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Kinetics studies of poly-o-toluidine/Multiwalled Carbon Nanotubes/Sn(IV)tungstate nanocomposite ion exchanger

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ABSTRACT: *Nanocomposite ion exchanger, poly-o-toluidine/Multiwalled Carbon Nanotubes/Sn(IV) tungstate (POT/MWCNT/ST) was chemically synthesized by mixing of organic polymers i.e. o-toluidine into inorganic gels of Sn(IV) tungstate (ST) and Multiwalled Carbon Nanotubes (MWCNT) with different mixing volume ratios. Ion-exchange kinetics for few divalent metal ions was evaluated by particle diffusion-controlled and ion-exchange phenomenon at four different temperatures. The particle diffusion mechanism is confirmed by the linear τ (dimensionless time parameter) Vs t (time) plots. The exchange processes were controlled by the diffusion within the exchanger particle for the systems studies. Some physical parameters like self-diffusion coefficient (D_0), energy of activation (Ea) and entropy of activation (ΔS_0) have been evaluated under conditions favouring a particle diffusion-controlled mechanism.*

KEYWORDS: *Cation exchanger, kinetics, physical parameters, MWCNT, nano composite.*

I. INTRODUCTION:

Conducting polymer Polyaniline (PANI), poly-o-toluidine (POT), polypyrrole (PPY), polythiophene (PTP), polyfuran (PFu) etc. have been extensively studied in literature because of their multiple uses especially in the field of electronics due to their pi electron conjugated structure. Among these, POT is has a greater significance because of its better conductivity, good environmental stability and ease of synthesis [**1-3**]. As a result, composites of POT have been synthesized with various organic, inorganic metal oxides, SWCNT, MWCNT, nanoparticles by chemical or electrochemical route, which have shown significant enhancement in their properties with respect to the conductivity, retention of charge, enhanced thermal stability, mechanical properties and kinetic properties [**4-6**]. However these composite materials face certain limitations as they are mostly infusible, insoluble and suffer from poor processibility mainly because of rigid high conjugated backbone.

Composite ion-exchanger has a variety of uses and applications owing to its selectivity for some specific metal ions, indicating their useful environmental applications [**7-9**]. To understand the ion-exchange process, investigations of some kinetic parameters such as the diffusion coefficient, energy and entropy of activation etc., are very much essential. It is noteworthy that these parameters tell us about the mechanism, rate determining step and rate laws obeyed by the ion-exchange process. These studies enable us to understand the viability of an ion-exchanger in separations of metal ions. Most of the earlier studies [**10-12**] of kinetic behaviour were based on the old Bt criterion [**13**], which is not very useful for a true ion-exchange (non-isotopic exchange) process because of the different effective diffusion coefficients and mobilities [**14**] of the exchanging ions involved. The Nernst [**15**] and Planck [**16**] equations with some additional assumptions provide more appropriate values in obtaining the values of the various kinetic parameters precisely [**17-18**].

In view of above advantages of organic–inorganic composite ion exchange materials and carbon nanotubes, poly-o-toluidine/multiwalled carbon nanotubes/Sn(IV)tungstate composite ion exchanger is prepared in our present work [**6**] in order to raise the possibility of its use in analytical and kinetics studies. Synthesis of POT/MWCNT/ST composite ion exchangers by the simple in situ oxidative polymerization of POT in the presence of MWCNTs and ST ion exchangers has been carried out. POT/MWCNT/ST composite ion-exchanger was selective for Pb(II) having good ion exchange capacity [**19**]. The mechanism of ion exchange can be explained by taking into account ion-exchange equilibrium with respect to time wherein the phenomenon of ion-exchange can be considered as diffusion of ions through particles of the exchanger and its adherent film. With the help of experimental data and mathematical computation some physical parameters like self diffusion co-efficient (D_0), energy of activation (E_a) and entropy of activation (ΔS_0) were obtained.

II. EXPERIMENTAL

2.1 Methods and materials

Synthesis, characterizations and other studies on POT/MWCNT/ST nanocomposite ion exchanger has already been reported in our previous publications [**6, 19**].

2.2. Kinetic measurements

The nanocomposite ion-exchanger samples were grounded and then sieved to obtain particles of definite mesh size (25-50, 50-70, 70-100 and100-125). Out of them the particles of mean radii ~125 µm (50-70 mesh) were selected to evaluate various kinetic parameters. The rate of exchange was determined by limited bath technique as follows:

The POT/MWCNT/ST nanocomposite ion exchanger was dipped in 1.0×10^{-1} M $Pb(NO_3)_2$ solution for 5, 10, 20, 30, 40, 50, and 60 s at 30, 40, 60 and 70 °C with constant shaking of the solution. The potential was recorded and plotted against time at different temperatures. The supernatant liquid was removed immediately and determinations were made, usually by EDTA titration [**20**]. Each set was repeated four times and the mean value was taken for calculations.

