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An advanced nano-composite cation-exchanger polypyrrole zirconium titanium phosphate as a Th(IV)-selective potentiometric sensor: preparation, characterization and its analytical application

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Abstract Polypyrrole has emerged as one of the highly pursued conducting polymers owing to its high electrical conductivity and good environmental stability. In spite of its excellent electrical properties, the chemical and thermal stability and processability are not very satisfactory. The incorporation of a polymer material into an inorganic ion-exchanger provides a high class of hybrid ion-exchangers with enhanced ion-exchange properties, high reproducibility, high stability, and good selectivity for heavy metals. A novel organic–inorganic composite-polypyrrole zirconium titanium phosphate has been synthesized using zirconium titanium phosphate, which is an advanced inorganic ion-exchange material with the qualities listed above. The physicochemical properties of this composite material are characterized by X-ray, TGA–DTA, AAS, FTIR, SEM, and TEM. The ion-exchange capacity, pH titrations, elution, and chemical stability were determined to study ion-exchange properties of the material. Distribution studies for various metal ions revealed that the nano-composite is highly selective for Th(IV). An ion-selective membrane electrode was fabricated using this material for the determination of Th(IV) ions in solutions. The analytical utility of this electrode was established by employing it as an indicator electrode in electrometric titrations.

Introduction

In recent years, hybrid nano-composites have attracted great interest both in industry and in academia because they often exhibit remarkable improvement in materials properties when compared with virgin polymers. This kind of hybrid organic–inorganic material in which the inorganic part and the organic entities interact at molecular level in the nanoscopic domain, often presents the best properties of each of its components in a synergic way, offering a unique opportunity to prepare tailor-made new materials with optimal, chemical, physical, and mechanical properties [1, 2]. The intrinsic multifunctional character of these materials makes them potentially useful in multiple fields. The growing interest of this subject matter has been reflected in two symposia organized recently by the Materials Research Society [3, 4].

Water pollution by heavy metals remains an important environmental issue. The increasing demand for chemical surveillance in environmental protection, medicine, and many industrial processes has created the need for sensors with features such as high selectivity, sensitivity, reliability, and sturdiness. The most exciting and fastest growing area of research is the use of a hybrid material as an electroactive material embedded in a polymer binder (inert) for fabrication of electrometric sensor [5–16] for analytical purposes [17–21], especially for the determination of heavy toxic metals [22–27]. An electrode selective for thorium using zirconium phosphoborate as an electroactive material has been reported [28].

Thorium is a naturally occurring radioactive substance that is surprisingly as abundant as lead and 3 times more abundant than uranium. Working in uranium, thorium, tin, and phosphate mining areas or gas mantle production industries and living near radioactive waste disposal sites

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may expose people to higher levels of thorium. Breathing high levels of thorium dust results in an increased chance of getting lung disease and high exposures may cause lung, pancreas, and blood cancer [29–32].

Efforts have been done to prepare Th(IV) ion-sensitive membrane electrode using polypyrrole zirconium titanium phosphate (PPZTP), which is a nano-composite cation-exchanger that uses polypyrrole as the organic polymeric part and an advanced inorganic ion-exchange material zirconium titanium phosphate (ZTP). New mixed materials of the class of bimetallic tetravalent metal acid (TMA) salts (such as compounds containing two different cations and a given anion or vice versa) are interesting since they show improved exchange properties and selectivity for particular metal ions as compared to single salts [33, 34]. An advanced and novel inorganic cation-exchanger ZTP is synthesized and its study on equilibrium and kinetics have been reported [35]. It is a sensing material used for the construction of novel solid-state ammonium ion-membrane sensor [36].

The following work summarizes the preparation, characterization, and analytical utility of nano-composite PPZTP.

Experimental

Reagents and instruments

The main reagents used for the synthesis of the material were obtained from CDH, Loba Chemie, E-merck, and Qualigens (India Ltd., used as received). All other reagents and chemicals were of analytical grade. The following instruments were used during present research work: A Fourier Transform Infra Red (FTIR) spectrophotometer (Perkin Elmer, USA, model Spectrum-BX); digital pH meter (Elico Li-10, India); X-ray diffractometer—Phillips (Holland), model PW 1148/89; UV/VIS spectrophotometer—Elico (India), model EI 301E; a double beam atomic absorption spectrophotometer (GBC 902, Australia); a thermal analyzer̄V2.2A DuPont 9900; Carlo-Erba, model 1108; a digital potentiometer (Equiptronics EQ 609, India; accuracy ±0.1 mV with a saturated calomel electrode as reference electrode; an electronic balance (digital, Sartorius-21OS, Japan); and an automatic temperature-controlled water bath incubator shaker̄Elcon (India) were used.

Preparation of reagents

0.1 M solution of titanium tetrachloride, $TiCl_4$ and a 0.1 M solution of zirconium oxychloride, $ZrOCl_2 \cdot 8H_2O$ were prepared in demineralized water (DMW) with different concentrations of H_2SO_4 and Na_2HPO_4. Pyrrole solutions were prepared in toluene at different percentage concentrations (v/v) and 0.1 M $FeCl_3$ was prepared in DMW.

Synthesis of polymer

Synthesis of polypyrrole

Polypyrrole samples were prepared by chemical oxidative polymerization [37, 38] by adding solutions of pyrrole (in toluene, at concentrations up to 33% by weight) dropwise to the 0.1 M $FeCl_3$ solutions (in DMW) in different volume ratios at room temperature with continuous magnetic stirring for 2 h. The black slurries obtained were kept for 24 h.

Synthesis of inorganic precipitate

Synthesis of ZTP

The method of preparation of the precipitated ZTP ion-exchanger was very similar to that of Alberti and Constantino [39], with a slight modification [40] by mixing a solution containing 0.1 M $TiCl_4$ and 0.1 M $ZrOCl_2 \cdot 8H_2O$ in H_2SO_4 at a flow rate of 0.5 mL min^{-1} with the aqueous solution of Na_2HPO_4 in different molarities. Constant stirring was maintained using a magnetic stirrer at room temperature (25 ± 2 °C) for 3 h. The white gel obtained was left for 24 h at room temperature for digestion.

Preparation of PPZTP composite cation-exchanger

The composite cation-exchanger was prepared by sol–gel mixing an organic polymer, polypyrrole, into the inorganic precipitate of ZTP. In this process, a 0.1 M $FeCl_3$ solution was first added to the white inorganic gel of ZTP, which turned the gel color into light yellow, then the solution of pyrrole (in toluene) was added dropwise with constant stirring for 1 h. The resultant mixture turned first to green and then slowly into black slurries, which was kept for 24 h at room temperature (25 ± 2 °C). The dried products were immersed in 1 M HNO_3 solution for 24 h to convert it in H^+-form. The excess acid was removed after several washing with DMW. The materials were finally dried at 40 °C and sieved to obtain shiny black granules of PPZTP. The composite cation-exchanger, having a higher capacity (3.68 mequiv dry g^{-1}) as compared to ZTP (3.36 mequiv dry g^{-1}), the PP-9 sample was selected for the detailed studies (Table 1).

