International Journal of
Research in Chemistry and Environment
Available online at: www.ijrce.org
IJRCE
ISSN 2248-9649

Research Paper

Ion Exchange Kinetics of Pb^{2+}, Cu^{2+}, Cd^{2+} and Mn^{2+} Ions on Thermally Stable Bimetallic Ion Exchange Material: TitaniumTin Tungstate

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(Received 29th June 2015, Accepted 25th September 2015)

Abstract: *Heavy metal contamination in the environment has been of great concern because of their increased discharge, toxic nature and other adverse effects on the receiving streams. Titaniumtin tungstate (TSW), an efficient bimetallic ion exchange material was synthesized by co-precipitation method and is used to study the ion exchange kinetics of some toxic heavy metal ions. The exchanger was characterized by some physicochemical properties like FTIR, XRD, TGA-DTA, SEM and ion exchange properties to validate the structure and ion exchange behavior. The exchanger shows high ion exchange capacity of 1.2 meqg*$^{-1}$ *as well as good chemical and thermal stability. Explicit Nernst-Plank approximation is applied to study the reaction kinetics for four heavy metal ions (*Pb^{2+}, Cu^{2+}, Cd^{2+} *and* Mn^{2+}*) on the surface of TSW. The kinetic studies carried out under particle diffusion controlled phenomenon. On the basis of kinetic studies, various physical parameters like fractional attainment of equilibrium* $U(\tau)$*, self diffusion coefficients (*D_0*), energy of activation (*E_a*) and entropy of activation (*ΔS^**) were estimated to evaluate the mechanism of ion exchange and indicated that the ion exchange process is feasible and spontaneous.*

Keywords: Bimetallic ion exchanger, ion exchange kinetics, particle diffusion etc.

Introduction

Removal and separation of toxic heavy metal ions have been studied by various methods [1-4]. During last few decades, ion exchange process has been considered as an efficient method for the removal and the recovery of heavy metals from wastewater [5-7]. For practical application of ion exchange process it is required to determine the kinetic parameters. Kinetics of exchange enables to understand the feasibility of an ion exchange material in separation of heavy metal ions. Advancement of inorganic ion exchangers is not only due to high thermal stability and resistivity but also for unusual selectivity for ionic species and versatility in separation sciences [8, 9].

It is understood that the most important parameter for the selection of a material for the practical application in wastewater treatment techniques is the validity of ion exchange mechanism. Kinetic studies envisage the three aspects of ion exchange process, viz, the mechanism of ion exchange, rate determining step and the rate laws obeyed by the ion exchange system. There are many approaches that can be used to describe the ion-exchange equilibrium. The Nernst Plank equations with some additional assumptions provide appropriate values in obtaining the values of the various kinetic parameters precisely [10, 11].

In our present work, bimetallic cation exchanger titaniumtin tungstate was synthesized and characterized. Determination of ion exchange equilibrium and kinetic models of different M^{2+}/H^+ systems (M^{2+} – Metal ions) were done on the selected ion exchange materials. The mechanism of ion exchange can be explained taking into account of ion exchange equilibrium with respect to time and the phenomenon of ion exchange is considered as diffusion of ion through particles of the exchanger and its adherent film. Also we are actively engaged to study the issues related to the ion exchange kinetics of Pb^{2+}, Cu^{2+}, Cd^{2+} and Mn^{2+} ions over the newly synthesized ion exchange material. Various kinetic parameters like self diffusion coefficient

(Do), energy of activation (Ea) and entropy of activation (ΔS^*) were evaluated.

Methods and Material

Reagents and chemicals: Titanium chloride, stannic chloride and sodium tungstate were obtained from Loba Chemie (India). All other chemicals and reagents used were of analytical grade.

Instrumentation: pH measurements were performed using an ELICO LI613 pH meter. Spectrophotometry was done on a UV-Visible Spectrophotometer model JASCO V660 with diffuse reflectance accessory (integrated sphere). IR studies were made using an FTIR spectrometer model Thermo Nicolet Avtar370and thermogram was run on Perkin Elmer Diamond TG/DTA Analyzer. X-ray diffractometer BrukerAXS D8 Advance for X-ray diffraction studies and an electric temperature controlled shaker was used for shaking. Chemical composition was determined using EDS. A glass column was used for column operations.

