

Full Length Research Paper

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

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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 antimonate has been studied. The thermodynamic parameters such as activation energy (E_a), entropy of activation ΔS^* and diffusion coefficient (D_o) have been evaluated and a correlation has been made of these parameters with the ion exchange characteristics of the material.

Key words: Synthesis, polyacrylamide ferric antimonite, adsorption, isotherm, diffusion, heavy metals.

INTRODUCTION

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 (Khan et al., 2003, 2003; Khan and Alam, 2004). Heavy metals contamination exists in aqueous waste stream from many industries such as metal plating, mining, tanneries, and painting, car radiator manufacturing, as well as agricultural sources where fertilizers and fungicidal spray were intensively used. The removal of heavy metal in an effective manner from water and waste water is, thus, ecologically very important. There are many reported and established technologies for the recovery of metals from waste water, which include chemical precipitation, flotation, electrolytic recovery, membrane separation and activated carbon adsorption. 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 (Khan et al., 2004). These materials were found selective for heavy toxic metal ions and utilized for analysis of water pollution as such materials have a great deal of attention because of their special mechanical and chemical stabilities (Khan et al., 2004). 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.

EXPERIMENTALS

Materials

All chemicals used in this work were of analytical grade and used

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without further purification.

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 $70 \pm 5^\circ C$ with continuous stirring.

Preparation of ferric antimonate

Ferric antimonate prepared from 0.5 M of ferric chloride was 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 $70 \pm 5^\circ C$. The resulting solution was precipitated by using ammonia solution drop by drop until the pH was about 0.13. This results in formation of red brown precipitate.

Preparation of polyacrylamide ferric antimonate

Polyacrylamide ferric antimonate was 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 was washed with distilled water several times. The supernatant liquid was decanted and the gel filtered using a centrifuge (about 10^4 rpm) and dried at $50 \pm 1^\circ C$. The product was crashed and sieved to obtain different mesh sizes of 0.12 to 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 at $1000^\circ C$ were determined using thermal analysis technique (TG and DTA) to be 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 6 M], as well as in potassium and sodium hydroxide (0.1, 1 M) by mixing 50 mg of ion exchanger samples and 50 ml of the desired solution with intermittent shaking for approximately three weeks at $25 \pm 1^\circ C$.

Data 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

The ion exchange capacity of polyacrylamide ferric antimonate for Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions were found to be 5.33, 4.31, 3.12, 2.51 and 2.35 respectively. It is indicated that the affinity sequence for all cations is $Pb^{2+} > Fe^{3+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$. This trend may be due to the electronegativity of $Pb^{2+} > Fe^{3+}$, Cu^{2+} , Cd^{2+} and Zn^{2+} and may be due to the hydrated ionic radii

according to the fact that increasing atomic number results in decreasing hydrated ionic radii (Abou-Mesalam and El-Naggar, 2003).

The effect of particle sizes on the rate of exchange of Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions on polyacrylamide ferric antimonate was studied at $25 \pm 1^\circ C$. Straight lines passing through the origin are obtained, which were taken as indication of a particle diffusion mechanism as shown in Figure 1. The results and figures of Lead were taken 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, 2012).

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 $65 \pm 1^\circ C$) on polyacrylamide ferric antimonate are presented in Figure 2. The results and figures of Lead were taken as example for the sake of brevity). straight lines were observed to be 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 $65 \pm 1^\circ C$. The relatively small activation energy values (E_a) obtained in Table 1, for Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions, indicated that the rate of exchange is particle diffusion mechanism (El-Naggar et al., 2012).

Adsorption isotherm

The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful applications in many adsorption processes of monolayer adsorption. For the case of adsorption in solution, the equation is represented by the following (Langmuir, 1916).

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} k_L} + \frac{C_e}{q_{\max}}$$

Where q_e (mol g^{-1}) 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^{-3}) 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 composite Figure 3 give a straight line of the slope $\frac{1}{q_{\max}}$ and intercept $\frac{1}{q_{\max} k_L}$.

