

Full Length Research Paper

Ion exchange kinetics of some heavy metals from aqueous solutions onto poly (acrylic acid-acrylonitrile) potassium titanate

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Heavy metals released by a number of industrial processes are major pollutants. Ground, industrial and even treated wastewaters, heavy metals can be extremely toxic as they damage nerves, liver, kidney and bones. So, our work was concerned to prepare composite inorganic-organic absorbers which represent a group of inorganic ion exchangers modified using binding organic materials. Polyacrylonitrile (PAN) has been used as a universal binding polymer for a number of inorganic ion exchangers. Acrylic acid-acrylonitrile (AA-AN) comonomer mixture was prepared at the optimum copolymerization process and potassium titanate was synthesized by adding 200 ml of 2.2 M TiCl_4 , and 800 ml of 2.8 M KOH were prepared and mixed with constant stirring to the 1000 ml of AA-AN. These composites have been tested for separation of various contaminants from aqueous solutions. Their high selectivity and sorption efficiency are advantageous for treatment of various industrial waste waters. The kinetic of lead (Pb^{2+}), cadmium (Cd^{2+}) and zinc (Zn^{2+}) ions on the prepared material were studied by applying the Nernst-plank 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. The selectivity order towards the ions was found: $\text{Pb (II)} > \text{Cd (II)} > \text{Zn (II)}$.

Key words: Adsorption, polyacrylic acid-acrylonitrile, heavy metals, potassium titanate, equilibrium.

INTRODUCTION

The presence of heavy metals in an environment has been of great concern to scientists because of their increased discharge. Toxic nature, heavy metals are generally refractory and cannot be degraded. Hence, safe and effective disposal of waste water containing heavy metals is always a challenge to industrialists and environmentalists, since cost-effective treatment are not available. Lead, cadmium and zinc are example of heavy metals that have been classified as priority pollutants by the US environmental protection agency (USEPA). Therefore, the elimination of these metals from water and

wastewaters is important to protect public health. The treatment method such as chemical precipitation, membrane filtration, reverse osmosis, ion exchange and adsorption has been practiced for the removal of heavy metals. The adsorption of heavy metals has been studied by a variety of materials such as activated carbons (Tan and Teo, 1987), clays (Bolto and Pawlowski, 1986), polymeric synthetic resins (Harland, 1994) and metal oxides (Schultz et al., 1987). Studies have been reported on the use of hydrous tin (IV) oxide (Inoue et al., 1985) and hydrous titanium (IV) oxide composites as adsorbents for the removal of certain metals from aqueous solutions.

Thus, the chemistry of the adsorbents surface rather than the extent of its surface area control the adsorption

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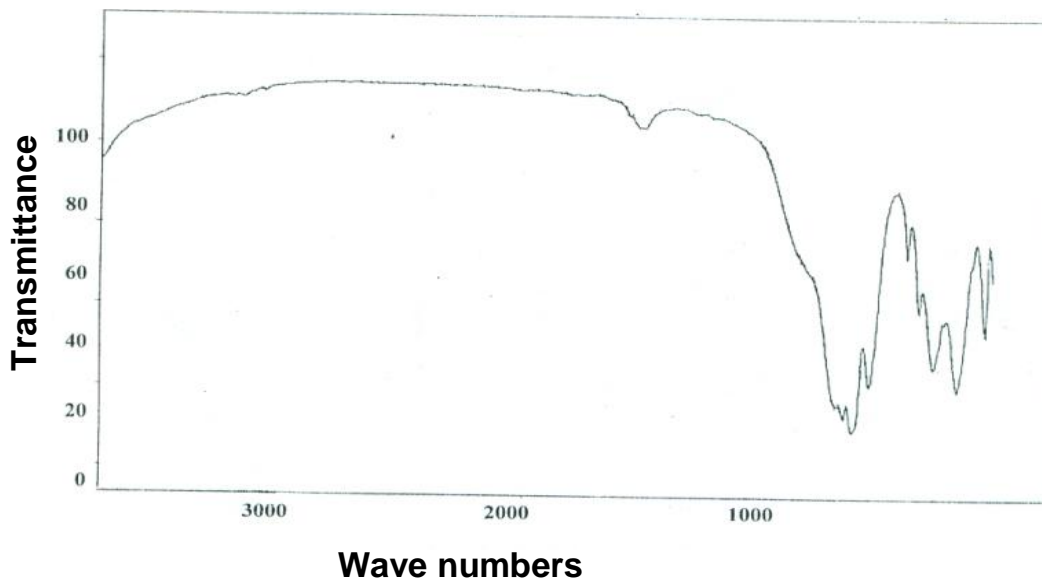