Ion-exchange properties of PPZTP

Ion-exchange capacity

The ion-exchange capacity (I.E.C.), which is generally taken as a measure of the hydrogen ions liberated by neutral salt to flow through the composite cation-exchanger, was determined by a standard column process. One

Table 1 Conditions of preparation and ion-exchange capacity of various sample of polypyrrole zirconium titanium phosphate composite cation-exchanger

Sample	Mixing volume ratio (v/v)			Mixing volume ratio (v/v)			Appearance of the beads after drying	Na^+ ion-exchange capacity (mequiv g^{-1})
	0.1 M $TiCl_4$ in H_2SO_4	0.1 M $ZrOCl_2$ in H_2SO_4	Na_2HPO_4 in DMW	% Pyrrole in toluene	Pyrrole in toluene	0.1 M $FeCl_3$ in DMW		
PP-1	1(1 M)	1(1 M)	1(2 M)	0.5	1	1	Grayish granules	1.02
PP-2	1(0.1 M)	1(4 M)	2(0.2 M)	0.1	1	1	Slate color granules	0.96
PP-3	1(0.1 M)	2(2 M)	1(0.2 M)	20	0.02	1	Black shiny granules	2.15
PP-4	1(1 M)	1(1 M)	2(1 M)	0.6	0.3	2	Dark brown granules	0.82
PP-5	1(1 M)	1(1 M)	1(0.2 M)	33	0.2	1	Black granules	1.28
PP-6	1(1 M)	1(2 M)	2(0.2 M)	33	0.05	1	Black granules	2.5
PP-7	1(0.2 M)	1(0.1 M)	2(0.2 M)	33	0.1	2	Black shiny granules	3.1
PP-8	1(0.2 M)	1(0.1 M)	2(0.2 M)	33	0.08	2	Black shiny granules	3.34
PP-9	1(0.2 M)	1(0.1 M)	2(0.2 M)	33	0.05	2	Blackish purple crystal	3.68
PP-10	1(0.2 M)	1(0.1 M)	2(0.2 M)	–	–	–	White granules	3.36
PP-11	–	–	–	33	0.05	2	Black granules	0.72

gram (1 g) of the dry cation-exchanger sample in the H^+-form was taken into a glass column with an internal diameter (i.d.) of ~1 cm and glass wool support at the bottom. The bed length was approximately 1.5 cm. Solutions of 1 M alkali and alkaline earth metal nitrates were used to completely elute the H^+ ions from the cation-exchange column while maintaining a very slow flow rate (~0.5 mL min^{-1}). The effluent was titrated against a standard 0.1 M NaOH solution using phenolphthalein indicator to determine the total numbers of ions liberated in the solution (I.E.C.) in mequiv g^{-1}.

Elution behavior and effect of eluant concentration

The optimum concentration of the eluants for complete elution of H^+ ions was determined by passing a fixed volume (250 mL) of sodium nitrate ($NaNO_3$) solution of varying concentrations through the column containing 1 g of the exchanger in the H^+-form with minimum flow rate. The effluent was titrated against a standard alkali solution (0.1 M NaOH). The efficiency of the column was determined by eluting different 10 mL fractions of $NaNO_3$ solution with minimum flow rate and each fraction of 10 mL effluent was titrated against a standard alkali solution for the H^+ ions eluted out.

pH titration

We performed pH-titration studies of PPZTP (PP-9) composite cation-exchanger using the method of Topp and Pepper [41]. The samples (in the H^+-form) were placed in each of the several 250 mL conical flasks in 500 mg portions followed by the addition of equimolar solutions of alkali metal chlorides and their hydroxides in different volume ratios, with the final volume set at 50 mL to maintain the ionic strength constant. The pH of the solution was recorded every 24 h until equilibrium was attained, which required about 5 days. The pH at equilibrium was plotted against the milliequivalents of OH^- ions added.

Chemical stability

The chemical stability also plays an important role in the elucidation of properties of the ion-exchangers. Portions of 250 mg of composites in H^+-form were treated with 20 mL of varying concentration of acids, bases, organic solvents and also in DMW for 24 h with occasional shaking. The supernatant liquids were analyzed for 'zirconium' and 'titanium' by atomic absorption spectrometer, while phosphorus was determined by phosphovanado molybdate method [42].

Thermal effect on ion-exchange capacity

To study the effect of temperature on the I.E.C., a 1 g sample of the composite cation-exchange material PP-9 in the H^+-form were heated at various temperatures in a muffle furnace for 1 h and the Na^+ I.E.C. was determined by a column process after cooling them at room temperature.

Thermal (TGA and DTA) studies

Simultaneous TGA and DTA studies of the composite cation-exchanger (PP-9), in original form were carried out by an automatic thermobalance on heating the material from 10 to 1000 °C at a constant rate (10 °C per minute) in the air atmosphere (air flow rate of 400 mL min^{-1}).

FTIR studies

The FTIR spectrum of polypyrrole (PP-11), inorganic precipitate of ZTP (PP-10), and PPZTP (PP-9) in the original form (dried at 40 °C) was taken using the KBr disc method at room temperature.

X-ray analysis

The powder X-ray diffraction (XRD) pattern was obtained in an aluminum sample holder for PP-9 in the original form using a PW 1148/89 diffractometer with Cu Kα radiation.

Transmission electron microscope studies

Micrographs of the organic–inorganic composite material PPZTP were obtained by transmission electron microscopy to determine the particle size of composite.

Scanning electron microscopy studies

Micrographs of the sample of polypyrrole (PP-11), the inorganic precipitate of ZTP (PP-10); and the composite material PPZTP (PP-9) were obtained by the scanning electron microscope at various magnifications.

Selectivity (sorption) studies

The distribution behavior of metal ions plays an important role in the determination of the material's selectivity. In certain practical applications, equilibrium is most conveniently expressed in terms of the distribution coefficients of the counter ions.

The distribution coefficient (K_d values) of various metal ions on PPZTP composites was determined by the batch method in various solvents systems. Portions of 200 mg of the composite cation-exchanger beads PP-9 in the H^+-form was put in Erlenmeyer flasks with 20 mL of different metal nitrate solutions in the required medium and kept for 24 h with continuous shaking for 6 h in a temperature-controlled incubator shaker at 25 ± 2 °C to attain equilibrium. The metal ion concentrations in the solution were determined before and after equilibrium by titrating against standard 0.005 M solution of EDTA [43]. In other words, the distribution coefficient is the measure of the fractional uptake of metal ions competing for H^+ ions by an ion-exchange material and hence mathematically can be calculated using the formula given as:

$$K_d = [(I - F)/F] \times V/M \left(\text{mL g}^{-1}\right) \tag{1}$$

where I is the initial amount of metal ion in the aqueous phase, F is the final amount of metal ion in the aqueous phase, V is the volume of the solution (mL), and M is the amount of cation-exchanger (g).

Separation factor

For the preferential uptake of metal ion, the separation factor is determined in the separation of a mixture of two metal ions. It can be defined and calculated as:

$$\text{Separation factor}\left(\alpha_B^A\right) = \frac{K_d(A)}{K_d(B)} \tag{2}$$

where K_d (A) and K_d (B) are the distribution coefficient for the two competing species A and B in the ion-exchange system.

Preparation of PPZTP membrane

Coetzee and Benson [8] method was employed for the preparation of PPZTP membrane. The electroactive material, the PPZTP cation-exchanger was ground to a fine powder and was mixed thoroughly with PVC, dissolved in 10 mL of tetrahydrofuran (THF) and finally mixed with 10 drops of dioctylphthalate, which act as a plasticizer [44]. The mixing ratio of the ion-exchanger was varied with a fixed content of PVC in order to obtain a composition with the highest-performing membrane and the resulting solutions were carefully poured into a glass-casting ring (diameter 5 mm) resting on a glass plate. These rings were left untouched so that the THF could evaporate slowly and leave thin films. Four sheets (master membranes) of different thicknesses (0.25, 0.30, 0.40, and 0.42 mm thick) were obtained.

Characterization of membrane

The performance of an ion-exchange membrane depends on its complete physicochemical properties, including those parameters that affect its electrochemical properties: porosity, water content, swelling, thickness, etc. These parameters were determined as described [45–47] after conditioning of the membrane as given below.

Conditioning of the membrane

The membranes were conditioned for measuring swelling and water content by equilibrating with 1 M sodium chloride; about 1 mL of sodium acetate was also added to adjust the pH to be in the range of 5–6.5 (to neutralize the excess acid present in the film).

Water content (% total wet weight)

The conditioned membranes were first soaked in water to elute diffusible salts, blotted quickly with Whatman filter paper to remove surface moisture, and immediately weighed. These were further dried to a constant weight in vacuum over P_2O_5 for 24 h. The water content (% total wet weight) was calculated as:

$$\begin{aligned} \%\ \text{Total wet weight} &= \%\ \text{Total wet weight} \\ &= \frac{W_\mathrm{w} - W_\mathrm{d}}{W_\mathrm{w}} \times 100 \end{aligned} \tag{3}$$

where W_d = weight of the dry membrane and W_w = weight of the soaked/wet membrane.

Porosity

The porosity (ε) was determined as the volume of water incorporated in the cavities per unit membrane volume from the water content data:

$$\varepsilon = \frac{W_\mathrm{w} - W_\mathrm{d}}{A\,L\,\rho_\mathrm{w}} \tag{4}$$

where W_w = weight of the soaked/wet membrane, W_d = weight of the dry membrane, A = area of the membrane, L = thickness of the membrane, and ρ_w = density of water.