Synthesis of the exchanger: Different samples of TSW were prepared by adding 0.05 M sodium tungstate solution to a mixture of 0.05M titanium trichloride solution and 0.05M stannic chloride solution in different volume ratios with intermittent shaking of the mixture and keeping the pH at 1.0 as given in table 1. The precipitates were filtered, washed with deionized water and dried. The exchangers were then converted in to the H^+ form by treating with 1M nitric acid for 24 hrs with occasional shaking and intermittent changing of acid. Then the samples were washed with deionized water to remove the excess acid, dried and sieved to obtain particles of 50-70 mesh. Properties like ion exchange capacity (IEC), chemical resistivity and pH titration studies, distribution studies and effect of temperature on IEC were carried out as reported earlier [12].

Kinetic studies

Concentration variation study

Concentration effect on exchange mechanism was studied by taking metal ion solution of different concentrations (0.005, 0.01, 0.02 and 0.03M) for ion exchange process. Metal ion solution (20 ml) of each concentration was shaken with 0.2g of exchanger (in H^+ form) in stoppered conical flasks at 30^0C for different time intervals (0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 min). Supernatant was removed after every time interval and metal ion concentration was evaluated by EDTA titration.

Temperature variation study

0.01M metal ion solution was shaken with 0.2g of the exchanger in stoppered conical flasks at different temperatures (30, 40, 50 and 60^0C) for different time intervals (0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 min). Supernatant was removed after every time interval and metal ion concentration was evaluated by EDTA titration.

Results and Discussion

Synthesis and characterization of the exchanger

Titaniumtin tungstate was obtained as ivory coloured solid. The Na^+ ion exchange capacity for the selected sample, evaluated by column method [13] at room temperature was 1.2meqg^{-1} (Table 1).

The FTIR spectrum (figure 1(a)) of TSW exhibits a broad band in the region 3544 cm^{-1}, which is attributed to asymmetric and symmetric hydroxyl –OH stretches. A sharp medium band at 1625 cm^{-1} is attributed to aqua (H–O–H) bending.

A band in the region 2364 cm^{-1} showed the presence of Ti-O bond [14]. The band in the region of 1496 cm^{-1} represents deformation vibrations of metal hydroxyl groups and interstitial water molecules and the bands at 1146 cm^{-1} and 416 cm^{-1} express the presence of metal-oxygen stretching vibrations [15]. X-ray diffractogram (figure 1(b)) of the material supports its amorphous nature. TGA of TSW (figure 1(c) shows a sharp change within the temperature up to 154^0C corresponding to the loss of external water molecules, after which a gradual weight loss is observed till 300^0C.

This may be due to the condensation of structural hydroxyl groups. After which the material is almost stable up to 600^0C. The scanning electron microscope image (figure 1(d)) of titaniumtin tungstate explains the particles were broad in size range, having an irregular shape and no sign of crystalline structure.

Table 1: Synthesis and properties of various samples of ZBW

Sample	Volume ratios			pH	Appearance	IEC (meq/g)
	Ti	Sn	W			
TSW-1	1	1	1	1	All Ivory coloured solids	0.65
TSW-2	1	1	2	1		0.79
TSW-3	1	1	3	1		0.92
TSW-4	1	2	3	1		0.86
TSW-5	2	1	4	1		0.99
TSW-6	1	2	4	1		1.20