Figure 1. FTIR spectra of poly(acrylic acid-acrylonitrile) K-titanate.

in many applications. Silica composite modified with pyridinium ions (Iamamoto and Gushikem, 1989) and clay impregnated with 2-mercaptobenzothiazole (Khanet al., 2004) have been developed for the adsorption of heavy metals such as Pb(II), Cd(II), Cu(II) and Zn(II). A limited study indicated the potential of surface modification of tree bark (Khan et al., 2003) and sawdust. The use of polymer grafted metal oxides for the removal of toxic heavy metals from wastewaters has continued to attract considerable attention in recent years, because they are capable of binding heavy metals by adsorption and ion exchange even at higher temperatures (Khan et al., 2005; Suzuki et al., 1987; Shubha, 1996). This work shows the use of prepared poly (acrylic acid-acrylonitrile) K-titanate composite to remove Pb(II), Cd(II) and Zn(II) from aqueous solutions. The organic resins have much greater interest than inorganic resins especially in industrial applications because they have higher capacity than inorganic resins.

MATERIALS AND METHODS

The chemicals used in this study were obtained from B.D.H (U.K). All reagents were of analytical grade and used without further purification.

Synthesis of poly (acrylic acid-acrylonitrile)

Acrylic acid-Acrylonitrile (AA-AN) comonomer mixture was prepared at the optimum copolymerization process (Egawa and Nonaka, 1986) at a molar ratio of (AA-AN) (0.75: 0.25) and comonomer concentration of 100%. The mixture was purged by the pure dry nitrogen gas and potassium titanate was synthesized by adding 200 ml of 2.2 M TiCl_4 , and 800 ml of 2.8 M KOH were prepared and mixed with constant stirring to the 1000 ml of AA-AN. The mixture

was subjected to γ -irradiation from Co-60 with adsorbate of 2.2 KGy/h. The polymer was precipitated by acetone from the irradiated samples. The polymer was dried under vacuum at 50°C overnight to a constant weight. The kinetics experiments were carried out by batch technique at different reaction temperatures. A certain weight of the composite was mixed with a certain volume of some heavy metals solutions at natural pH value and 10^{-4} M concentration. The mixture was shaken in a shaker thermostat adjusted to the desired temperatures (25, 40 and 60°C); the v/m rate used was $500 \text{ cm}^{-3} \text{ g}^{-1}$ in all cases. At each time the solutions were separated and the concentration of these ions was determined by atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Characterization of adsorbent

Infrared studies of the synthesized compound of the poly (acrylic acid-acrylonitrile) potassium titanate are shown in Figure 1. This figure shows that the absorption band at 1600 cm^{-1} is due to the bending mode of water adsorbed on the titanate sample. The absorption band at 980 cm^{-1} for the symmetric vibrations of C-C and the absorption band at 500 to 300 cm^{-1} indicates the presence of Ti-O bonds in the synthesized compound (Aly et al., 2008). X-ray diffraction patterns were carried out using a Shimadzu XD-D1 obtained from Shimadzu Kyoto, "Japan", X-ray diffractometer with Cu $K\alpha$ radiation tube source and graphite monochromator operating at 30 kV and 30 mA. The measurements were done in 2θ ranges from 5 to 90 with scan speed $2^\circ/\text{min}$. Figure 2 manifested that the prepared compound is amorphous structure and poor in crystallinity. Table 1 clearly shows that the component of the composite and their percent, which shows that the poly (acrylic acid-acrylonitrile) K-titanate contains mainly