Thickness and swelling

The thickness of the membrane was measured by taking the average thickness of the membrane by using screw gauze. The swelling is measured as the difference between the average thicknesses of the membrane equilibrated with 1 M NaCl for 24 h and the dry membrane.

Fabrication of ion-selective membrane electrode

The membrane sheet (M-2) of 0.25 mm of PPZTP thickness, as obtained by the above procedure, was cut in the shape of a disc and mounted at the lower end of a Pyrex glass tube (o.d. 0.8 cm, i.d. 0.6) with PVC. Finally, the assembly was allowed to dry in air for 24 h. The glass tube was filled with 0.1 M thorium nitrate, $Th(NO_3)_4$ solution. A saturated calomel electrode was inserted in the tube for electrical contact and another saturated calomel electrode was used as an external reference electrode. The whole arrangement can be shown as:

Internal reference electrode (SCE)	Internal electrolyte 0.1 Th^{4+}	Membrane	Sample solution	External reference electrode (SCE)

The lower detection limit, electrode response curve, response time, and working pH range were evaluated to study the characteristics of the electrode.

Electrode response or membrane potential

The response of the electrode in terms of the electrode potential (at 25 ± 2 °C), corresponding to the concentration of a series of standard solutions of $Th(NO_3)_4$ (10^{-10}–10^{-1} M), was determined at a constant ionic strength as described by IUPAC Commission for Analytical Nomenclature [48]. Potential measurements of the membrane electrode were plotted against the selected concentrations of the respective ions in an aqueous medium using the electrode assembly. The calibration graphs were plotted 3 times to check the reproducibility of the system.

Effect of pH

A series of pH solutions ranging from 1 to 13 were prepared at constant ionic concentration, i.e., 1×10^{-3} M. The pH variations were brought about by the addition of dilute acid (HCl) and alkali (NaOH) solution. The value of electrode potential at each pH was recorded and plotted against the pH.

Dynamic response time of the electrode

In order to measure the response time of the prepared electrode, the potential of a Th^{4+} solution was recorded as a function of time by a stepwise change of the metal ion concentration from 1×10^{-7} M up to 1×10^{-1} M. The potential was read at 0 s just after dipping of the electrode in the second solution, and subsequently recorded at intervals of 5 s.

Selectivity coefficient of interfering cations

The selectivity of the electrode towards thorium ions over some mono-, di-, and trivalent ions was tested using a mixed solution method [49]. A specified amount of the interfering (M^{n+}) ions (1×10^{-3} M) were added to varying concentrations (1×10^{-1}–1×10^{-9} M) of the primary ion (here Th^{4+}) and the potential was recorded.

Stability of the electrode

In order to assess the electrode lifetime, the slope of the potential versus concentration over the concentration range of 1×10^{-7} M up to 1×10^{-1} M of thorium ions was measured each week over a period of 6 weeks while the electrode was in continuous use.

Analytical application of the electrode

The analytical utility of this membrane electrode has been established by employing it as an indicator electrode in the potentiometric titration of a 0.01 M $Th(NO_3)_4$ solution against an EDTA solution. Potential values are plotted against the volume of EDTA used.

Results and discussion

In this study a novel organic–inorganic nano-composite cation-exchange material is introduced to the field of hybrid composites by the incorporation of organic polymer polypyrrole into the matrix of inorganic ZTP using a sol–gel mixing method. The ion-exchange behavior of crystalline ZTP has been already studied [50, 51], but its hybrid composites are not yet reported, so efforts have been made done to prepare and study the analytical utility this hybrid organic–inorganic composite material. The composite PPZTP is used as an electroactive material as it is made up of the conducting polymer polypyrrole formed by oxidative polymerization [52] of pyrrole. The binding of polymer into the inorganic matrix can be explained in Scheme 1.

Among the various samples prepared, the composite cation-exchanger PPZTP (PP-9) possessed a better Na^+ exchange capacity (3.68 mequiv g^{-1}) as compared to the inorganic ion-exchanger ZTP (3.36 mequiv g^{-1}), as evident from Table 1. Thus, it was selected for further studies.

The effect of the size and charge of the exchanging ion on the I.E.C. was also observed for this material. The alkali metals show a decreasing trend for the I.E.C. ($K^+ > Na > Li^+$) while the alkaline earth metal ions follow the order $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. The size and charge of the exchanging ions affect the I.E.C. of exchanger. This sequence is in accordance with the hydrated radii of the exchanging ions (Table 2). Ions with the smaller hydrated radii easily enter the pores of the exchanger, which results in higher adsorption.

The column elution experiments indicated the concentration of the eluents depends on the rate of elution. It is evident from the Fig. 1 that the minimum molar concentration of $NaNO_3$ was 1.4 M for PP-9 for the maximum elution of H^+ ions from 1 g of the cation-exchanger. This elution behavior indicates that the exchange is quite fast as only 190 mL of sodium nitrate solution (1.4 M) is enough to release all the exchangeable H^+ from 1 g of PPZTP sample (Fig. 2).

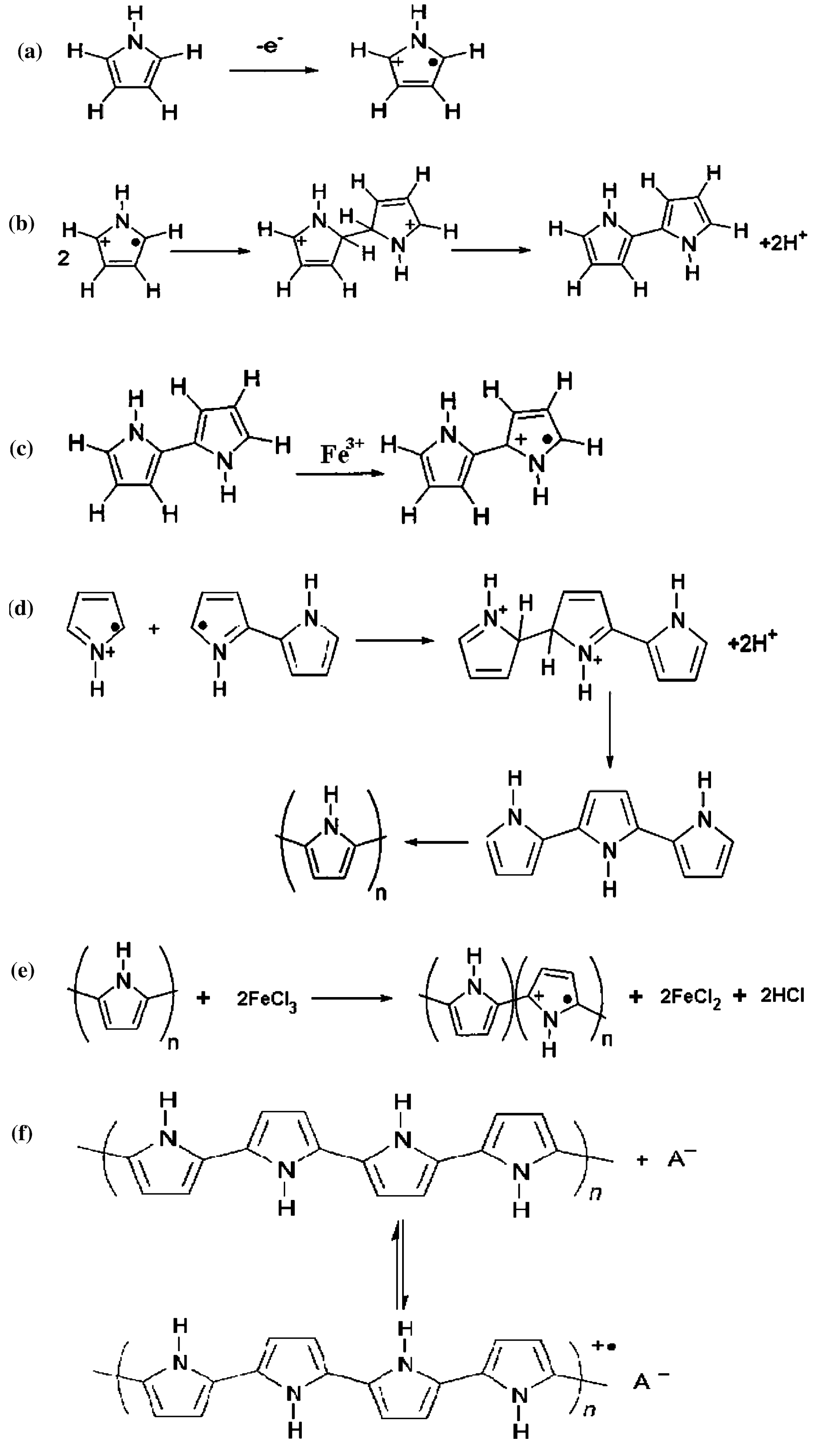
The pH-titration curves for nano-composite sample PP-9 was obtained under equilibrium conditions with NaOH/NaCl, KOH/KCl, and LiOH/LiCl. These systems indicated bifunctional behavior of the material. The nano-composite material PPZTP appears to be a strong cation exchanger, as indicated by the low pH value, 2.63 of the solution when no OH^- ions were added to the system as evident from Fig. 3. The rate of H^+–Na^+ exchange was faster than the H^+–Li^+ and H^+–K^+ exchanges.