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 4. Accordingly the values of ΔH at saturation are calculated

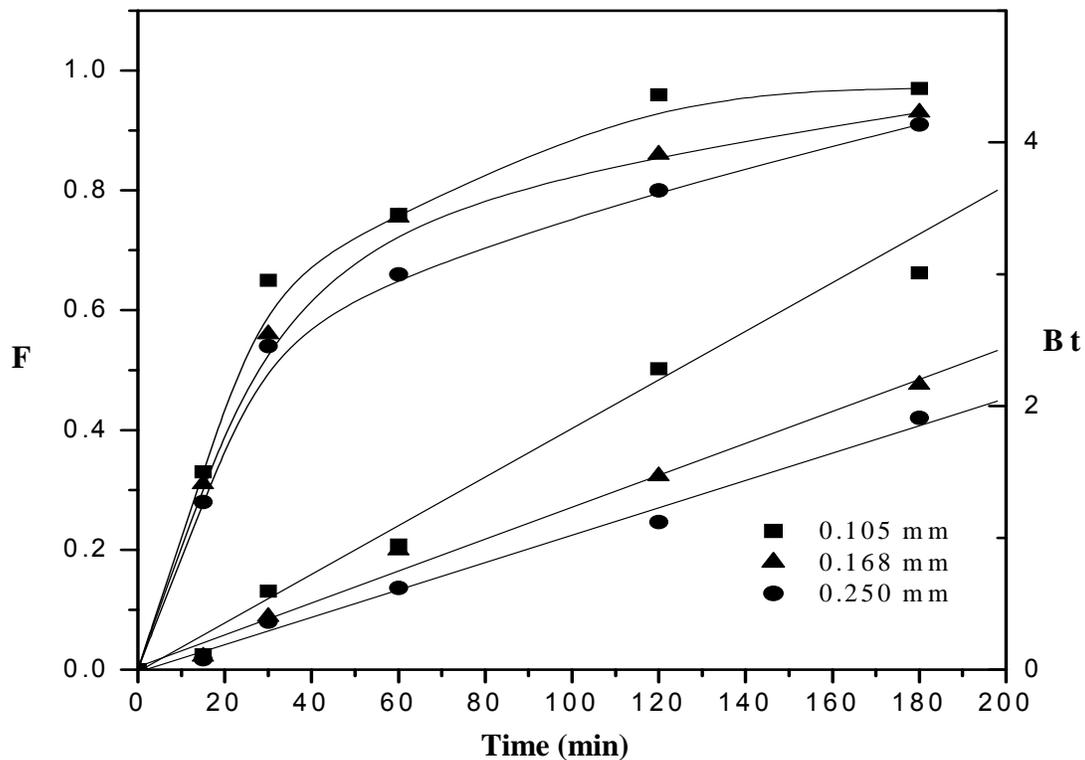


Figure 1. Plots of F and Bt against time for exchange of Pb(II) on polycrylamid ferric antimonate at different particle diameters.