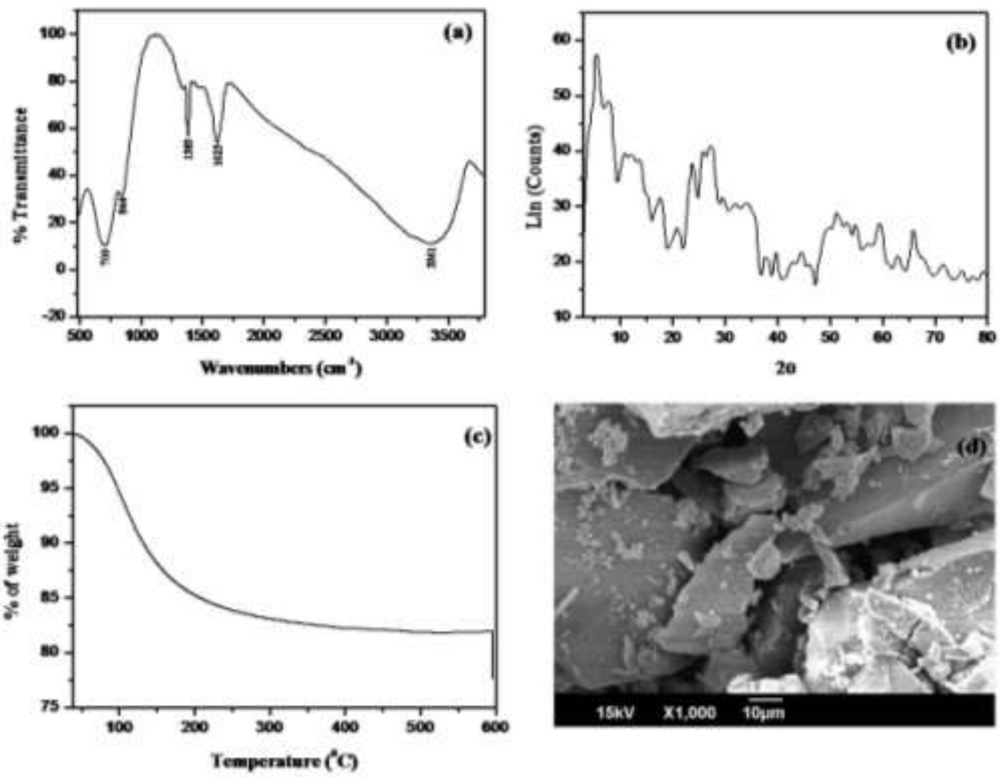

Figure 1: **(a) FTIR, (b) XRD, (c) TGA and (d) SEM of TSW**

Kinetic studies

This study was carried out to ascertain the use of this bimetallic ion exchange material for the removal and separation of toxic heavy metal ions from aqueous solution. As the ion exchange process is basically the exchange of ions between the mobile phase and stationary phases, the rate of exchange process determined through the ion exchange kinetics will be responsible for the fate of a particular ion exchange material used for the treatment of wastewater streams. The rate of ion exchange process is basically governing by the inter-diffusion of the exchanging ions either within the ion exchange material particle (Particle diffusion) or in an adherent liquid film (film diffusion) which is not affected by agitation of the solution. A simple kinetic criterion is used to predict whether particle or film diffusion will be rate controlling step under a given set of conditions. The infinite time of exchange is the time necessary to obtain equilibrium in an ion exchange process. Thus, ion exchange rate becomes independent of time after this time interval. Figure 2(a) shows that 20 minutes were required for the establishment of equilibrium at 30^0C for Pb^{2+}-H^+ exchange. Similar behavior was also observed for Cu^{2+}-H^+, Cd^{2+}-H^+ and Mn^{2+}-H^+ exchanges. Therefore, 20 minutes was assumed to be the infinite time of exchange for all exchange systems.

