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Heavy metal ion-exchange kinetic studies over cellulose acetate Zr(IV) molybdophosphate composite cation-exchanger

Tansir Ahamad[a], Mu. Naushad[a], Inamuddin[b,*]

[a]*Department of Chemistry, College of Science, Building #5, King Saud University, Riyadh, Saudi Arabia*
[b]*Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202002, India*
Tel. +91-571-2700920 Ext. 3009; email: inamuddin@rediffmail.com

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ABSTRACT

Explicit Nernst–Planck approximation is applied to study the reaction kinetics for four heavy metal ions (Cd^{2+}, Cu^{2+}, Zn^{2} and Pb^{2+}) of environmental importance on the surface of cellulose acetate Zr(IV) molybdophosphate composite cation-exchanger. The composite cation-exchanger possessed ion exchange capacity of 1.96 meq g^{-1}. The kinetic studies are carried out under particle diffusion controlled phenomenon. On the basis of kinetic studies various physical parameters i.e. fractional attainment of equilibrium $U(\tau)$, self diffusion coefficients (D_0), energy of activation (E_a) and entropy of activation (ΔS^*) are estimated to evaluate the mechanism of ion exchange on the surface of composite ion exchange material. The activation entropy and energy revealed that the greater degree and minimum energy was achieved during forward ion exchange process.

Keywords: Cellulose acetate Zr(IV) molybdophosphate; Cation-exchanger; Ion-exchange kinetics

1. Introduction

Pollution by heavy toxic metal ions in natural and wastewater systems is a matter of great concern throughout the world [1–3] due to their detrimental effects on environment and human health [4]. Heavy metals are being discharged to the aquatic environment from natural and anthropogenic sources including painting, smelting, electroplating, mining, leather tanning, alloy and battery manufacturing, etc. Heavy metals are considered non-biodegradable, carcinogenic and easily accumulative in human body through food. They can possess toxicity to the environment even at very low concentration levels [5]. For that reason, economical, effective and reliable treatment methods are required for removal of heavy metals from polluted aquatic environment. A large number of separation and preconcentration techniques including adsorption, ion exchange, coagulation, precipitation, membrane process, etc. are available for the removal of toxic metals from polluted aquatic environment [6–13]. However, among all these techniques, ion exchange is considered as an effective, efficient and economic method for the treatment of polluted aquatic environment. Various types of ion exchange materials have been synthesized and characterized in academic institutions throughout the world [14–16] and some of the important research groups working in this field are mentioned in the literature cited [17–23]. They

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*Corresponding author.

have carried out experimental studies of different types of ion exchange materials and have proposed their separation and removal capabilities. The practical applicability of these ion exchange materials is missing in spite of their high chemical, mechanical and radiation stabilities as well as high ion exchange capacities. 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. Thus, our group is actively engaged to study the issues related to the ion-exchange kinetics and the mobility of counter ions in the lattice structure of newly synthesized ion exchange materials. The composite cation-exchanger cellulose acetate Zr(IV) molybdophosphate showed good thermal and mechanical stabilities, selectivity and separation capabilities for heavy metal ions of environmental importance as proposed by Nabi and Naushad [24]. Therefore, in this research study, cellulose acetate Zr (IV) molybdophosphate composite cation-exchange material was selected to evaluate the ion-exchange mechanism occurring over the surface of the ion-exchanger.

2. Experimental

2.1. Materials and instruments

The main reagents used for the synthesis of the material were zirconium oxychloride octahydrate, sodium molybdate, orthophosphoric acid and cellulose acetate (Sigma, Saudi Arabia). Solutions for kinetic measurement were made using analytical reagent grade nitrate salts of Cd, Cu, Zn and Pb (99%) (Sigma, Saudi Arabia). Nitric acid, HNO_3, (35%) and hydrochloric acid, HCl, (35%) were also obtained from Sigma, Saudi Arabia. All other reagents and chemicals were of analytical reagent grade. A single electrode pH metre (744, Metrohm, Switzerland) and a water bath incubator shaker (SW22/9550322, Julabo) were used.

2.2. Methods

Composite cation-exchanger cellulose acetate Zr (IV) molybdophosphate was prepared as reported by Nabi and Naushad [24]. The procedure for the preparation is given below.