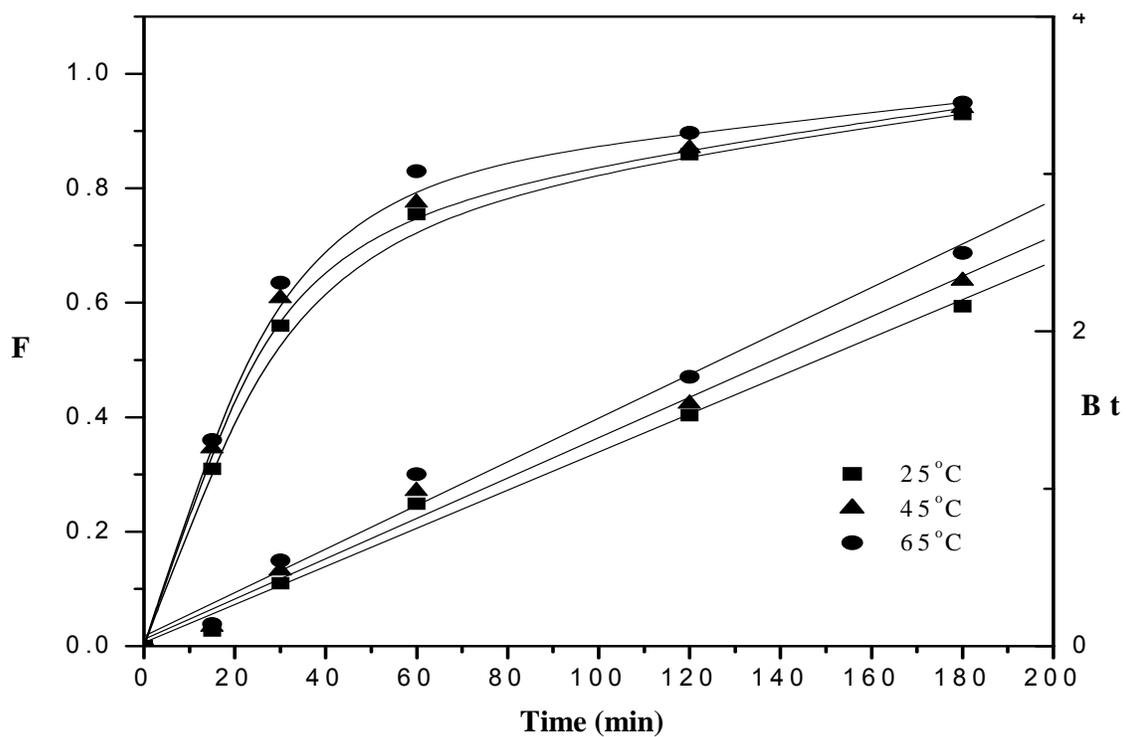


Figure 2. Plots of F and Bt against time for exchange of Pb(II) on polycrylamid ferric antimonate at different reaction temperatures.

Table 1. Thermodynamic parameters for the exchange of Fe³⁺, Pb²⁺, Cd²⁺, Cu²⁺, and Zn²⁺ on polyacrylamide ferric antimonate, at different reaction temperatures.

Metal ion	Reaction temperature	$D_i \times 10^8$ (cm ² s ⁻¹)	$D_o \times 10^5$ (cm ² s ⁻¹)	E_a (KJ mol ⁻¹)	ΔS^* (mol ⁻¹ k ⁻¹)
Pb(II)	25	0.57	1.83	2.86	-121
	45	0.61	1.82		-122.3
	65	0.65	1.83		-122.8
Cd(II)	25	0.59	3.44	4.37	-116.4
	45	0.67	3.54		-116.8
	65	0.73	3.44		-117.6
Zn(II)	25	0.59	3.8	4.56	-115.7
	45	0.69	3.89		-116
	65	0.75	3.8		-116.8
Cu(II)	25	0.81	8.55	6.27	-107.2
	45	1.04	9.3		-107.4
	65	1.08	8.56		-108.6
Fe(III)	25	0.44	17.9	9.14	-102.8
	45	0.62	20.04		-102.4
	65	0.67	17.9		-103.9