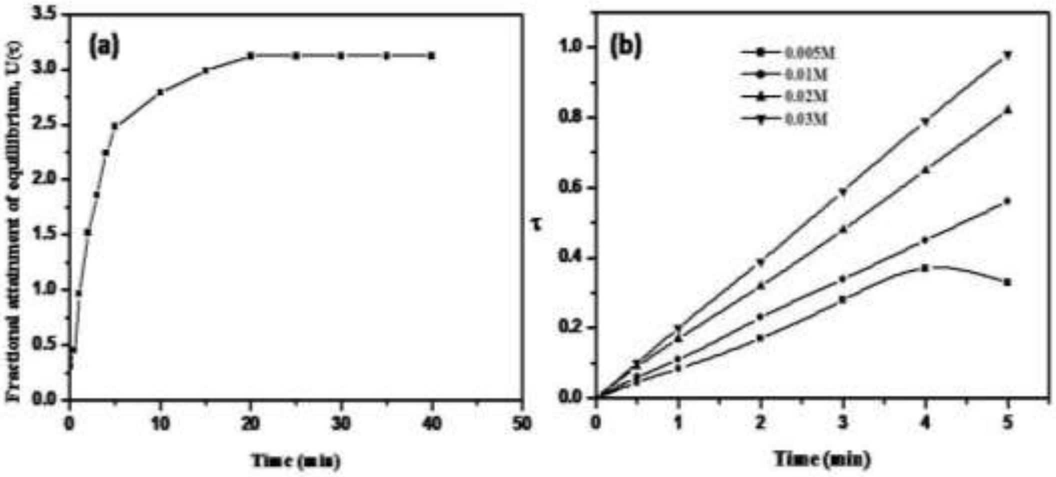

Figure 2: (a) Plot of U(τ) vs. time (t) for M^{2+}-H^+ exchanges at 30^0C on TSW and (b) Plots of τ versus time (t) for M^{2+}-H^+ exchanges at 30^0C on TSW