It was observed that PP-9 has reasonably good stability in different chemicals. The PPZTP composite was resistant to 2.0 M H_2SO_4, 2.5 M HNO_3, 2.0 M HCl, only slight decomposition of phosphate group was observed. Chemical dissolution was very feeble in DMW, alkaline media, and organic solvents. The results are summarized in Table 3. The chemical stability may be due to the presence of the binding polymer, which can prevent the dissolution of heteropolyacids sols or leaching of any constituent element into the solution.

The material was found to possess good thermal stability. The weight loss starts at 100 °C but, with respect to the I.E.C. and appearance, the material was found stable up to 150 °C and it retained about 49% of its I.E.C. and 70% of its initial mass without any change in color or physical appearance till 250 °C (Table 4). This relative stability might be due to the loss of external water molecules and condensation of material. Above 250 °C, the color of the material starts changing with loss of mass, which indicates the decomposition of materials. These results also support the TGA studies.

The TGA curve (Fig. 4) of the nano-composite PPZTP shows that until 100 °C, only 9% weight loss was observed, which may be due to the removal of external H_2O molecules present at the surface of the composite materials [53]. A steep weight loss (12%) in the PPZTP composite was observed between 100 and 250 °C due to conversion of inorganic phosphate into pyrophosphate. Further slow weight loss of about 8% mass between 250 and 750 °C, in the PPZTP composite may be due to the slight decomposition of organic material. From 750 °C onwards, a smooth horizontal line represents the complete formation of the oxide form of the material. A broad peak near 250 °C in the DTA curve shows that reaction was exothermic during the change of phase of the material.

The FTIR spectrum of polypyrrole, ZTP, and PPZTP are shown in Fig. 5. The FTIR spectrum of the nano-composite PP-9 (Fig. 5c) indicates the presence of extra water molecules in addition to the –OH groups and metal oxides present internally in the material. A strong broad band around 3400 cm^{-1} could be attributed to the –OH stretching frequency. A sharp peak at 1700 cm^{-1} can be ascribed to the H–O–H bending band, which shows interstitial water present in the composite material. The assembly of peaks in the region of 950–1100 cm^{-1} is due to the presence of an ionic phosphate group [54] and peaks at 800 cm^{-1} are attributed to M–O bonding. The stretching vibration of C–N observed at 1350 cm^{-1} indicates that the material contains a considerable amount of pyrrole [55].



Scheme 1 Polypyrrole zirconium titanium phosphate. **a** Formation of radical cation of pyrrole, **b** coupling of radical cations, **c** formation of dimer, **d** chain propagation, **e** polymer oxidation, **f** hybrid composite formation. A stands for ZTP

Table 2 Ion-exchange capacity of various exchanging ions on PPZTP composite cation exchanger

Exchanging metal ions	pH of the metal solution	Ionic radii (Å)	Hydrated ionic radii (Å)	Ion-exchange capacity (mequiv g^{-1})
Na^+	6.30	0.97	2.76	3.68
K^+	6.2	1.33	2.32	3.52
Li^+	6.9	0.68	3.40	3.04
Mg^{2+}	6.0	0.78	7.00	3.51
Ca^{2+}	6.5	1.06	6.30	4.04
Sr^{2+}	6.3	1.27	–	5.38
Ba^{2+}	6.2	1.43	5.90	5.76

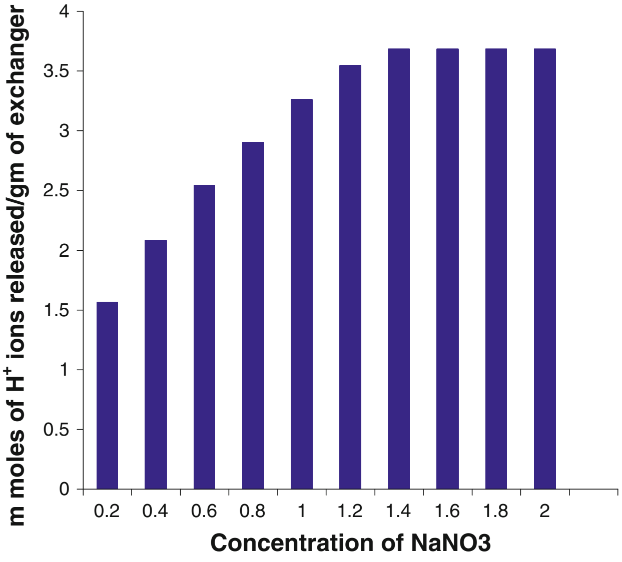


Fig. 1 Effect of eluant concentration on ion-exchange capacity of polypyrrole zirconium titanium phosphate cation exchanger

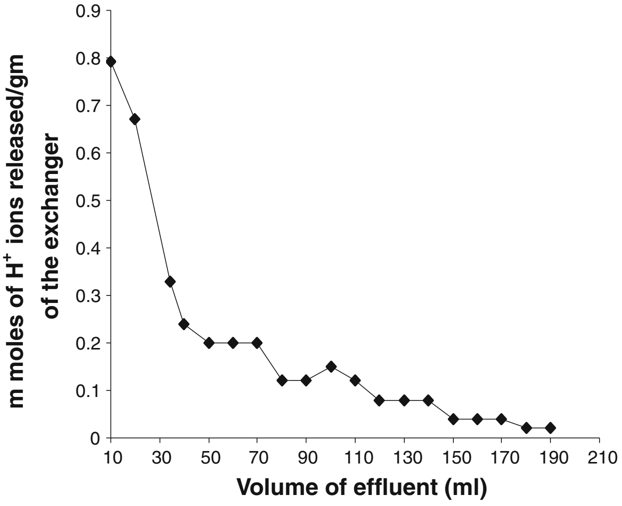


Fig. 2 Elution behavior of polypyrrole zirconium titanium phosphate cation exchanger

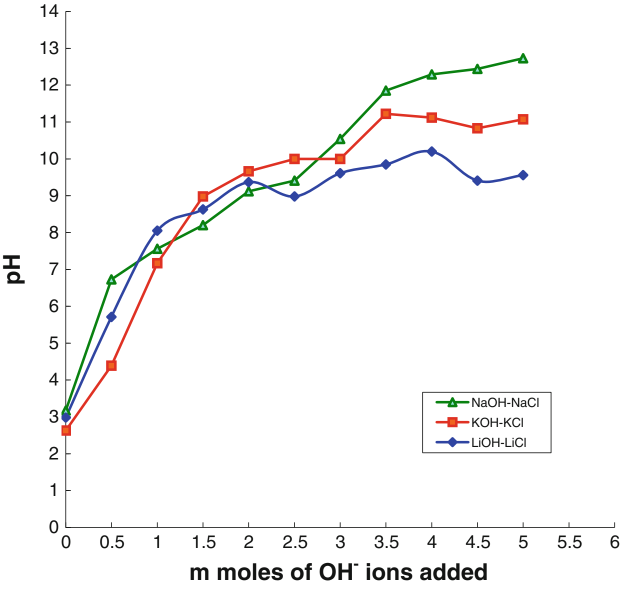


Fig. 3 pH-titration curves for polypyrrole zirconium titanium phosphate cation-exchanger

Table 3 Chemical stability of PPZTP in various solvents

Solvent used (20 mL)	Amount dissolved (mg/20 mL)		
	Zr(IV)	Ti(IV)	Phosphorus
DMW	0.00	0.00	0.00
1 M HCl	0.04	0.03	0.152
1.5 M HCl	0.29	0.18	0.48
2.0 M HCl	1.08	0.81	1.05
1 M HNO_3	0.06	0.09	0.74
1.5 M HNO_3	0.23	0.56	1.08
2.0 M HNO_3	1.01	0.92	1.21
2.5 M HNO_3	1.37	1.19	1.72
1 M H_2SO_4	0.10	0.07	0.67
1.5 M H_2SO_4	0.66	0.42	1.26
2.0 M H_2SO_4	1.05	0.98	1.61
0.1 M NaOH	0.03	0.00	0.21
0.1 M KOH	0.05	0.02	0.38
10% Acetone	0.00	0.00	0.08
10% Butanol	0.02	0.00	0.12
10% Dimethylsulphoxide	0.05	0.04	0.42

These characteristic stretching frequencies show close resemblance to ZTP (Fig. 5b) and PPZTP (Fig. 5c), which indicates the binding of the inorganic precipitate with the organic polymer and also shows the formation of an ‘organic–inorganic’ composite.