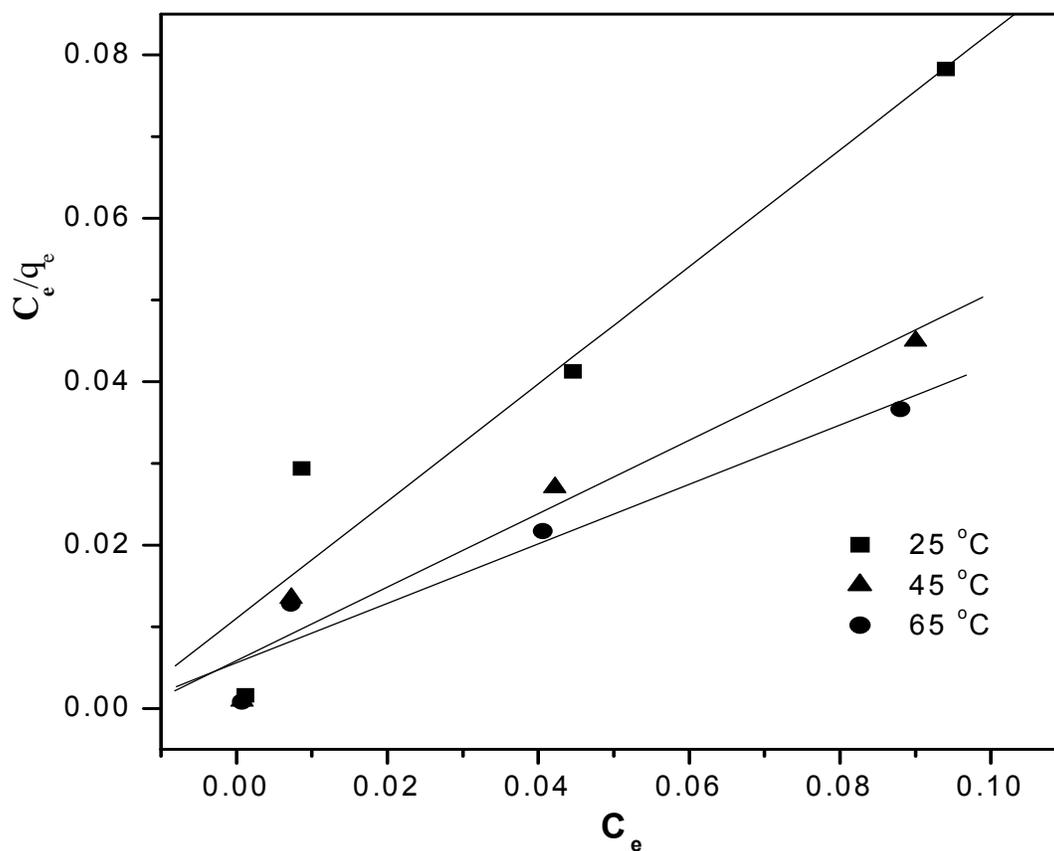


Figure 3. Plots of C_e / q_e against C_e for exchange of Pb(II) on polyacrylamid ferric antimonate at different reaction temperatures.

