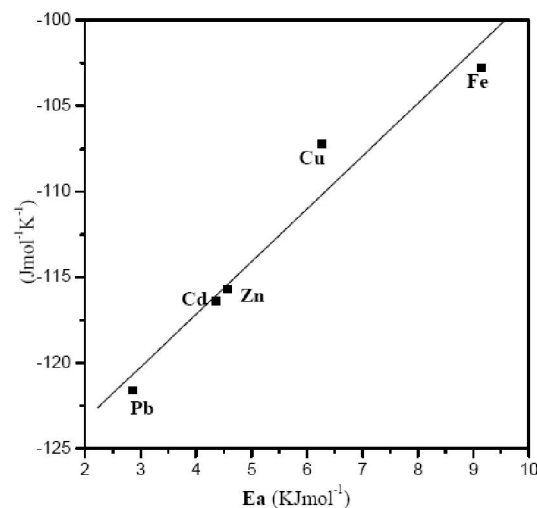
**TABLE 3 : Thermodynamic parameters for the exchange of Fe<sup>3+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup> on polyacrylamide ferric antimonate, at different reaction temperatures.**

Metal ion	Reaction temperature	$D_i \times 10^8$ $\text{cm}^2 \text{s}^{-1}$	$D_o \times 10^5$ $\text{cm}^2 \text{s}^{-1}$	$E_a$ $\text{KJ mol}^{-1}$	$\Delta S^*$ $\text{J mol}^{-1} \text{K}^{-1}$
Pb(II)	25	0.57	1.83		-121.6
	45	0.61	1.82	2.86	-122.3
	65	0.65	1.83		-122.8
Cd(II)	25	0.59	3.44		-116.4
	45	0.67	3.54	4.37	-116.8
	65	0.73	3.44		-117.6
Zn(II)	25	0.59	3.80		-115.7
	45	0.69	3.89	4.56	-116.0
	65	0.75	3.80		-116.8
Cu(II)	25	0.81	8.55		-107.2
	45	1.04	9.30	6.27	-107.4
	65	1.08	8.56		-108.6
Fe(III)	25	0.44	17.9		-102.8
	45	0.62	20.04	9.14	-102.4
	65	0.67	17.90		-103.9

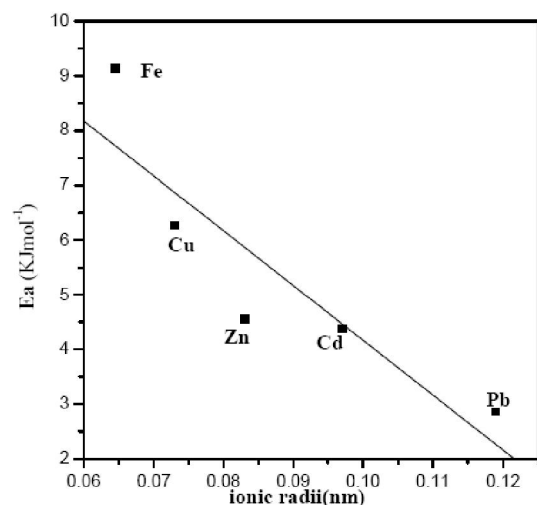
The values of diffusion coefficient for all metals take the order. Cu(II) > Zn(II) > Cd(II) > Fe(III) > Pb(II), this may be attributed to the decrease in the electrostatic interaction of the counter ions with the exchange sites, hydrated ionic radius and electronegativity of the metals ion studied.

The relatively small activation energy values which are given in TABLE 3, for Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions suggest that the rate of exchange is particle diffusion mechanism. The values of  $D_o$ ,  $E_a$  and  $\Delta S^*$  thus obtained are summarized in TABLE 3. These results show that there is a linear relation between the  $E_a$  and  $\Delta S^*$  value Figure 5, but the increase in ionic radii of the metal ion leads to decreases the energy of activation<sup>[7]</sup> Figure 6, these results also indicate that the

entropy change increases in order. Pb(II) < Cd(II) < Zn(II) < Cu(II) < Fe(III) thus showing a maximum entropy change being for Fe(III) exchange. The negative values of the entropy of activation indicate the presence of more active sites in its structure and suggest that no significant structural change occurred in polyacrylamide ferric antimonate.