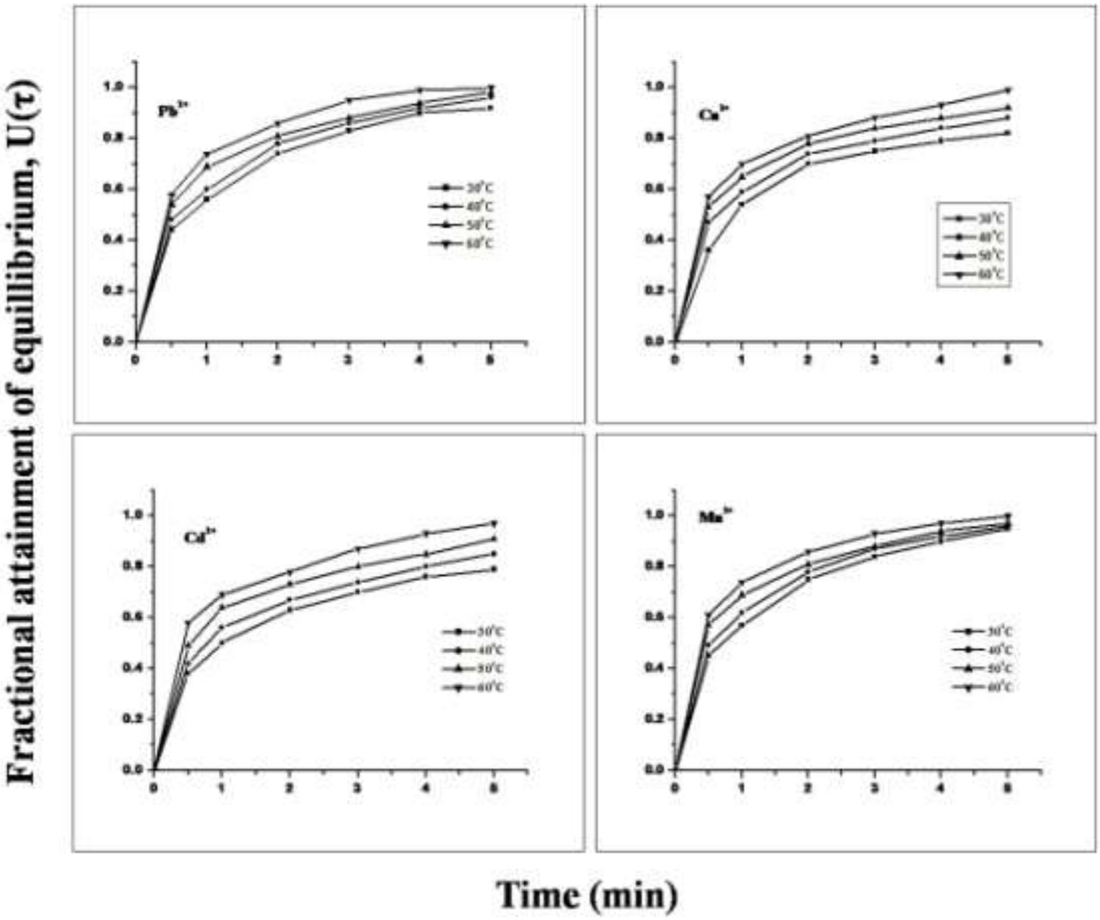

Figure 3: **Plots of U(τ) versus time (t) for Pb^{2+}-H^+, Cu^{2+}-H^+, Cd^{2+}-H^+ and Mn^{2+}-H^+ exchanges at different temperatures on TSW**

A study of the concentration effect on the rate of exchange at 30^0C showed that the initial rate of exchange was proportional to the metal ion concentration and τ versus time (t in min) plots are also straight lines passing through the origin at and above 0.01M concentration of metal ion (Figure 2(b)), which confirms the particle diffusion controlled phenomenon. However, below the metal ion concentration of 0.01M, film diffusion control phenomenon was more prominent. Hence, the kinetic studies for exchange of Pb^{2+}-H^+, Cu^{2+}-H^+, Cd^{2+}-H^+ and Mn^{2+}-H^+ were made under particle diffusion controlled phenomenon. The ion exchange kinetic results for all heavy metal ions under particle diffusion controlled phenomenon are expressed in terms of the fractional attainment of equilibrium, U(τ) with time according to the equation,

$$U(\tau) = \frac{\text{the amount of exchange at time (t)}}{\text{the amount of exchange at infinite time}} = 1 - \left(\frac{Q_H t}{Q_H^0}\right) = \left[\frac{C_0 - C_t}{C_t - C_\infty}\right] \qquad (1)$$

Where $Q_H t$ is the H^+ ion content present at time t and Q_H^0 is the amount present initially in the ion exchanger while C_t, C_∞ and C_0 are concentrations of metal ion at time t, equilibrium concentration and initial concentration respectively. Plots of U(τ) versus time (t in min), for metal-hydrogen ion exchanges showed that the fractional attainment of equilibrium was faster at a higher temperature suggesting that the mobility of the ions increased with an increase in temperature (Figure 3).

On the basis of Nernst-Plank equation, each value of U(τ) will have a corresponding value of τ, a dimensionless parameter and the numerical results for corresponding value of τ can be expressed by explicit approximation [16-18]:

$$U(\tau) = [1-\exp\{\pi^2 (f_1(\propto)\, \tau + f_2 (\propto)\, \tau^2 + f_3 (\propto)\, \tau^3)\}]^{1/2} \qquad (2)$$

Where $\tau = D_H^+ \, t / r_o^2$, $\propto$ is the mobility ratio $= D_H^+/D_M^+$. D_H^+ and D_M^+ are the inter diffusion coefficients of counter ions H^+ and M^{2+}, respectively, in the exchanger phase, r_0 is the particle radius which is 125×10^{-6}m (50-70 mesh in the present study. The three functions f_1 (∝), f_2 (∝) and f_3 (∝) depend upon the mobility ratio (∝) and the charge ratio (Z_H^+/Z_M^{2+})

of the exchanging ions. Thus they have different expressions as given below. When the exchanger is taken in the H^+ form and the exchanging ion is M^{2+}, for $1 \leq \propto \leq 20$, as in the present case the three functions have the values:

$$f_1(\propto) = -\frac{1}{0.64 + 0.36 \propto^{0.668}}$$
$$f_2(\propto) = -\frac{1}{0.96 + 2.0 \propto^{0.4635}}$$
$$f_3(\propto) = -\frac{1}{0.27 + 0.096 \propto^{1.140}}$$