The X-ray diffraction pattern of the cation-exchanger (PP-9 as prepared) was recorded in a powdered sample exhibited very sharp peaks in the spectrum (Fig. 6) that suggest a semi-crystalline nature of the composite material.

Table 4 Thermal stability of PPZTP composite cation-exchanger after heating at various temperature

Heating temperature (°C)	Appearance (color)	% Weight loss	Na^+ ion-exchange capacity (mequiv g^{-1})	% Retention of I.E.C.
50	Black	–	3.68	100
100	Black	04	3.68	100
150	Black	08	3.1	84.23
200	Black	10	2.7	73.36
250	Grayish black	35	1.8	48.91
300	Grayish black	55	1.51	41.03
350	Grayish black	58	0.08	24.34
400	Grayish black	62	0.39	10.59
500	Buff color	65	0.08	2.14
600	Dirty white color	70	0	0
650	White	74	0	0

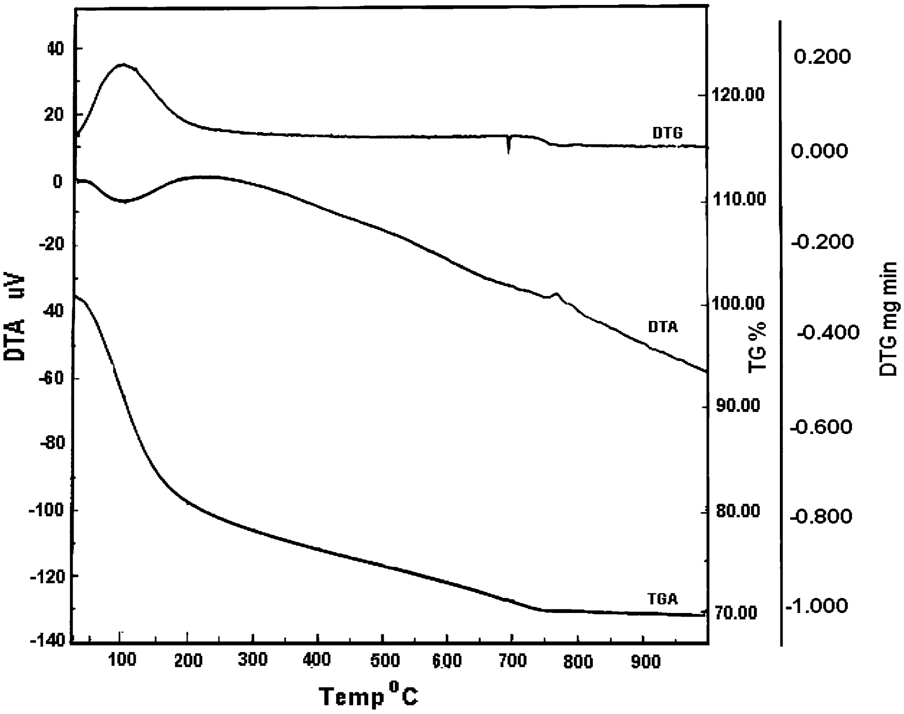


Fig. 4 Simultaneous TGA–DTA curves of polypyrrole zirconium titanium phosphate (as prepared)

From TEM micrographs the particle sizes of PPZTP observed are 31, 42, and 60 nm (Fig. 7) which proves that the proposed cation-exchanger is a nano-composite since the particle sizes are in nano-range.

The SEM images of polypyrrole, inorganic precipitate ZTP, and PPZTP (PP-9) at different magnifications are shown in Fig. 8. The SEM image shows the difference in the surface morphology after incorporation of the organic polymer into the inorganic ZTP, which indicates the binding of the inorganic ion-exchange material to the organic polymer (polypyrrole) and the formation of a composite material was observed.

In order to explore the selectivity potential of the composite material PP-9, distribution studies (K_d) for 17 metal ions were performed in 15 solvent systems. It was observed from the data given in Table 5 that the K_d-values vary with the nature of the contacting solvents. It was also observed from the sorption studies (K_d values) that Th^{4+} was strongly adsorbed on the surface of ion-exchange material PPZTP while the remaining metal ions are poorly adsorbed.

Some factors that affect the distribution coefficient of cations are the charge, size, swellings, formation of complexes, nature of the chemical bond, solvent distribution, and nature of the ion exchanger. Three main factors that affect the ability of an ion to compete effectively with one another are the charge on the ion, its ionic radius and the hydrated energy of the competing ion. For an ion to be

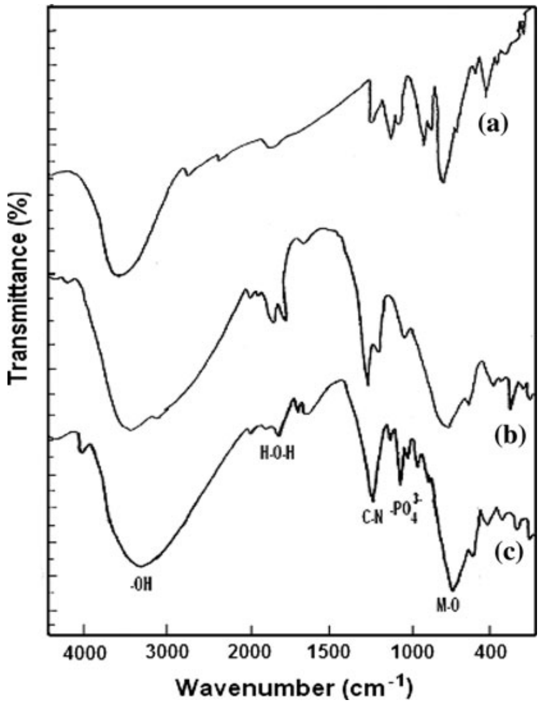


Fig. 5 FTIR spectra of as prepared polypyrrole (*a*), zirconium titanium phosphate (*b*), and polypyrrole zirconium titanium phosphate (*c*) nano-composite cation exchanger

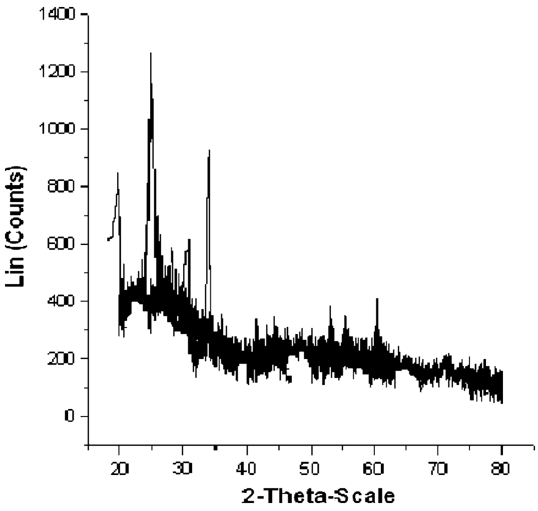


Fig. 6 Powder X-ray diffraction pattern of polypyrrole zirconium titanium phosphate nano-composite (as prepared)

effective in a competition reaction its charge and hydration energy must be high and its radius should be small. The radius of Th^{4+} is 0.9 Å which is less than some metal ions and is about that of Na^{+}. Some metals like Sr^{2+} have lower radius values but their hydration energies are quite low. A few heavy metals like Al^{3+} and Cr^{3+} have high hydration radius values but the charge on their ions is less than that of Th^{4+}, so they should be at a much higher concentration to become a competitor. Therefore, the charge on the ion is a very important factor. Below, a pictorial representation of the adsorption and regeneration process is shown:

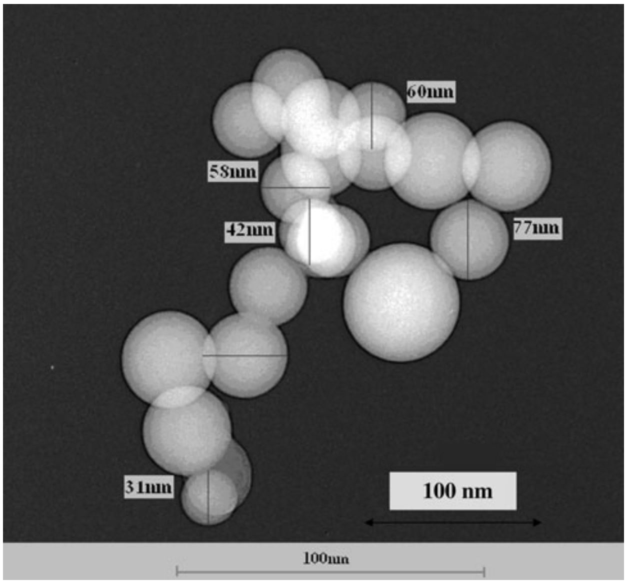
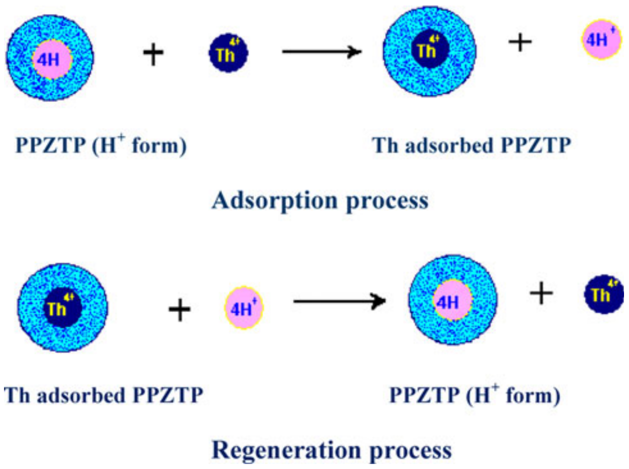


Fig. 7 Transmission electron microphotographs (TEM) of polypyrrole zirconium titanium phosphate showing different particle size



The small hydrated radii of Th(IV) (2–2.45 Å) may be attracted easily by co-ions (phosphates and amines) present in the matrix of the material. Thus, this study showed that the composite PPZTP has maximum selectivity for Th(IV) and can be utilized for the determination and separation of Th(IV) from waste effluents.

The separation factor is the preference of the ion-exchangers for one of the two counter ion species. If the ion A is preferred, the factor is larger than unity, and if B is preferred, the factor is smaller than unity. The numerical value of the separation factor is not affected by the choice of the concentration units and it shows that the sample is highly preferential and selective for Th(IV) (Table 6).

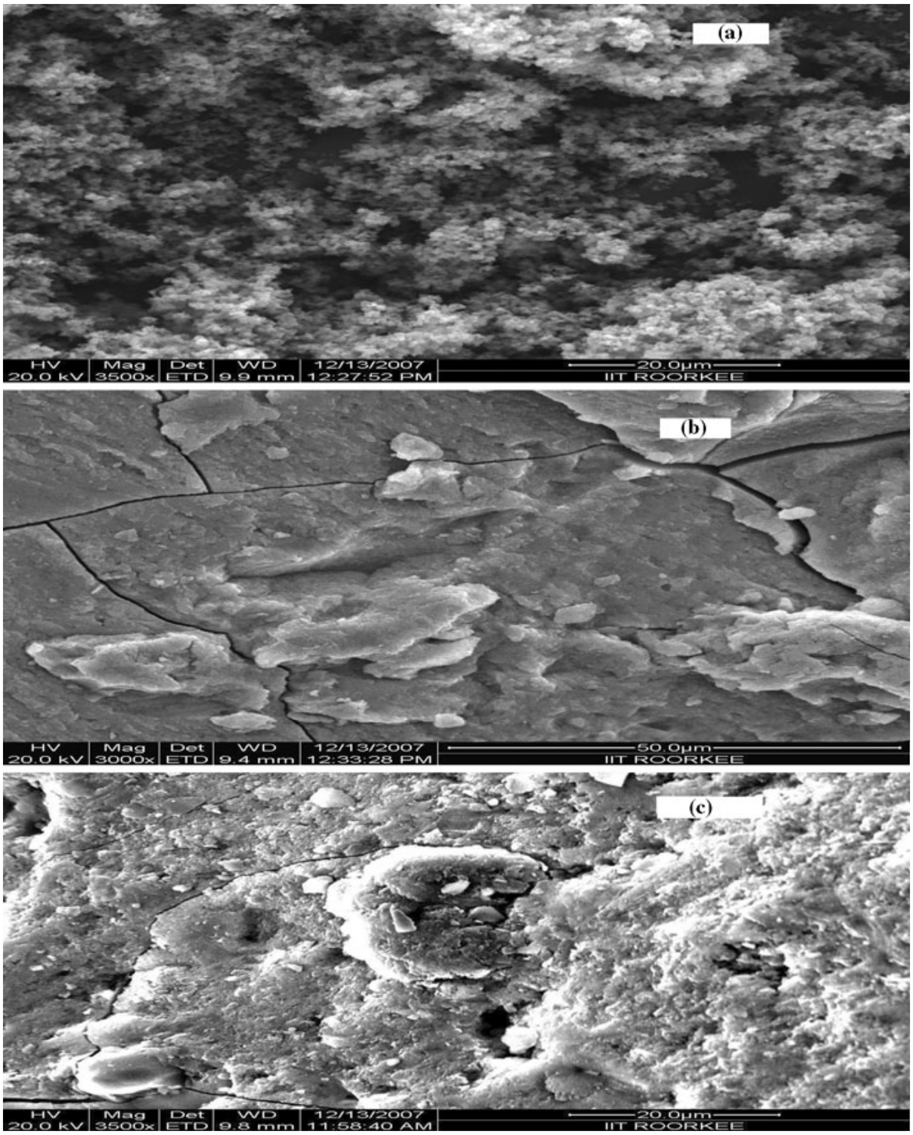


Fig. 8 Scanning electron microphotographs (SEM) of chemically prepared **a** polypyrrole at the magnification of 3500×, **b** zirconium titanium phosphate at the magnification of 3500×, and **c** polypyrrole zirconium titanium phosphate composite system at the magnification of 3500×

A number of samples of the PPZTP nano-composite membranes were prepared with different amounts of composites and a fixed amount of PVC and were checked for the mechanical stability, surface uniformity, materials distribution, cracks and thickness, etc. Characterization of the membrane is important before its use as an ion-selective electrode. Thus, some properties like swelling, thickness, porosity, and water content capacities were determined (Table 7).

The PPZTP composite membrane sample M-2 (thickness 0.25 mm) was selected for making of ion-selective electrode. The low order of water content, the swelling, porosity, and lesser thickness of these membranes suggest that interstices are negligible and diffusion across the membranes would occur mainly through the exchanger sites. The sensitivity and selectivity of the ion-selective electrode depend upon the nature of the electroactive material. When a membrane of such materials is placed between two electrolyte solutions of the same nature, at the same pressure and temperature, but at different concentrations, some ions (to which the membrane is selective) pass from the solution of higher concentration through the membrane to that of lower concentration, thus producing an electrical potential difference. This membrane potential can be used for electroanalytical studies.