III. RESULTS and DISCUSSION

In this POT/MWCNT/ST nanocomposite ion exchanger was synthesized by the incorporation of organic polymer o-toluidine into the matrix of inorganic Sn(IV) tungstate and MWCNTs using *in-situ* polymerization method. Detail kinetics studies were done on selected sample on the basis of their ion exchange capabilities as done in our previous publications **[21-22].**

3.1. Ion-Exchange Kinetic Studies on POT/MWCNT/ST nanocomposite ion exchanger

Kinetic measurements were made under conditions favoring a particle diffusion-controlled ion-exchange phenomenon for the exchange of Ni^{2+}–H^+, Cu^{2+}–H^+, Ba^{2+}–H^+ and Zn^{2+}-H^+. The particle diffusion controlled phenomenon was favored by a high metal ion concentration, a relatively small particle size of the exchanger and vigorous shaking of the exchanging mixture.

The infinite time of exchange is the time necessary to obtain equilibrium in an ion-exchange process. The ion-exchange rate becomes independent of time after this interval. (**Fig. 1)** shows that 30 min was required for the establishment of equilibrium at 40°C for Mg^{2+}–H^+ exchange for POT/MWCNT/ST. Similar behavior was observed for Ni^{2+}–H^+, Cu^{2+}–H^+, Ba^{2+}–H^+, and Zn^{2+}-H^+ exchanges. Therefore, 50 and 45 min were assumed to be the infinite time of exchange for the systems.

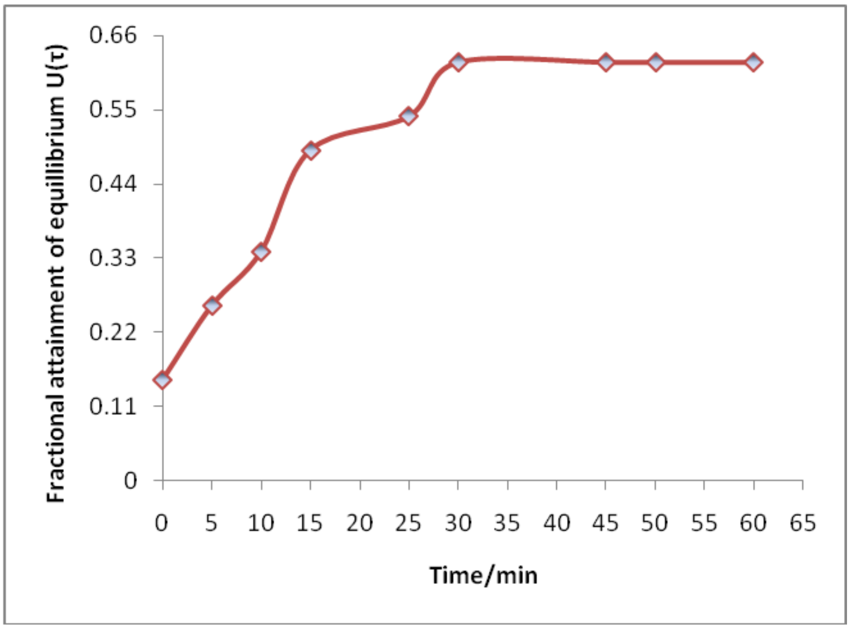

Fig. 1. A plot of U(τ) versus t (time) for M^{2+}–H^+ exchanger at 30°C on POT/MWCNT/ST nanocomposite cation-exchanger for the determination of infinite time

A study of the concentration effect on the rate of exchange at 40°C showed that the initial rate of exchange was proportional to the metal ion concentration at and above 0.03 M for POT/MWCNT/ST (**Fig. 2)**.