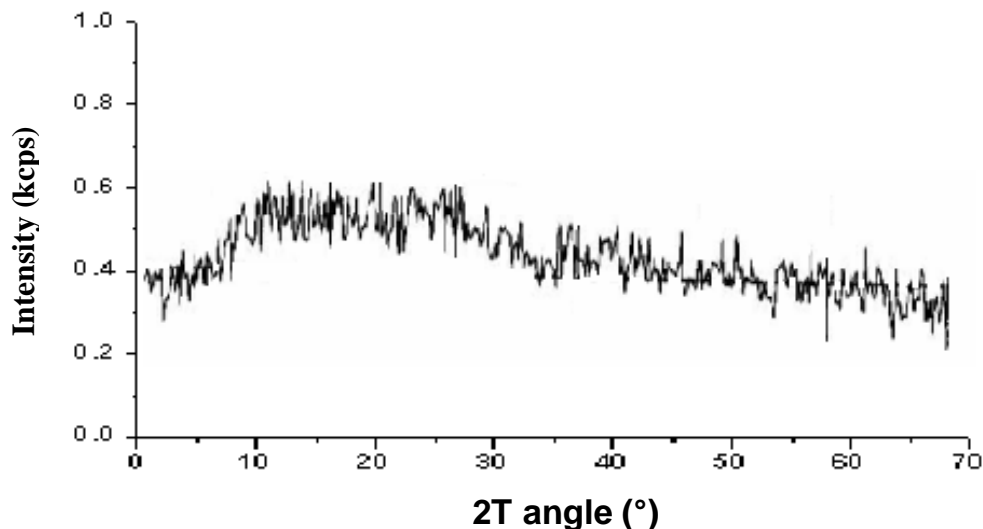


Figure 2. X-ray diffraction on poly(acrylic acid-acrylonitrile) K-titanate.

Table 1. X-ray fluorescence analysis of poly(acrylic acid-acrylonitrile) potassium titanate.

Component	Percentage (%)
K ₂ O	4.23
TiO ₂	48.88
Al ₂ O ₃	0.54
SiO ₂	0.98
CaO	0.50
ZrO ₂	2.44
SnO ₂	0.39
Sb ₂ O ₃	0.83
SO ₃	0.33
Cl	0.25
P ₂ O ₅	0.27

(TiO₂, K₂O and ZrO₂) compounds.

Effect of pH

At pH equilibrium the amount of metal ions removed was found to be a function of the pH of the solution. Figure 3 indicate that the removal of percentage of the metals as a function of pH within the range of 1 to 6. The removal of Pb(II), Cd(II) and Zn(II) by poly (acrylic acid-acrylonitrile) potassium titanate composite increased with increasing pH up to pH 4.5. The maximum removal of Pb(II) (95%), Cd(II) (75%) and Zn(II) (69%) by the composite. Above and below this pH, the extent of removal was found to be considerably low. It is clear that this composite is effective for quantitative removal of Pb(II), Cd(II) and Zn(II) at pH 4.5. Above this pH value, the removal was

found to decrease, this reflecting the higher selectivity of the adsorbent for Pb(II) than Cd(II) and Zn(II).

Kinetic studies

Effect of ions concentration

The study of the effect of concentration on the rate of exchange for the metal ions studied on the H⁺ form of poly (acrylic acid-acrylonitrile) K-Tit at 25±1°C for Cd(II) case only is shown in Figure 4. From Figure 4, it is found that the rate of exchange is independent on the metal ion concentrations; this is the first proof that particle diffusion control is the main mechanism at the concentration studied. Particle diffusion control at such concentrations has been proofed also in case of inorganic ion-exchangers (El-Naggar et al., 2007) where F is the fractional attainment of equilibrium. The effect of the particle size on the rate of exchange of Pb(II) on H⁺ form of composite was investigated at different particle diameters at 25±1°C and the results are given in Figure 5 as a relation between F and Bt against time. The figure shows that, straight lines passing through the origin are obtained for Bt and t relation at all metal ions studied which is a further indication of particle diffusion mechanism (Abou-Mesalam and El-Naggar, 2003). The same trend was reported by others (El-Naggar et al., 1999), which also indicates that the exchange rate of the studied Pb²⁺ is increasing with the decrease of particle sizes which is again verifies the particle diffusion control (Figure 5). The experimental conditions of the present work were set to study the particle diffusion mechanism only as a limited batch technique. In this condition the rate of exchange is controlled by diffusion of ions through the spherical particles of the exchanger (Boyd et al.,