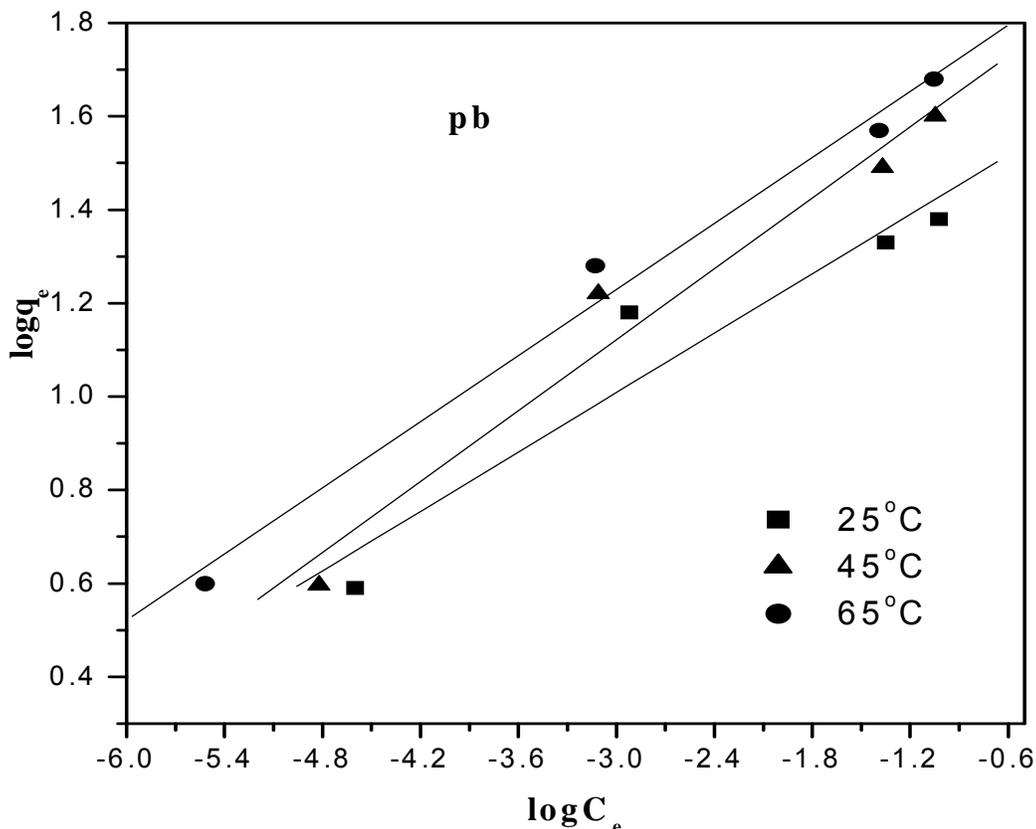


Figure 4. Freundlich adsorption isotherm for the sorption of Fe(III), Pb(II), Cd(II), Cu(II) and Zn(II) ions on polyacrylamid ferric antimonate at different reaction temperatures.

for Pb(II), Fe(III), Cd(II), Cu(II) and Zn(II) ions on polyacrylamide ferric antimonate and represented in the Table 2. These values indicate the exothermic behavior of polyacrylamide ferric antimonate. The linearized form of the Freundlich isotherm equation (Freundlich, 1906) is.

$$\log q_e = \log k_F + \frac{1}{n} \log C_e$$

Where K_F ($\text{dm}^3 \text{g}^{-1}$) 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.

The free energy ΔG° were associated to the adsorption process and were determined using the following equation

$$\Delta G^\circ = -RT \ln K_L$$

The results given in Table 2 show that the change of free energy for physisorption is generally between -20 and 0 kJ mol^{-1} ; the physisorption together with chemisorption is at the range of -20 to -80 kJ mol^{-1} and chemisorptions is

at a range of -80 to -400 kJ mol^{-1} (Jaycock and Parfitt, 1981). The negative value of the enthalpy change of Pb(II) ion indicates an exothermic behavior; 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 [Pb(II), Fe(III), Cd(II), Cu(II) and Zn(II)] ions and composite, thereby demonstrating that the adsorption process is stable energetically (Yu et al., 2001). The Freundlich constant n is a measure of the deviation from linearity of the adsorption. If a value for n is below unity, this implies that adsorption process is governed by a chemical mechanism; however, if a value for n is above unity, adsorption is favorably a physical process. The K_F and n were calculated from the slopes of the Freundlich plots as shown in Figure 4. The results and figures of Lead were taken as example for the sake of brevity) and were found to be (1.64 to 2.57) and (2.70 to 4.76) respectively. The magnitudes of K_F and n show easy separation of heavy metal ion from wastewater and high adsorption capacity (Saifuddin and Raziah, 2007). The value of n , which is related to the distribution of bonded ions on the sorbent surface, represent beneficial adsorption if it is between 1 and 10 (Kadirvelu and

Table 2. Isotherm parameters for adsorption of Pb (II), Fe (III), Cd (II), Cu (II) and Zn (II) ions on polyacrylamid ferric antimonate.

Elements	Langmuir		Freundlich	
	ΔH (KJ/mol)	ΔG° (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

Namasivayam, 2000; Solener et al., 2008). The values of n at equilibrium represents favorable adsorption at studied temperatures and therefore this would seem to suggest that a physical mechanism, referred to as the adsorption bond becomes weak (Jiang et al., 2002) and conducted with van der Waals forces. Table 2 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 thus 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 [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.

Conflict of Interests

The author(s) have not declared any conflict of interests.

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