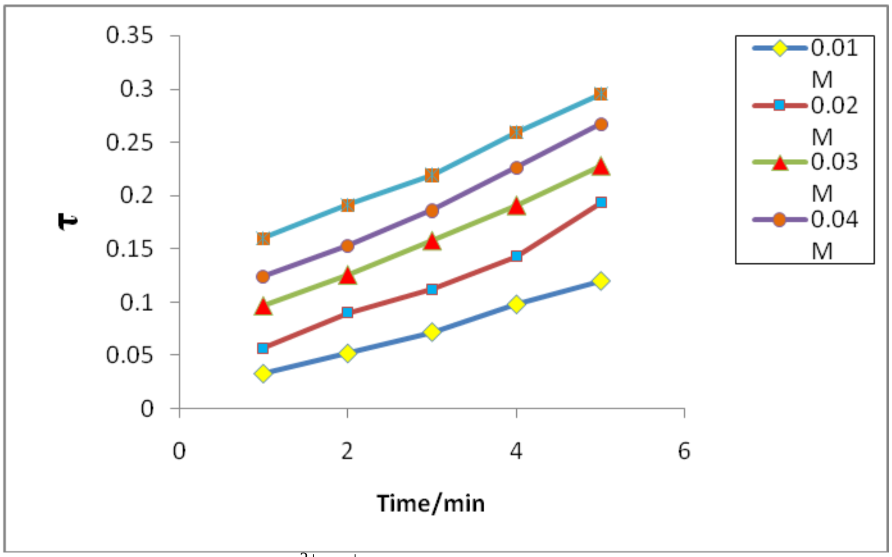

Fig 2. A plot of U(τ) versus t (time) for M^{2+}–H^{+} exchanges at 40◦C on POT/MWCNT/ST nanocomposite cation exchanger using different concentrations of metal solution.

The results are expressed in terms of the fractional attainment of equilibrium, $U(\tau)$ with time according to the equation 1:

$$U(\tau) = \frac{\textit{the amount of exchange at time 't'}}{\textit{the amount of exchange at inite time}}. \quad \text{……... (1)}$$

Plots of $U(\tau)$ versus t (min), for some metal ions (**Fig. 3)** indicated that the fractional attainment of equilibrium was faster at a higher temperature suggesting that the mobility of the ions increased with the 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.

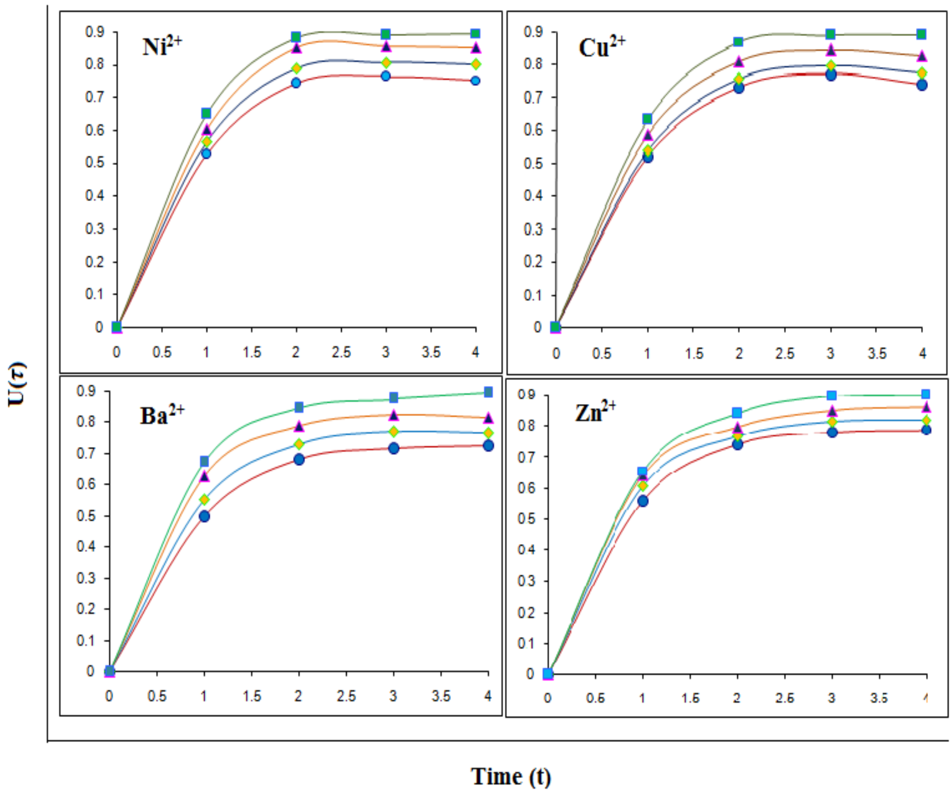

Fig.3. Plots of U(τ) versus t (time) for different M^{2+}–H^{+} exchanges at different temperatures: , ● 30 ºC; ◆ 40 ºC; ▲ 60 ºC; and ■ 70 ºC, of POT/MWCNT/ST nanocomposite cation exchanger.