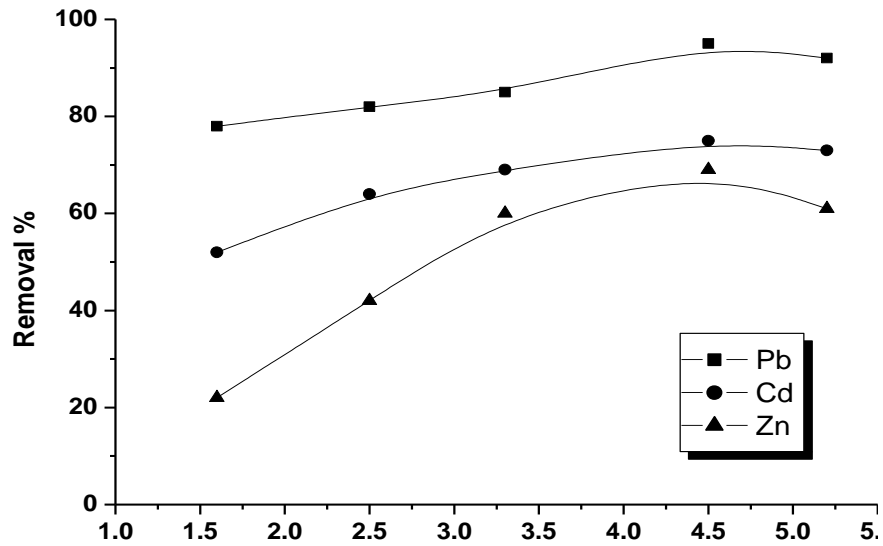


Figure 3. Effect pH on the distribution of metal ions onto poly (acrylic acid-acrylonitrile) potassium titanate.

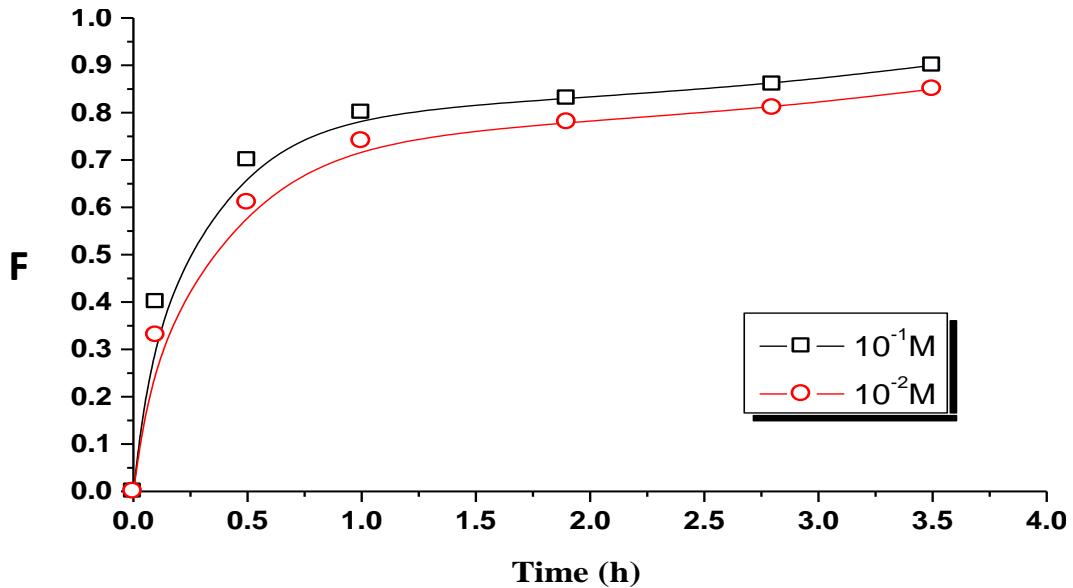


Figure 4. Plots of F against time for exchange of Cd(I) on poly(acrylic acid-acrylonitrile) K-Tit. at different metal ion concentrations at 25 ± 1°C.

1947). The equation developed by Boyd et al. (1947) is used for evaluating the kinetic parameters as follows.