The τ versus time (t) for heavy metal exchanges at four different temperatures are shown in figure 4. The particle diffusion controlled phenomenon is verified as the straight lines passing through the origin. The slopes (S) of the lines of various τ versus time (t) plots are given in table 2 and are related to D_{H^+} as follows:

$$S = D_{H^+}/r_0^2 \tag{3}$$

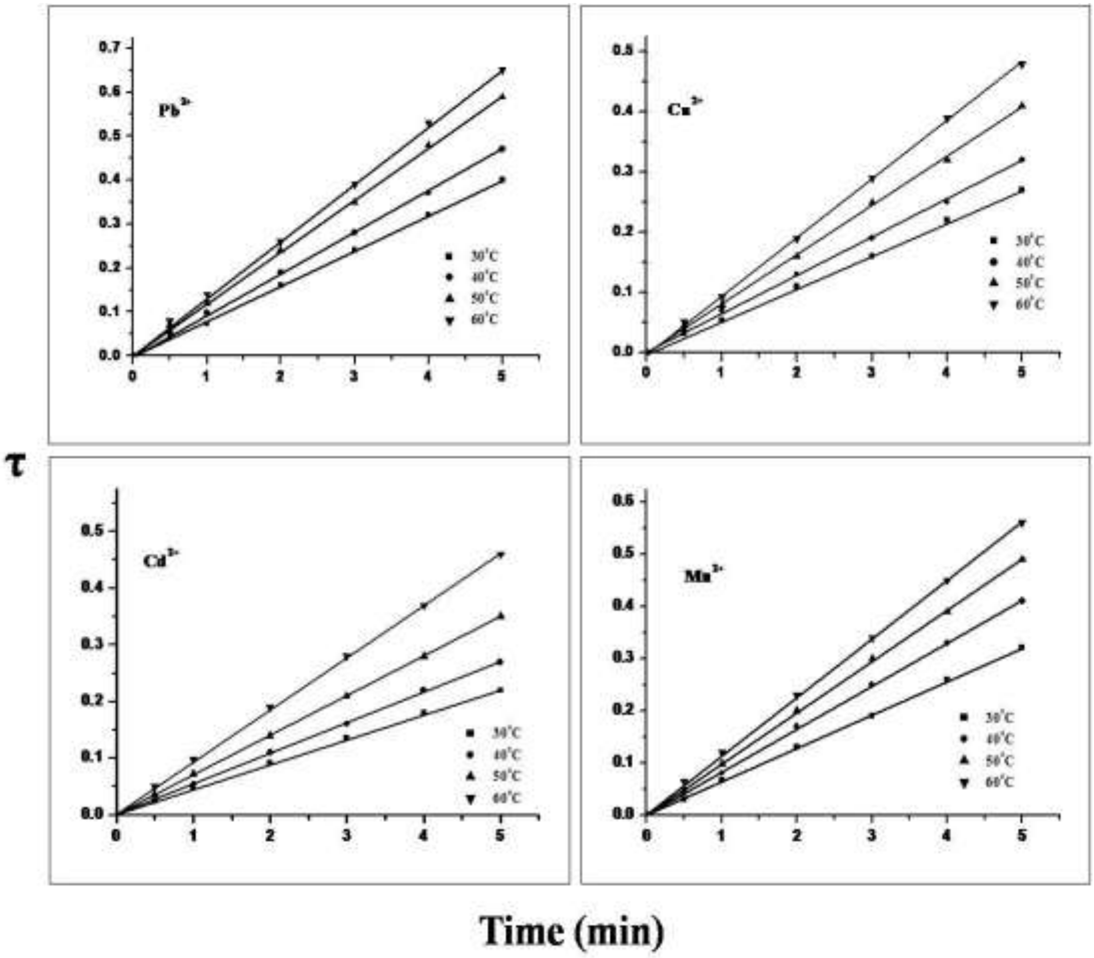

Figure 4: **Plots of τ versus time (t) for Pb^{2+}-H^+, Cu^{2+}-H^+, Cd^{2+}-H^+ and Mn^{2+}-H^+ exchanges at different temperatures on TSW**