On the basis of the Nernst–Planck equation, the numerical results can be expressed by explicit approximation **[23-25].**

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

Where τ is the half time of exchange= $\bar{D}_{H^+} t / r_o^2$, α is the mobility ratio = $\bar{D}_{H^+} / \bar{D}_{M^{2+}}$, r_0 is the particle radius, $\bar{D}_{H^+}$ and $\bar{D}_{M^{2+}}$ 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 ($Z_{H^+} / Z_{M^{2+}}$) 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 $1 \le \alpha \le 20$, as in the present case, the three functions have the values:

$$f_1(\alpha) = -\frac{1}{0.64 + 0.36\alpha^{0.668}} \quad \text{...... (3)}$$

$$f_2(\alpha) = -\frac{1}{0.96 - 2.0\alpha^{0.4635}} \quad \text{....... (4)}$$

$$f_3(\alpha) = -\frac{1}{0.27 + 0.09\alpha^{1.140}} \quad \text{...... (5)}$$

Each value of $U(\tau)$ will have a corresponding value of τ which is obtained on solving equation 2 using a computer. The plots of τ versus time (t) at the four temperatures, as shown in (**Fig. 4)** are straight lines passing through the origin, confirming the particle diffusion control phenomenon for M^{2+}–H^+ exchanges at a metal ion concentration of 0.03 M for POT/MWCNT/ST.

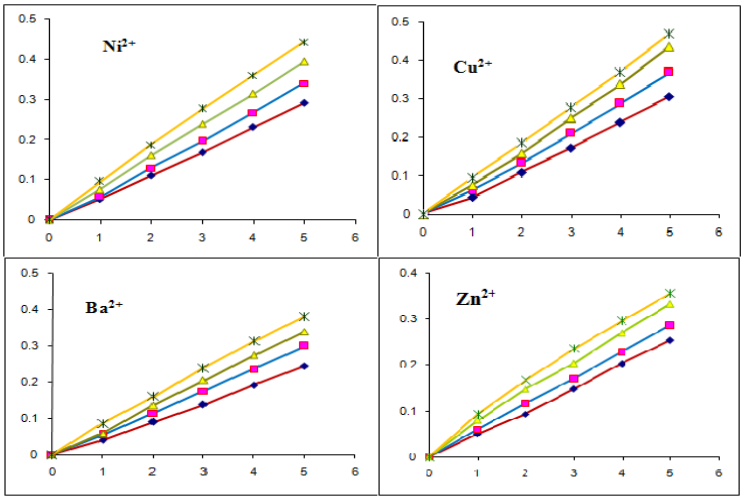

Fig. 4. Plots of τ versus t (time) for different M^{2+}–H^+ exchanges at different temperatures: , —◆— 30 ºC; —■— 40 ºC; —▲— 60 ºC; and —✳— 70 ºC, of POT/MWCNT/ST nanocomposite cation exchanger.

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

$$S = \bar{D}_{H^+} / r_0^2 \quad \text{.......... (6)}$$

Table 1 Slopes of various τ versus time (t) plots on POT/MWCNT/ST nanocomposite cation exchanger at different temperatures

Migrating ions	**10^2 S (s^{-1})**			
	30˚C	**40˚C**	**60˚C**	**70˚C**
Ni^{2+}	8.84	7.87	6.84	5.83
Cu^{2+}	9.33	8.76	7.43	6.23
Ba^{2+}	7.60	6.89	6.01	4.92
Zn^{2+}	7.02	6.55	5.73	5.10

The values of $-\log \bar{D}_{H^+}$ obtained by using equation 6 plotted against 1000/ T (K) are straight lines (**Fig. 5**) thus verifying the validity of the Arrhenius relation;

……….. (7)