2.2.1. Preparation of reagent solutions

Solutions of 0.1 M zirconium oxychloride and cellulose acetate were prepared in 0.1 M HCl and concentrated formic acid, respectively, while solutions of orthophosphoric acid and sodium molybdate were prepared in demineralized water (DMW).

2.2.2. Preparation of cellulose acetate Zr(IV) molybdophosphate composite cation-exchange material

Zr(IV) molybdophosphate was prepared by mixing 1:2 by volume of (equivolumes of 0.1 M orthophosphoric acid and sodium molybdate) and 0.1 M Zr(IV) oxychloride solution, gradually with continuous shaking of the mixture. The pH 1 was achieved by adding 1 M nitric acid or 1 M ammonia solutions. The cellulose acetate was dissolved in concentrated formic acid in 2:1 (wt.%/volume) ratio and added into the inorganic precipitate of Zr(IV) molybdophosphate and mixed thoroughly with constant stirring for 1 h. The gelatinous precipitate so formed, was allowed to stand for 24 h in the mother liquor for digestion. The supernatant liquid was get rid of and the precipitate was washed with DMW several times to remove excess reagents and finally dried at 50˚C. The composite cation-exchanger was crushed and the particle size of approximately 125 μm was obtained by sieving and stored in desiccator.

2.2.3. Method for the measurement of ion exchange capacity

The ion exchange capacity was determined by standard column process. For this purpose, one gram (1 g) of the dry cation-exchanger in the H^+-form was taken into a glass column having an internal diameter (i.d.) ~1 cm and fitted with glass wool support at the bottom. The bed length was approximately 1.5 cm long. 1 M $NaNO_3$ as eluent was used to elute the H^+ ions completely from the cation-exchange column, maintaining a very slow flow rate (~0.5 ml min^{-1}). The effluent was titrated against a standard 0.1 M NaOH solution for the total ions liberated in the solution using phenolphthalein indicator and the ion exchange capacity was determined. The ion exchange capacity of this composite cation-exchanger was found to be 1.96 meq g^{-1}.

2.3. Determination of theoretical approach

Composite cation-exchanger particles of mean radii ~125 μm (50–70 mesh) in H^+ form were used to evaluate various kinetic parameters. The rate of exchange was calculated as follows.

A total of 20 ml fractions of the 0.02 M metal ion solutions (Cd, Cu, Zn and Pb) were shaken with 200 mg of the cation-exchanger in H^+-form in several stoppered conical flasks at desired temperatures [25, 33, 50 and 65 (± 0.5)˚C] for different time intervals (0.5, 1.0, 2.0, 3.0 and 4.0 min). The supernatant liquid was removed immediately and determinations were made as usual by ethylene diamine tetra-acetic acid, disodium salt (EDTA) titrations [25]. Each set was repeated four times and the mean values were taken for calculation.

3. Results and discussion

Various studies have been carried out to elucidate the rate of ion exchange [26–29]. These studies are based on old *Bt* criterion which is true only for the exchange of two isotopic counter ions. In the case of isotopic exchange, the diffusion coefficient is constant. Boyd et al. [30] derived an equation for through analysis of ion exchange kinetics based on the Nernst concept of a liquid diffusion layer and calculated fractional attainment of equilibrium from a series of values of *Bt*. However, the most useful form of the tabulation is that of *Bt* for a series of values of fractional attainment of equilibrium. Further, Reichenberg [31] studied that the equations of the type derived by Boyd et al. [30] obeyed the mechanism derived for film diffusion and particle diffusion control phenomenon for non-isotopic exchange. Nernst–Planck equation [32] has been tasted for the exchanging ions of different effective diffusion coefficients and different mobilities. Similarly, it provided more appropriate values of the various kinetic parameters by using some additional assumptions.

In principle 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. In an ion exchange process, the inter-diffusion of counter ions is occurring either by particle diffusion or film diffusion control. 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, the ion-exchange rate becomes independent of time after this time interval. Fig. 1 shows that 15 min were required for the establishment of equilibrium at 33˚C for Mg^{2+}–H^+ exchange. Similar behaviour was also observed for Cd^{2+}–H^+, Cu^{2+}–H^+, Zn^{2+}–H^+ and Pb^{2+}–H^+ exchanges. Therefore, 15 min was assumed to be the infinite time of exchange for all exchange systems.

