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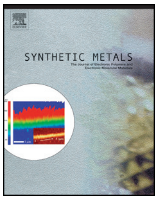

Determination of ion-exchange kinetic parameters for the conducting nanocomposite polyaniline zirconium titanium phosphate

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ABSTRACT

The kinetics and mechanism for the ion-exchange processes like Mg(II)–H(I), Ca(II)–H(I), Sr(II)–H(I), Ba(II)–H(I), Ni(II)–H(I), Cu(II)–H(I), Mn(II)–H(I) and Zn(II)–H(I) at different temperatures using approximated Nernst–Plank equation under the particle diffusion controlled phenomenon were studied for the polyaniline zirconium titanium phosphate nanocomposite cation-exchanger. Some 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°) have been estimated. These investigations revealed that the equilibrium is attained faster at higher temperature probably due to availability of thermally enlarged matrix of polyaniline zirconium titanium phosphate (PANI-ZTP) nanocomposite cation exchange material. These results are useful for predicting the ion exchange process occurring on the surface of this cation-exchanger.

1. Introduction

Composite materials were considered to be the best way to solve the limitations of poor thermal and radiation stabilities and less stability in high acidic and basic medium associated with the use of organic as well as inorganic ion exchange materials, respectively. Hybrid framework composite, including both metal–organic coordination polymers and systems that contain extended inorganic connectivity (extended inorganic hybrids), have recently developed into an important new class of solid-state materials as ion-exchanger and has been of great interest in our laboratory [1–8]. Various applications of ion exchangers can be found in pharmaceuticals and medicine [9–11], recuperation of metals, biotechnology [12], catalysis [13], food production [14,15], recycling of industrial waste [16], microelectronics, nuclear industry [17], potable water preparation [18], solid polymer electrolyte membrane fuel cells [19–22] and many other areas [23–32]. In most of these fields, information related to the ion exchange kinetics and the mobility of counter ions in the lattice structure is needed. Kinetics 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. Moreover, the earlier approaches [33–35] of kinetic behavior are based on the old Bt criterion [36,37] which is not very useful for a true ion-exchange (non-isotopic exchange) process because of the different effective diffusion coefficients and different mobilities [38] of the exchanging ions involved. The Nernst–Planck [39,40] equations with some additional assumptions provide more appropriate values in obtaining the values of the various kinetic parameters precisely. Though many studies on the kinetics of ion exchange on organic and inorganic ion exchangers have been reported [41–43], relatively less information exists on the kinetics of exchange on composite ion.

Hence, in the present research work, we evaluate the ion-exchange mechanism occurring over the surface of nanocomposite cation-exchanger polyaniline zirconium titanium phosphate (PANI-ZTP). The synthesis and physico-chemical characterization of this electrically conducting nanocomposite has also been studied and results are published [6]. The nanocomposite was found highly selective for toxic metal ion mercury and successfully used as indicator electrode indicating its utility for the removal of Hg(II)from waste stream [2].

2. Experimental

2.1. Reagents and instruments

The main reagents used were obtained from CDH, Loba Chemie, E-Merck and Qualigens (India Ltd., used as received). All other reagents and chemicals were of analytical grade.

Following instruments were used during present research work: digital pH meter (Elico Li-10, India); a digital potentiome-

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ter (Equiptronics EQ 609, India); an electronic balance (digital, Sartorius-21OS, Japan) and an automatic temperature controlled water bath incubator shaker—Elcon (India) were used.

2.2. Preparation of nanocomposite polyaniline zirconium titanium phosphate (PANI-ZTP)

The nanocomposite cation-exchanger was prepared by sol–gel mixing of polyaniline (an organic polymer) into the inorganic precipitate of zirconium titanium phosphate (ZTP) with varying mixing ratio. The conditions of preparation, the ion-exchange capacity, and physical appearances of the organic, inorganic and composite cation-exchangers are given in Table 1. The ion exchange capacity was determined by standard column process as described in our previous work [6]. On the basis of Na^+ exchange capacity (I.E.C.) and yield percentage, sample PA-7 was selected for further studies.

2.3. Ion-exchange kinetics

Nanocomposite cation-exchanger was grounded and then sieved to obtain particles of definite mesh size (25–50, 50–70, 70–100 and 100–125). Out of them the particles of mean radii ~125 μm (50–70 mesh) in H^+ were selected to evaluate various kinetic parameters. The rate of exchange was determined by limited batch technique.

20 ml fractions of the 0.01 M metal ion solutions (Mg, Ca, Sr, Ba, Ni, Cu, Mn and Zn) were shaken with 200 mg of the cation-exchanger in H^+-form in several conical flasks at the desired temperatures [25,40, 55 and 70 °C] for different time intervals (0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 min). The supernatant liquid was removed immediately and determinations were made by EDTA titration [44]. Each set was repeated four times and the mean values were taken for calculation.