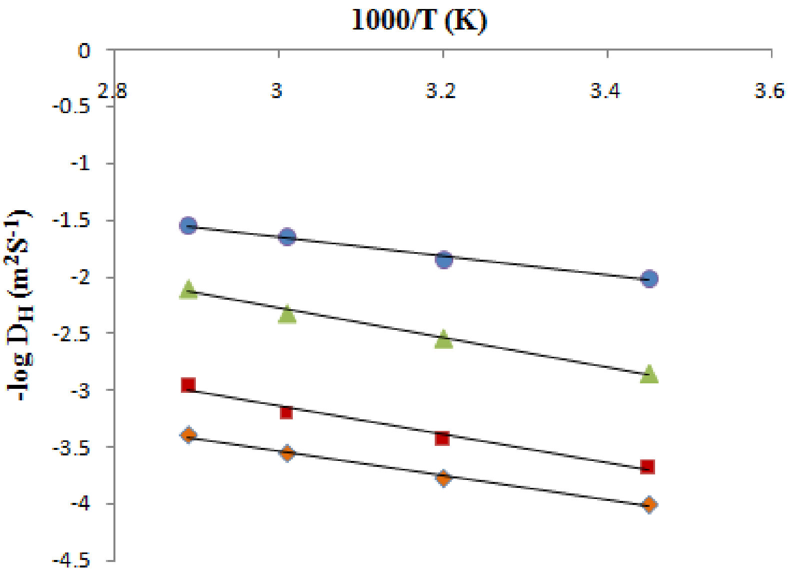

Fig. 5. Plots of $-\log D^{H+}$ versus 1000/T (K) for (a) ◆ Ni^{2+}, ■ Cu^{2+}, ▲ Ba^{2+}, and ● Zn^{2+} on the POT/MWCNT/ST nanocomposite cation exchanger.

D_0 is obtained by extrapolating these lines and using the intercepts at the origin. The activation energy (E_a) is then calculated with the help of the equation 7, putting the value of $\bar{D}_{H^+}$ at 273 *K*. The entropy of activation ($\Delta S°$) was then calculated by substituting D_0;

$$D_\circ = 2.72d^2(kT/h)\exp(\Delta S^\circ/R) \quad ....(8)$$

Where d is the ionic jump distance taken as 5 A° **[26],** k is the *Boltzmann* constant, *R* is the gas constant, *h* is *Plank's* constant and *T* is taken as 273 *K.*

The values of the diffusion coefficient (D_0), energy of activation (E_a) and entropy of activation ($\Delta S°$), thus obtained are summarized in (**Table 2).**

Table 2 Values of $D_{\circ}$, E_a and ΔS° for the exchange of H^+ with some metal ions on POT/MWCNT/ST nano composite cation exchanger

Metal ion exchange with H(I)	**10^9 Ionic mobility (m^2 V^{-1} s^{-1})**	**10^2 ionic radii (nm)**	**10^{10} $D_{\circ}$ (m^2 s^{-1})**	**E_a (k $Jmol^{-1}$)**	**ΔS° (J K^{-1} mol^{-1})**
Ni(II)	52	6.9	12.08	20.54	-52.7
Cu(II)	57	7.3	10.12	16.53	-51.6
Ba(II	62	13.5	18.23	23.18	-59.5
Zn(II)	56	7.5	7.85	9.63	-51.4

The kinetic study reveals that equilibrium is attained faster at a higher temperature, probably because of a higher diffusion rate of ions through the thermally enlarged interstitial positions of the ion-exchange matrix. The particle diffusion phenomenon is evident from the straight lines passing through the origin for the τ versus time (t) plots, as shown above in **Fig. 4**. Negative values of the entropy of activation suggest a greater degree of order achieved during the forward ion-exchange in M^{2+}–H^+ process. From the Table 2, it is observed that the self-diffusion co-efficient is highest for Ba^{2+} ion. As ionic radii of Ba^{2+} ion is greater, the Ba^{2+} ion is least hydrated and therefore its self-diffusion co-efficient is higher.

According to the value of self-diffusion co-efficient, the selectivity order of metal ions by POT/MWCNT/ST is $Ba^{2+} > Ni^{2+} > Cu^{2+} > Zn^{2+}$ was found. Further, it is observed that Ea (activation energy) values of metal ions on the composite is in the order $Ba^{2+} > Ni^{2+} > Cu^{2+} > Zn^{2+}$ indicate the order of exchange process of metal ions. Lower the activation energy (*Ea*) stronger the preference for metal ion by the exchanger site. Similarly smaller the standard entropy change ($\Delta S°$) values indicate the preference of more active exchangeable site in the exchanger and strong preference for those metal ions **[27].**

IV. CONCLUSION

In the present study, the mechanism of ion exchange suggest the particle diffusion as confirmed by the linear τ (dimensionless time parameter) Vs t (time) plots. Further, various kinetic parameters like self-diffusion coefficient (D_0), Energy of activation (Ea) and entropies of activation (ΔS°) have been evaluated under condition favouring a particle diffusion controlled mechanism. The above studies thus reveal the promising use of POT/MWCNT/ST as a cation-exchanger. The chemical, thermal and mechanical strength of this electro-active material can make the material more important for the electro analytical purpose.

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