Fig. 2 shows that the τ vs. time (t) (t in min) plots are also straight lines passing through the origin at and above 0.02 M of metal ion concentration confirming the particle diffusion control phenomenon. However, below the metal ion concentration of 0.02 M, film diffusion control phenomenon was more prominent. Therefore, the kinetic studies for exchange of Cd^{2+}–H^+, Cu^{2+}–H^+, Zn^{2+}–H^+ and Pb^{2+}–H^+ were made under particle diffusion controlled phenomenon. The kinetic results are expressed in terms of the fractional attainment of equilibrium $U(\tau)$ with time according to the equation:

$$U(\tau) = \frac{\text{the amount of exchange at time } (t)}{\text{the amount of exchange at infinite time}} \tag{1}$$

Fig. 3 shows plots of $U(\tau)$ vs. time (t) (t in min), for Cd^{2+}–H^+, Cu^{2+}–H^+, Zn^{2+}–H^+ and Pb^{2+}–H^+ exchanges

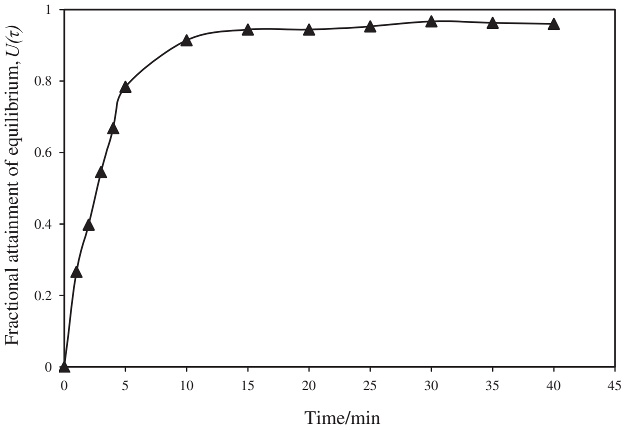

Fig. 1. A plot of $U(\tau)$ vs. t (time) for M^{2+}–H^+ exchanges at 33˚C on cellulose acetate Zr(IV) molybdophosphate composite cation-exchanger for the determination of infinite time.

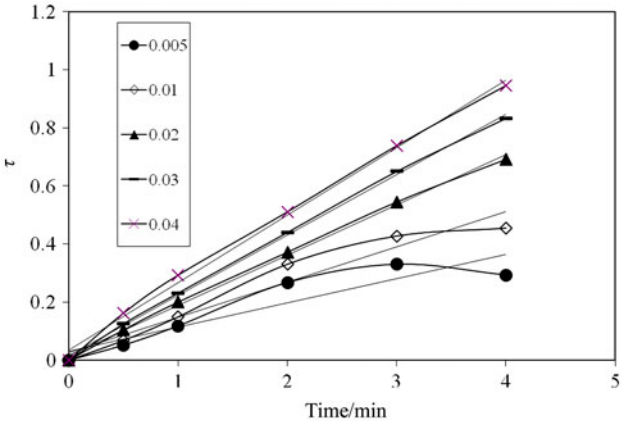

Fig. 2. Plots of τ vs. t (time) for M^{2+}–H^+ exchanges using different metal solution concentrations at 33˚C on cellulose acetate Zr(IV) molybdophosphate composite cation-exchanger.

which indicated 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 and the uptake decreased with time.

Each value of $U(\tau)$ will have a corresponding value of τ, a dimensionless time parameter. On the basis of the Nernst–Planck equation, the numerical results can be expressed by explicit approximation [33–35]:

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

where τ is the half-time of exchange = $\overline{D}_{\mathrm{H}^+}t/r_o^2$, α is the mobility ratio = $\overline{D}_{\mathrm{H}^+}/\overline{D}_{\mathrm{M}^{2+}}, r_o$ is the particle radius, $\overline{D}_{\mathrm{H}^+}$ and $\overline{D}_{\mathrm{M}^{2+}}$ are the inter diffusion coefficients of counter ions H^+ and M^{2+}, respectively, in the exchanger phase. The three functions $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ depend upon the mobility ratio (α) and the charge ratio ($Z_{\mathrm{H}^+}/Z_{\mathrm{M}^{2+}}$) of the exchanging ions. Thus, they have different expressions as given below [36]. When the exchanger is taken in the H^+-form and the exchanging ion is M^{2+}, for $1 \le \alpha \le 20$, as in the present case, the three functions have the values:

$$f_1(\alpha) = -\frac{1}{0.64 + 0.36\alpha^{0.668}}$$

$$f_2(\alpha) = -\frac{1}{0.96 - 2.0\alpha^{0.4635}}$$

$$f_2(\alpha) = -\frac{1}{0.27 + 0.09\alpha^{1.140}}$$

The Nernst–Planck explicit approximation equation (2) was used to calculate various τ values corresponding to each $U(\tau)$ using a computer. Fig. 4 shows the plots of τ vs. time (t) at four different temperatures for heavy metal ion–hydrogen exchanges. The straight lines passing through the origin confirming the particle diffusion control phenomenon for M^{2+}–H^+ exchanges at a metal ion concentration of 0.02 M.

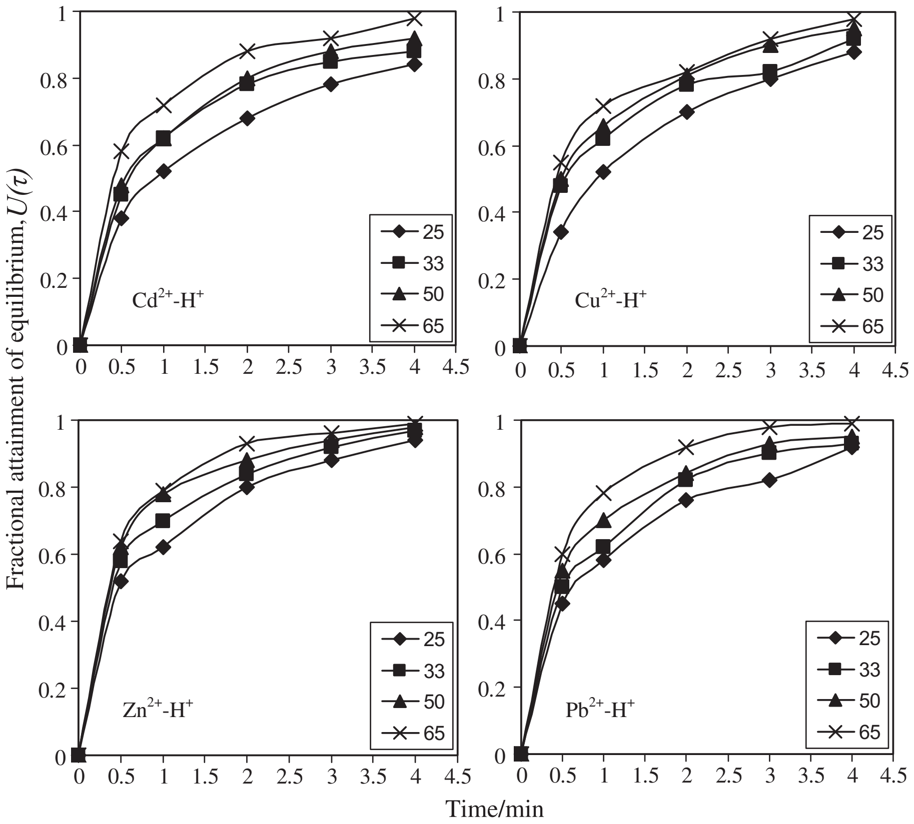

Fig. 3. Plots of $U(\tau)$ vs. t (time) for Cd^{2+}–H^+, Cu^{2+}–H^+, Zn^{2+}–H^+ and Pb^{2+}–H^+ exchanges at different temperatures on cellulose acetate Zr(IV) molybdophosphate composite cation-exchanger.