Table 2: Slops of various τ vs. time plots on TSW at different temperatures

Ions present in the ion exchanger	**Migrating ions**	**S (s^{-1}) at different temperatures**			
		30^0C	**40^0C**	**50^0C**	**60^0C**
H^+	Pb^{2+}	0.0799	0.0925	0.1172	0.1308
H^+	Cu^{2+}	0.0536	0.0618	0.0817	0.0955
H^+	Cd^{2+}	0.0433	0.0528	0.0689	0.0914
H^+	Mn^{2+}	0.0644	0.0825	0.0982	0.1114

Table 3: Values of D_0, E_a and ΔS* for ion exchanges over TSW

Migrating ions	Ionic radii (A^0)	D_0 (10^{-7}) (m^2s^{-1})	E_a ($KJmol^{-1}$)	ΔS* ($JK^{-1}mol^{-1}$)
Pb^{2+}	1.32	3.3884	6.2087	-21.0298
Cu^{2+}	0.70	2.5021	6.8683	-23.5510
Cd^{2+}	1.03	2.3983	9.5989	-23.9034
Mn^{2+}	0.91	2.8668	5.3447	-22.4238

The values of $-\log D_{H}^{+}$ obtained from equation (3) plotted against 1/T are straight lines as shown in figure 5, verifying the validity of Arrhenius equation:

$$D_{H}^{+} = D_0 \exp(-E_a/RT) \qquad (4)$$

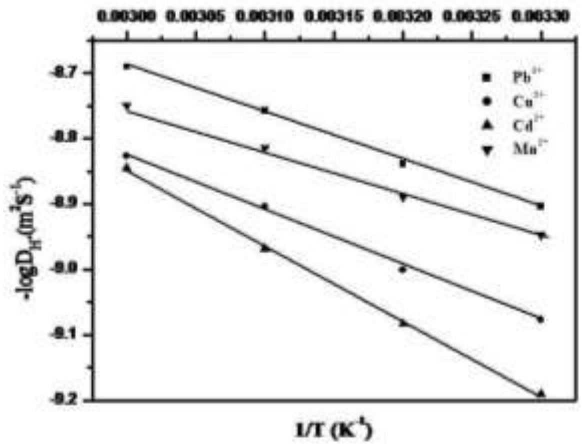

Figure 5: **Plots of $-\log D_{H}^{+}$ vs. 1/T for Pb^{2+}-H^{+}, Cu^{2+}-H^{+}, Cd^{2+}-H^{+} and Mn^{2+}-H^{+} exchanges on TSW**

The energy of activation, E_a and the constant D_0 can be evaluated from the slope and intercept of these plots. The entropy of activation, ΔS* was calculated using the equation,

$$D_0 = 2.72d^2 \frac{KT}{h} \exp(\frac{\Delta S^*}{R}) \qquad (5)$$

Where *d* is the average distance between two exchanging sites, taken as 5×10^{-10} m, *K* is the Boltzman constant, *R* is gas constant and *h* is Plank's constant. T is taken as 273 K.

Table 3 shows the values of diffusion coefficient (D_0), energy of activation (E_a) and entropy of activation (ΔS*). The positive values of activation energy indicated that minimum energy is required to facilitate the forward (M^{2+}-H^{+}) ion exchange process [19,20]. $\triangle S^*$ is found to be negative in all cases showing decrease in degree of randomness at exchanger surface during ion exchange process, indicating increased selectivity to metal ions when the exchanger phase is in H^+ form and feasibility of metal ion exchange.

Conclusion

Bimetallic ion exchange material titaniumtin tungstate was synthesized and characterized. Studies of ion exchange kinetics of heavy metal ions over the exchanger reveals that the equilibrium is attained faster at a higher temperature with particle diffusion controlled phenomenon, which is confirmed by the linear τ versus time (t) plots. Evaluation of various kinetic parameters like self diffusion coefficient (D_0), energy of activation (E_a) and entropy of activation (ΔS*) showed the feasibility of the ion exchange reaction. The overall studies reveal the promising use of TSW as a cation exchanger.

Acknowledgement

Author acknowledges the Council of Scientific and Industrial Research for awarding Junior Research Fellowship and STIC, Cochin, School of Chemical Sciences, M G University, Kottayam for providing technical facilities.

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