3. Results and discussion

In this study, nanocomposite polyaniline zirconium titanium phosphate (PANI-ZTP) was prepared by sol–gel mixing method. It was also noticed that the nanocomposite material has extraordinary high Na^+ exchange capacity (4.52 meq g^{-1}) as compared to its inorganic counterpart ZTP (3.36 meq g^{-1}) (Table 1). Improvement in ion exchange and granulometric properties are considered due to the presence of binding polymer, polyaniline.

In order to check the reproducibility of prepared composite, it was synthesized five times under identical condition of concentration of reagents, mixing ratio and drying temperature. The composition and ion exchange capacity and yield of each product were examined. The averages and standard deviation of the ion exchange capacity and yield were found to be 4.52 meq g^{-1} and ±0.03%, respectively.

3.1. Kinetic studies on nanocomposite PANI-ZTP

The rate determining step in an ion exchange process is interdiffusion of the exchanging counter ions either within the ion exchanger itself (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 rate-controlling mechanism can be film diffusion, if the slow step is diffusion across the hydrodynamic film that surrounds the exchanger particles or particle diffusion, if the slow step is diffusion inside the exchanger beads themselves.

In the first case, a concentration gradient is set up within the liquid film, whereas inside the exchanger a uniform concentration of ion, prevails. In the second case the concentration gradient occurs within the exchanger, while the film has a uniform composition. High metal ion concentration, relatively large particle size of the exchanger and vigorous shaking of the exchanging mixture favour a particle diffusion-controlled process.

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

$$U(\tau) = \frac{\text{the amount of exchange at time } 't'}{\text{the amount of exchange at infinite time}}. \qquad (1)$$

In an ion-exchange process the time necessary to obtain equilibrium is the infinite time of exchange, after which the rate becomes independent of time. Plots of $U(\tau)$ versus time (t) (t in min) (Fig. 1) shows that 35 min was required for the establishment of equilibrium at 35 °C on PANI-ZTP for Mg^{2+}–H^+ and Ca^{2+}–H^+ exchanges respectively. Similar behavior was observed for Sr^{2+}–H^+, Ba^{2+}–H^+, Ni^{2+}–H^+, Cu^{2+}–H^+, Mn^{2+}–H^+ and Zn^{2+}–H^+ exchanges. Therefore 35 min was assumed to be the infinite time of exchange for all exchange systems.

A study of the concentration effect on the rate of exchange at 35 °C showed that the initial rate of exchange was proportional to the metal ion concentration and τ versus time (t) (t in min) plots are straight lines passing through the origin at and above 0.03 M as shown in Fig. 2. Below the concentration of 0.03 M, film diffusion control phenomenon was more prominent. Thus, kinetic measurements were made under conditions favoring a particle diffusion-controlled ion-exchange phenomenon for the exchanges of Mg^{2+}–H^+, Ca^{2+}–H^+, Sr^{2+}–H^+, Ba^{2+}–H^+, Ni^{2+}+–H^+, Cu^{2+}–H^+, Mn^{2+}–H^+ and Zn^{2+}–H^+. This phenomenon is favored by a high metal ion concentration, a relatively large particle size of the exchanger and vigorous shaking of the exchanging mixture.

Table 1
Conditions of preparation and the ion-exchange capacity of polyaniline zirconium titanium phosphate (PANI-ZTP).

Sample No.	Mixing volume ratio (v/v) of inorganic			Mixing volume ratio (v/v) of Organic		Appearance of the sample	I.E.C. (meq g^{-1})
	$TiCl_4$ in H_2SO_4	$ZrOCl_2$ in H_2SO_4	Na_2HPO_4 inDMW	0.1 M Aniline in 1 M HCl	$(NH_4)_2S_2O_8$ in 1 M HCl		
PA-1	1 (1 M)	1 (1 M)	1 (2 M)	1	1	Black shiny	3.7
PA-2	1 (0.1 M)	1 (4 M)	2 (1 M)	2	1	Black shiny	1.12
PA -3	1 (0.1 M)	1 (2 M)	2 (0.2 M)	1	2	Blackish purple	1.6
PA -4	1 (1 M)	1 (1 M)	2 (1 M)	1	1	Greenish	0.72
PA -5	1 (0.2 M)	1 (0.1 M)	2 (0.2 M)	1	1	Greenish	2.5
PA -6	1 (0.1 M)	1 (0.1 M)	2 (0.2 M)	1	2	Blackish	3
PA -7	**1 (0.2 M)**	**1 (0.1 M)**	**2 (0.2 M)**	**1**	**2**	**Black shiny**	**4.52**
PA -8	1 (0.2 M)	1 (0.1 M)	2 (0.2 M)	0.25	2	Black shiny	4.2
PA -9	1 (0.1 M)	1 (0.1 M)	2 (0.2 M)	1	2	Purple	3
PA -10	1 (0.2 M)	1 (0.1 M)	2 (0.2 M)	–	–	White Granules	3.36
PA -11	–	–	–	1	1	Dark Green Granules	0.20

Bold letters significance is that this sample selective for further studies.