The potentiometric response of the PPZTP membrane electrode (M-2) over a wide concentration range (1×10^{-1}–1×10^{-10} M) is shown in Fig. 9. The electrode showed a linear Nernstian response in the range of 1×10^{-1}–1×10^{-7} M with an average slope of 16.65 mV per decade change of activity. The limit of detection, was determined from the intersection of the two extrapolated

Table 5 K_d values of some metal ions on PPZTP composite cation-exchanger column in different solvent system

Metal ions	Ionic radii (Å)	Hydrated radii (Å)	DMW	10^{-1} M HNO_3	10^{-2} M HNO_3	10^{-3} M HNO_3	10^{-1} M H_2SO_4	10^{-2} M H_2SO_4	10^{-1} M HCl	10^{-2} M HCl	10^{-3} M HCl	pH 5.75	10% HCOOH	10^{-2} M $HClO_4$	10% C_2H_5OH	20% Acetone	Buffer 10
Ba^{2+}	1.35	5.90	142	42	14	158	100	30	51	72	290	–	18	44	130	440	146
Mg^{2+}	0.65	7.00	188	22	134	5	50	6	39	38	17	–	6	20	24	86	726
Cu^{2+}	0.92		800	89	116	104	27	36	65	72	379	412	111	50	364	650	123
Cd^{2+}	0.97	4.26	400	–	–	164	77	–	18	116	92	172	30	25	525	473	580
Co^{2+}	0.72		134	–	17	77	–	50	50	19	46	345	17	108	89	23	–
Sr^{2+}	1.18	4.08	213	20	91	110	219	67	–	8	59	307	18	15	110	18	83
Ca^{2+}	1.00	6.30	5	40	42	160	40	46	145	100	120	56	93	53	126	11	454
Mn^{2+}	0.80		38	–	–	80	–	–	–	–	157	600	200	30	52	59	556
Pb^{2+}	1.18	4.01	1000	119	850	–	212	70	45	53	78	480	342	384	525	720	420
Al^{3+}	1.87	3.14	30	53	286	–	–	–	–	227	17	167	42	147	–	423	400
Ni^{2+}	0.69	2.08	10	131	40	342	140	65	15	–	20	65	–	25	89	–	38
Cr^{3+}	0.76		50	450	131	–	31	45	115	100	–	145	130	115	777	–	–
Th^{4+}	0.94	2.45	1415	TA	1480	637	155	110	136	269	1136	–	567	648	–	900	TA
Zn^{2+}	0.75	4.25	14	58	8	19	–	–	5	13	47	223	–	73	243	56	136
Fe^{2+}	0.63		–	16	–	150	356	86	94	35	–	107	–	–	–	73	35
Tl^{+}	0.89	2.21	200	250	–	247	–	–	–	34	234	25	108	8	108	200	16

Table 6 Separation factor of different metal ions on PPZTP composite cation exchanger

Separation factor	DMW	1×10^{-2} M $HClO_4$	1×10^{-3} M HCl	1×10^{-2} M HNO_3
$\alpha^{Th...Ni}$	141.50	25.9	56.8	37
$\alpha^{Th...Pb}$	0	1.86	14.6	1.8
$\alpha^{Th...Mg}$	7.52	32.4	66.8	11.04
$\alpha^{Th...Zn}$	101.07	8.87	24.17	185
$\alpha^{Th...Ba}$	9.76	162	3.92	105.71
$\alpha^{Th...Al}$	41.66	1.56	58.8	7.34
$\alpha^{Th...Ca}$	250	4.32	8.33	50
$\alpha^{Th...Sr}$	5.86	15.2	16.95	23.07
$\alpha^{Th...Zn}$	89.29	3.13	21.27	262.5
$\alpha^{Th...Co}$	9.32	2.12	21.74	123.53

Table 7 Characterization of ion-exchange membranes of PPZTP

Polypyrrole zirconium titanium phosphate membranes	Thickness (mm)	Water content as % weight of wet membranes	Porosity	Swelling as % weight of wet membranes
M-1	0.30	2.1647	9.5×10^{-4}	0.662
M-2	0.25	1.1111	2.19×10^{-4}	0.3984
M-3	0.40	3.3113	1.8×10^{-4}	1.139
M-4	0.42	5.1241	4.37×10^{-4}	1.176

segments of the calibration graph according to the IUPAC recommendation [56, 57], was found to be 1×10^{-7}M for the PPZTP based electrode. Thus, the working concentration range for the selective membrane was found to be 1×10^{-1}–1×10^{-7} M having detection limit 1×10^{-7} M for Th^{4+} ions with a higher Nernstian slope of 16.65 mV per decade change in Th^{4+} ion concentration.

The dependency of the potential response of the sensor on the pH is shown in Fig. 10. The potential is independent of pH and remains constant in the range of 4.0–9.0. The dependency of potential on the pH values out of this range can be attributed to the metal hydroxide formation at the higher pH values. At lower pH the electrode shows a stronger response to the hydrogen ion than the Th^{4+} ions in the solution.

For analytical applications dynamic response time is an important factor for any ion-selective electrode. The potential was recorded as a function of time over a concentration range of thorium ions and the results are summarized in Fig. 11. An average response time of about 15 s was found in the entire examined concentration range.

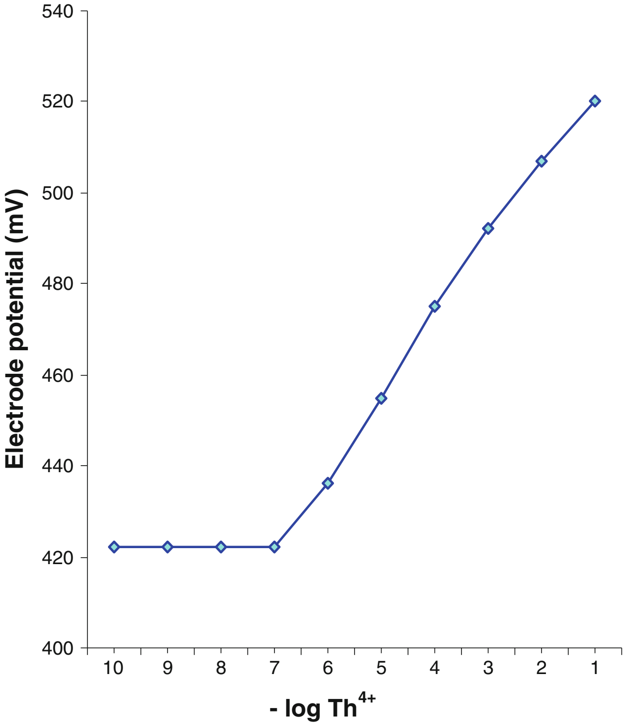


Fig. 9 Calibration curve for PPZTP membrane (M-2) electrode in aqueous solution of $Th(NO_3)_4$

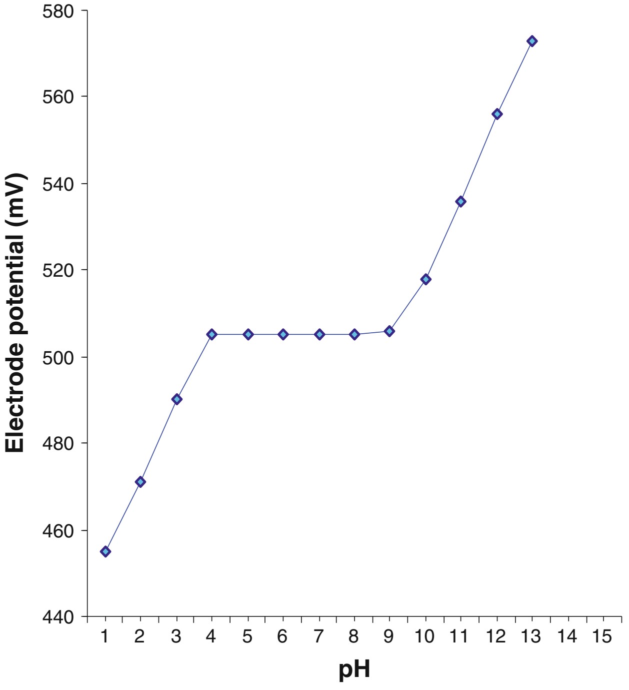


Fig. 10 Effect of pH on the potential response of the PPZTP membrane electrode at 1×10^{-3} M Th^{4+} ion concentration

The stability of the Th(IV)-selective electrode was tested over a period of 6 weeks. During this period, the electrode was in daily use over an extended period of time (1 h per day), and the results are provided in Table 8. The measured potential of Th(IV) ions in concentration range of 1×10^{-1}–1×10^{-7} M was reproducible within ±1.7 mV and there was no significant change observed in the slope of the Nernst plot during the experiment over a