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

Where, F is the fractional attainment of equilibrium, n is

an integer number, D_i is the effective diffusion coefficient of exchanging ion inside exchanger and r is the particle radius. This equation was improved by Reichenberg (1953) and can be written in the following form:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 B t} \quad (2)$$

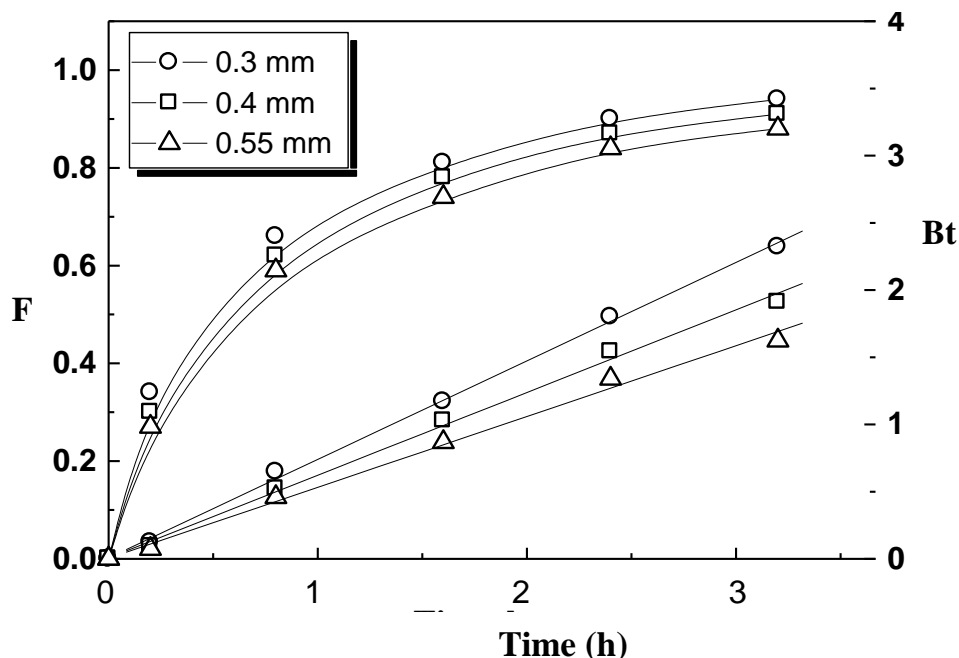


Figure 5. Plots of F and Bt against time for exchange of Pb(II) on poly(acrylic acid-acrylonitrile) K-titanate dried at 50°C at different particle diameter.

Where,

$$B = \pi^2 D_i / r^2 \quad (3)$$

F is a mathematical function of Bt. D_i is obtained from Bt and t plots which should give straight lines passing by the origin in the case of particle diffusion mechanism. The values of Bt at the respective values of F are obtained from Reichenberg's data (Reichenberg, 1953). As shown in Figure 6, the plots of Bt vs t for Pb(II), Cd(II) and Zn(II) exchange at 25, 40 and 60°C on the composite which shows a good straight lines passing by the origin, proving a particle diffusion mechanism. As D_i increases with temperature, this means that the mobility of the ions increases with temperatures. The D_i values computed from B-values are given in Tables 2 to 4 which give the sequence for 25, 40 and 60°C (Nancollas and Paterson, 1967) inferred that the crystallinity of the exchanger affect the D_i - values at all reaction temperatures. The linearity of $\log D_i$ vs $1/T$ (Figure 7) indicates the validity of Arrhenius equation:

$$D_i = D_o \exp(-E_a/RT) \quad (4)$$

The small activation energy (E_a) of cations diffusion process reflects the ease with which cations can pass through the exchanger particles. From Tables 2 to 4, the E_a -values given are relatively small which suggest that the rate is particle diffusion controlled (Zakaria et al.,

2009). The Arrhenius equation was also used for calculated D_o which in turn is used to obtain ΔS^\ddagger by means of the following equation, proposed by Barrer et al. (1961)

$$D_o = 2.72 d^2 kT^2 / h \exp(\Delta S^\ddagger/R) \quad (5)$$

Where k is the Boltzmann constant, h is the planks constant; d is the distance between the adjacent exchanging sites in the exchanger and T is the absolute temperature. It is evident from Tables 2 to 4 that the relatively small activation energy values for Pb^{2+} , Cd^{2+} and Zn^{2+} suggest that the rate of exchange is particle diffusion. Moreover, the negative value of entropy of activation, where the entropy change is small in the solid phase, suggesting that no significant change occurred in the composite.