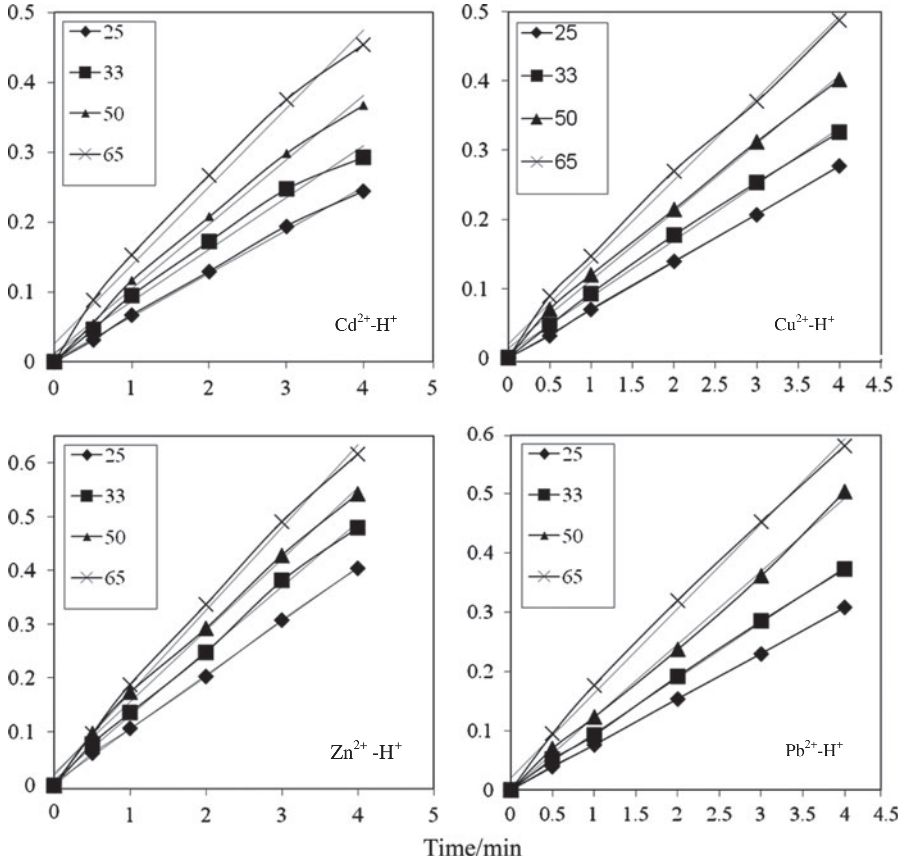

Fig. 4. Plots of τ vs. t (time) for Cd^{2+}–H^+, Cu^{2+}–H^+, Zn^{2+}–H^+ and Pb^{2+}–H^+ exchanges at different temperatures on cellulose acetate Zr(IV) molybdophosphate composite cation-exchanger.

Table 1
Slopes of various τ vs. time (t) plots on cellulose acetate Zr(IV) molybdophosphate cation-exchanger at different temperatures

Ion present in the ion exchanger	Migrating ions ⇓	S (s^{-1})			
	Temperature ⇒	25℃	33℃	50℃	65℃
H^+	Cd^{2+}	0.0619	0.0743	0.0921	0.1122
H^+	Cu^{2+}	0.0694	0.0813	0.0986	0.1184
H^+	Zn^{2+}	0.1002	0.1196	0.1329	0.1537
H^+	Pb^{2+}	0.0768	0.0934	0.1232	0.1430

The slopes (S values) of various τ vs. time (t) plots are given in Table 1. The S values are related to $\overline{D}_{H^+}$ as follows:

$$S = \overline{D}_{H^+}/r_o^2 \tag{3}$$

The values of—log$\overline{D}_{H^+}$ obtained by using Eq. (3) plotted against $1/T$ are straight lines as shown in Fig. 5, thus verifying the validity of the Arrhenius relation:

$$\overline{D}_{H^+} = D_0 \exp(-E_a/RT) \tag{4}$$

The pre-exponential constants D_0 are obtained by extrapolating these lines and using the intercepts at the origin. The activation energy (E_a) values are then calculated from the slope of plots. The entropy of activation (ΔS^*) vales were then calculated by substituting D_0 in Eq. (5).