**Figure 5 : The correlation between  $\Delta S^*$  and  $E_a$  for Fe(III), Pb(II), Cd(II), Cu(II), and Zn(II) ions on polyacrylamide ferric antimonate at 25 C°**



**Figure 6 : The correlation between ionic radii and  $E_a$  for Fe(III), Pb(II), Cd(II), Cu(II), and Zn(II) ions on polyacrylamide ferric antimonate at 25 C°**

## ADSORPTION ISOTHERM

The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful applications in

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many adsorption processes of monolayer adsorption. For the case of adsorption in solution, the equation is represented by the following<sup>[24]</sup>.

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (8)$$

Where  $q_e$  (mol g<sup>-1</sup>) is the adsorption capacity for Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions on the adsorbent at the equilibrium,  $C_e$  (mol dm<sup>-3</sup>) is the equilibrium ions concentration in the solution,  $q_{\max}$  is the monolayer adsorption capacity of the adsorbent, and  $K_L$  is the Langmuir adsorption constant. The plots of  $C_e/q_e$  vs.  $C_e$  for the adsorption of pb(II) ion onto com-

posite Figure 7 give a straight line of the slope,  $\frac{1}{q_{\max}}$

and intercept,  $\frac{1}{q_{\max} K_L}$ .

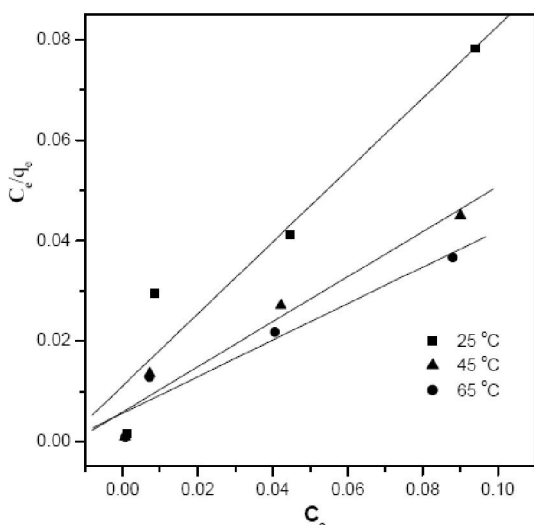


Figure 7 : Plots of  $C_e/q_e$  against  $C_e$  for the exchange of pb(II) on polyacrylamide ferric antimonate at different reaction temperatures.

We took the results and figures of lead as example for the sake of brevity. The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The plot of  $\ln K_L$  vs.  $1/T$  for Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions is given in Figure 8. Accordingly the values of  $\Delta H$  at saturation are calculated for Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions on polyacrylamide ferric antimonate and represented in the TABLE 4. These values indicate the exothermic behavior of polyacrylamide ferric antimonate. The linearized form of the Freundlich isotherm equation is<sup>[25]</sup>.

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (9)$$

Where  $K_F$  (dm<sup>3</sup> g<sup>-1</sup>) and  $n$  (dimensionless) are Freundlich adsorption isotherm constants, being indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively.

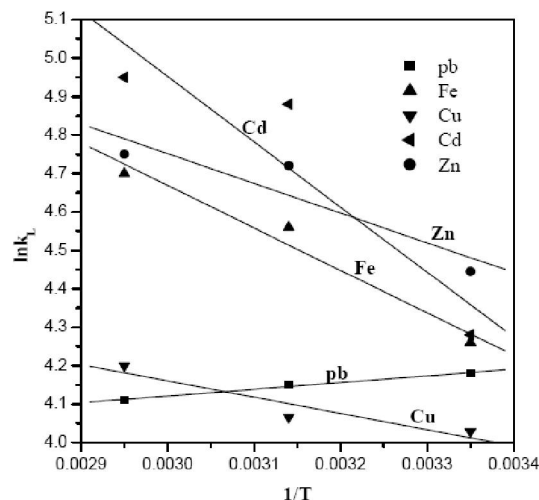


Figure 8 : Langmuir adsorption isotherm for the sorption of Fe(III), Pb(II), Cd(II), Cu(II), and Zn(II) ions on polyacrylamid ferric antimonate at different reaction temperatures.

TABLE 4 : Isotherm parameters for adsorption of Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions on polyacrylamid ferric antimonate.