Conclusion

The exchange kinetics of Pb(II), Cd(II) and Zn(II) on the prepared poly (acrylic acid-acrylonitrile) potassium titanate was studied as a function of concentrations, particle size, reaction temperatures and drying temperature. The rate of exchange increase with decreasing the particle size and drying temperature of the exchange materials, however the rate of exchange increases with increasing the reaction temperature. The rate of exchange is independent on the metal ion concentration and this is evident that the condition in this

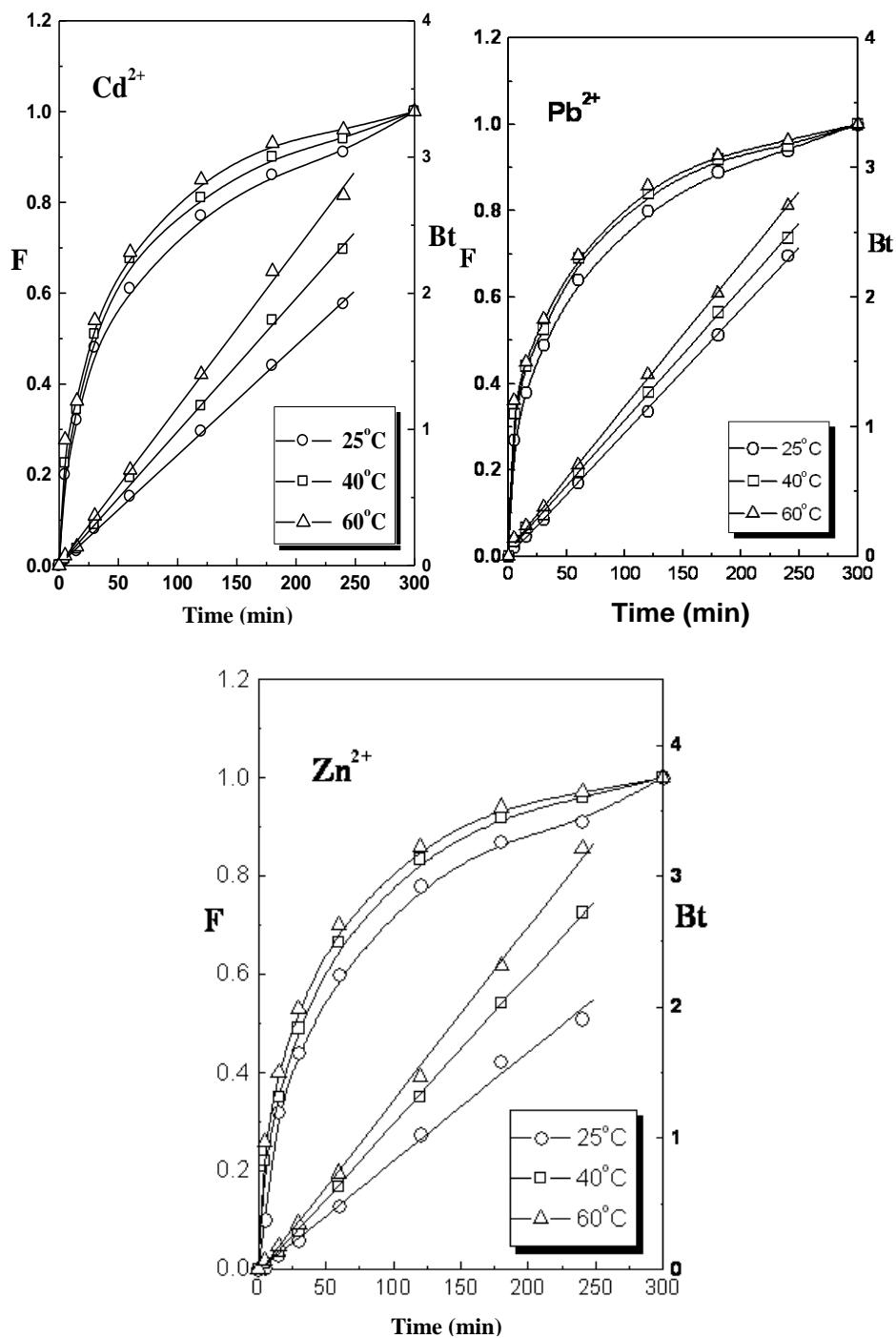


Figure 6. Plots of F and Bt against time for the exchange of pb(II), Cd(II) and Zn(II) on poly (acrylic acid-acrylonitrile)K-titanate.