Table 2
Values of D_0, E_a and ΔS^* for the exchange of H^+ ions with some metal ions on cellulose acetate Zr(IV) molybdophosphate composite cation-exchange material

Ion present in the ion exchanger	Migrating ions	Ionic mobility/$cm^2\ V^{-1}\ s^{-1}$	Ionic radii/Å	D_0 /$m^2\ s^{-1}$	$10^2\ E_a$/kJ mol^{-1}	ΔS^*/J $K^{-1}\ mol^{-1}$
H^+	Pb^{2+}	0.00061	1.32	4.6270×10^{-7}	43.37	−676.8428
H^+	Cu^{2+}	0.00046	0.70	8.9331×10^{-7}	56.88	−674.4675
H^+	Cd^{2+}	0.00046	1.03	1.3122×10^{-6}	63.28	−673.0791
H^+	Zn^{2+}	0.00047	0.83	2.3399×10^{-6}	67.85	−579.5366

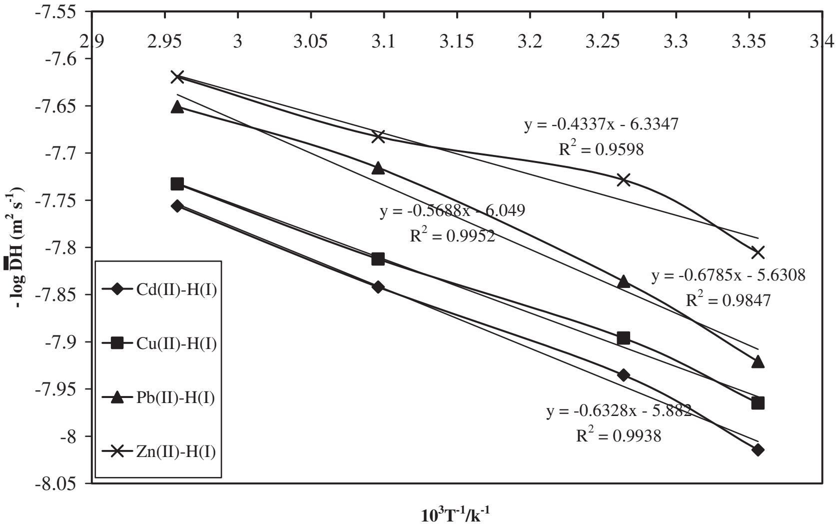

Fig. 5. Plots of –log $\overline{D}_H$ vs. $10^3\ T^{-1}/K^{-1}$ for Cd^{2+}–H^+, Cu^{2+}–H^+, Zn^{2+}–H^+ and Pb^{2+}–H^+ exchanges on cellulose acetate Zr (IV) molybdophosphate composite cation-exchanger.

$$D_o = 2.72d^2(kT/h)\exp(\Delta S^*/R) \tag{5}$$

where d is the ionic jump distance taken as 5×10^{-10} m, k is the Boltzmann constant, R is the gas constant, h is Planck's constant and T is taken as 273 K. The values of the diffusion coefficient (D_o), energy of activation (E_a) and entropy of activation (ΔS^*), thus obtained are summarized in Table 2. The results showed that there is no definite relation among the ionic mobility and ionic radii of migrating ions with the values of D_0, E_a and ΔS^*. The positive values of activation energy indicated that minimum energy is required to facilitate the forward (M^{2+}–H^+) ion-exchange process. Negative values of the entropy of activation (ΔS^*) suggest a greater degree of order achieved during the forward ion-exchange (M^{2+}–H^+) process.

Conclusion

On the basis of kinetic studies of heavy metal ions various physical parameters are determined. These parameters indicated that the exchange of heavy metal ions over this composite cation-exchanger takes place through particle diffusion controlled phenomenon. It is also evident that the ion-exchange process is feasible on this composite cation-exchanger and the material can be used for the separation and pre-concentration of heavy metal ions of practical importance.

Abbreviation used

$U(\tau)$ — fractional attainment of equilibrium
D_o — self diffusion coefficient
E_a — energy of activation
ΔS^* — entropy of activation
i.d. — internal diameter
DMW — demineralized water
EDTA — ethylene diamine terta acetic acid, disodium salt
$\overline{D}_{H^+}$ — inter diffusion coefficient of counter ion H^+
$\overline{D}_{M^{2+}}$ — inter diffusion coefficient of counter ion M^{2+}

r_o — particle radius
α — mobility ratio
$Z_{H^+}/Z_{M^{2+}}$ — charge ratio
τ — a dimensionless time parameter
H^+ — hydrogen ion
M^{2+} — metal ion
S — slope
D — the ionic jump distance
k — Boltzmann constant
R — the gas constant
h — Planck's constant
T — Temperature

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