Elements	Langmuir		Freundlich	
	$\Delta H$ KJ/mol	$\Delta G^\circ$ KJ/mol	$K_F$	$n$
Pb	-3.34	-10.33	1.64	4.76
Fe	21.17	-10.55	2.57	2.33
Cu	8.09	-9.98	1.87	2.77
Cd	32.5	-10.60	1.67	3.45
Zn	14.78	-11	1.84	2.70

The free energy  $\Delta G^\circ$  associated to the adsorption process and they were determined by using following equation.

$$\Delta G^\circ = -RT \ln K_L \quad (10)$$

The results are given in TABLE 4 show that the change of free energy for physisorption is generally between -20 and 0 kJ mol<sup>-1</sup>, the physisorption together with chemisorption is at the range of -20 to -80 kJ mol<sup>-1</sup> and chemisorptions is at a range of -80 to -400 kJ mol<sup>-1</sup><sup>[26]</sup>. As can be seen from TABLE 4, the overall standard free energy changes during the adsorption process were negative for the experimental range of temperatures,

corresponding to a spontaneous and a boundary of physisorption process of Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions on poly acrylamide ferric antimonate.

The negative value of the enthalpy change of Pb(II) ion indicates that exothermic behavior, and the positive value of the enthalpy change indicates that the adsorption process is endothermic and this value also indicates that the adsorption follows a physisorption mechanism in nature involving weak forces of attraction between the adsorbed of (Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions) and composite, thereby demonstrating that the adsorption process is stable energetically<sup>[27]</sup>. The Freundlich constant  $n$  is a measure of the deviation from linearity of the adsorption. If a value for  $n$  is below to unity, this implies that adsorption process is govern by a chemical mechanism, but a value for  $n$  is above to unity, adsorption is favorable a physical process. The  $K_F$  and  $n$  were calculated from the slopes of the Freundlich plots as shown in (Figure 9, we took the results and figures of lead as example for the sake of brevity) and were found to be (1.64-2.57) and (2.70-4.76) respectively. The magnitudes of  $K_F$  and  $n$  show easy separation of heavy metal ion from wastewater and high adsorption capacity<sup>[28]</sup>. The value of  $n$ , which is related to the distribution of bonded ions on the sorbent surface, represent beneficial adsorption if is between 1 and 10<sup>[29,30]</sup>. The values of  $n$  at equilibrium are representing favorable adsorption at studied temperatures and therefore this would seem to suggest that a physical mechanism, which is referred the adsorption bond becomes weak<sup>[31]</sup> and conducted with van der

Waals forces. TABLE 4 gives the isotherm parameters for both Langmuir and Freundlich isotherms. From these parameters of the adsorption isotherm, it was noted that the Freundlich isotherm model exhibits better data than the Langmuir isotherm model.

## CONCLUSION

The present study shows that polyacrylamide ferric antimonate is an effective adsorbent for the removal of Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions from aqueous solutions. The following results have been obtained:

- 1- polyacrylamide ferric antimonate has a good ion exchange capacity, high stability and high selectivity for Pb (II) and Fe (III) than Cd (II), Cu (II) and Zn (II) ions.
- 2- the adsorption follows a physisorption mechanism in nature involving weak forces of attraction between the adsorbed of Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions and polyacrylamide ferric antimonite..
- 3- it was noted that the Freundlich isotherm model exhibits better data than the Langmuir isotherm model.

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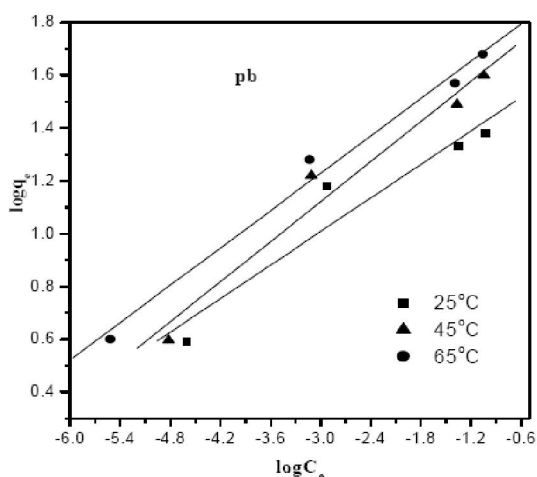


Figure 9 : Freundlich adsorption isotherm for the sorption of Fe(III), Pb(II), Cd(II), Cu(II), and Zn(II) ions on polyacrylamide ferric antimonate at different reaction temperatures



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