Table 2. Thermodynamic parameters for exchange of Pb(II) on poly(acrylic acid-acrylonitrile) K-titanate at different reaction temperatures and particle diameters 0.4 ± 0.02 mm.

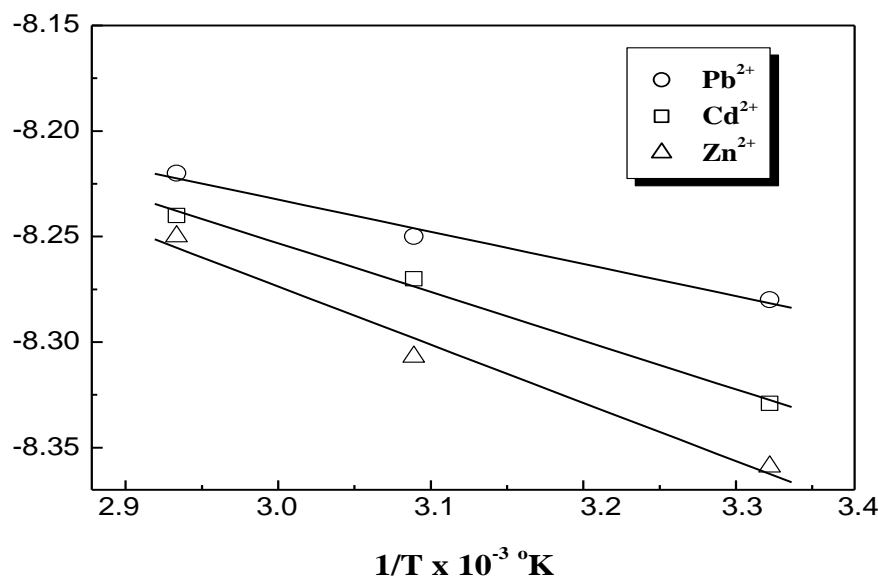
Temperature (°C)	$D_i \times 10^9$ (cm ² s ⁻¹)	$D_o \times 10^6$ (cm ² s ⁻¹)	E_a (kJ mol ⁻¹)	ΔS (J mol ⁻¹ k ⁻¹)
25	5.32	0.95	11.92	-213.3
40	6.80	0.62		-216.4
60	9.12	0.66		-218.6

Table 3. Thermodynamic parameters for exchange of Cd(II) on poly (acrylic acid-acrylonitrile) K-titanate at different reaction temperatures and particle diameters 0.4 ± 0.02 mm.

Temperature (°C)	$D_i \times 10^9$ (cm ² s ⁻¹)	$D_o \times 10^6$ (cm ² s ⁻¹)	E_a (kJ mol ⁻¹)	ΔS (J mol ⁻¹ k ⁻¹)
25	2.2	0.90	11.60	-215.2
40	6.3	0.55		-218.4
60	8.6	0.58		-222.3

Table 4. Thermodynamic parameters for exchange of Zn(II) on poly(acrylic acid-acrylonitrile) K-titanate at different reaction temperatures and particle diameters 0.4 ± 0.02 mm.

Temperature (°C)	$D_i \times 10^9$ (cm ² s ⁻¹)	$D_o \times 10^6$ (cm ² s ⁻¹)	E_a (kJ mol ⁻¹)	ΔS (J mol ⁻¹ k ⁻¹)
25	5.1	0.88	11.35	-216.2
40	6.0	0.50		-220.1
60	8.3	0.52		-224.2

**Figure 7.** Arrhenius plots for exchange of pb(II), Cd(II) and Zn(II) on poly(acrylic acid-acrylonitrile) K-Tit at different reaction temperatures.

work proves particle diffusions mechanism for all investigated metal ions. The diffusion coefficient values (D_i) of Pb(II), Cd(II) and Zn(II) on composite at 25°C decrease with increasing the drying temperatures from 50 to 400°C.

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