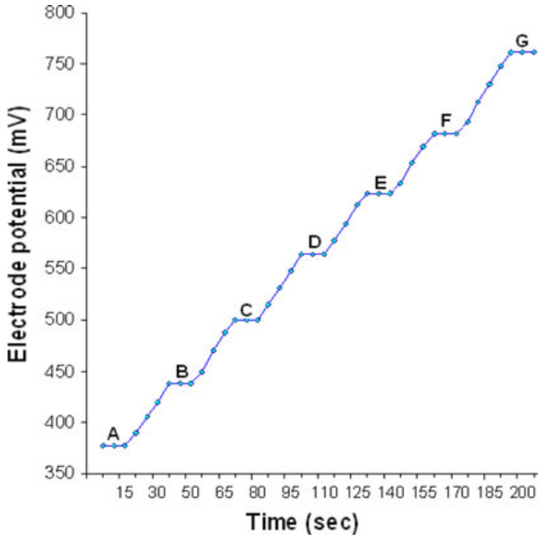


Fig. 11 Dynamic response time of PPZTP electrode for different Th^{4+} concentration: (*A*) 1×10^{-7} M, (*B*) 1×10^{-6} M, (*C*) 1×10^{-5} M, (*D*) 1×10^{-4} M, (*E*) 1×10^{-3} M, (*F*) 1×10^{-2} M, (*G*) 1×10^{-1} M

Table 8 The stability of the Th^{4+}-selective PPZTP membrane electrode

Week	Slope (mV decade^{-1})	DL (M)
First	16.65 ± 0.3	1×10^{-7}
Second	16.4 ± 0.5	9.2×10^{-6}
Third	16 ± 0.3	7.5×10^{-6}
Fourth	15.7 ± 0.4	6.7×10^{-6}
Fifth	15.3 ± 0.2	6.1×10^{-6}
Sixth	15.1 ± 0.3	5.4×10^{-6}

time period of 6 weeks. This suggests a longer life, quick response, and stable electrode performance.

Potentiometric selectivity coefficients describing the membrane preference towards an interfering ion were determined by a mixed solution method (FIM) [58].The resulting values are given in Table 9; they indicate the extent to which a foreign ion interferes with the response of the electrode towards its primary ion (Th^{4+}). The bivalent metal ions like Pb(II), Cu(II), Ni(II), Cd(II) interfere to small extent, as shown in Fig. 12. For the diverse set of ions used, the selectivity coefficients are on the order of 4.7×10^{-2} or smaller, indicating that they would not significantly interfere with the Th^{4+}-selective electrode function. Therefore, the proposed PPZTP material interacts relatively strongly with Th(IV) ions and can be successfully used as a sensing agent.

Table 9 The selectivity coefficient of various interfering cations for Th^{4+}-selective PPZTP membrane electrode

Interfering ion (M^{n+})	Selectivity coefficients (K_{MSM})
K^+	4.5×10^{-3}
Na^+	4.5×10^{-3}
Mg^{2+}	2.5×10^{-2}
Cu^{2+}	8×10^{-2}
Pb^{2+}	8×10^{-2}
Ca^{2+}	2.5×10^{-2}
Al^{3+}	1×10^{-3}
Sr^{2+}	4.7×10^{-2}
Mn^{2+}	4.7×10^{-2}
Fe^{3+}	1×10^{-3}
Ni^{2+}	8×10^{-2}
Cd^{2+}	4.7×10^{-2}

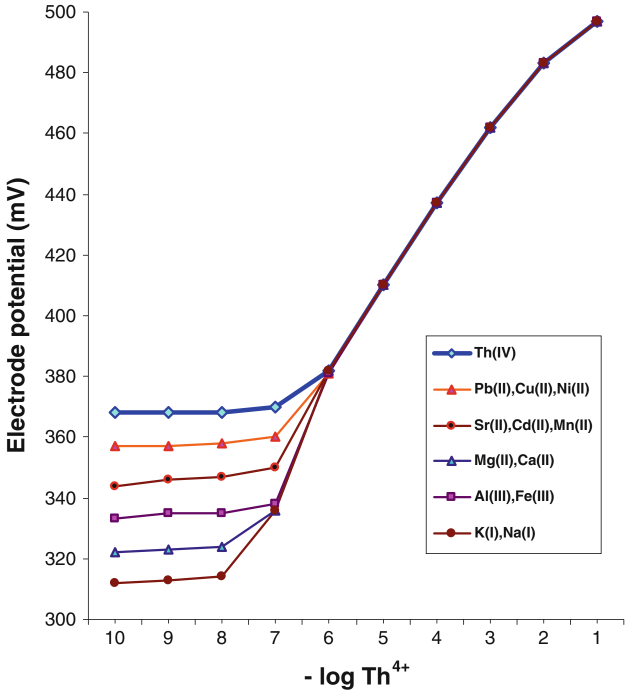


Fig. 12 Selectivity coefficient curve of various interfering ions for Th(IV)-selective PPZTP membrane electrode

Table 10 compares the detection limit, linear range, pH range, and response time of the proposed sensor with the previously reported thorium electrodes [28, 59–63]. The results clearly indicated the superiority of the proposed electrode in terms of linear range, pH range, and detection limit.

Owing to the good selectivity of the Th^{4+}-selective electrode it has been employed as an indicator electrode for the selective titration of a $Th(NO_3)_4$ solution against an EDTA solution. The addition of EDTA causes a decrease in potential as a result of the decrease in free metal ion concentration due to its complexation with EDTA (Fig. 13). The amount of Th(IV) ion in solution can be accurately determined from the resulting neat titration curve which

Table 10 Comparison of the selectivity coefficient of the best Th^{4+} sensors with the proposed sensor

Reference	Detection limit (M)	Linear range (M)	Response time (s)	pH range
[59]	1.4×10^{-6}	1.0×10^{-1}–8.0×10^{-6}	15	2.5–9.0
[60]	6.3×10^{-7}	1.0×10^{-2}–1.0×10^{-6}	30	3.0–9.0
[61]	7.9×10^{-6}	1.0×10^{-3}–1.0×10^{-5}	15	2.3–4.0
[62]	8.0×10^{-7}	1.0×10^{-1}–1.0×10^{-6}	10	3.5–9.5
[28]	5×10^{-5}	1.0×10^{-1}–1.0×10^{-4}	10	3–5
[63]	1.6×10^{-6}	1.0×10^{-1}–5.0×10^{-6}	30	3–5
This work	1.0×10^{-7}	1.0×10^{-1}–1.0×10^{-7}	15	4.0–9.0

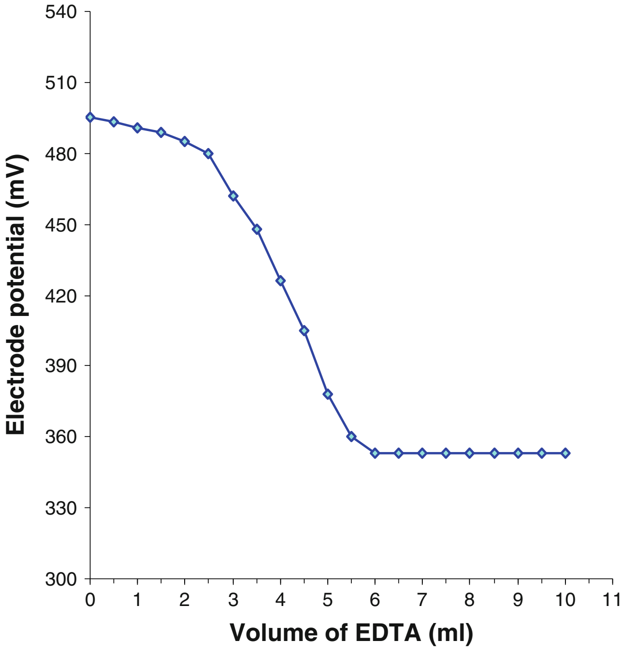


Fig. 13 Potentiometric titration of Th(IV) against EDTA solution using PPZTP membrane sensor as an indicator electrode

provides a sharp equivalence point. This study established the practical and analytical utility of the proposed composite cation-exchanger membrane electrode.

Conclusion

In this piece of work, a thorium selective nano-composite cation-exchanger PPZTP synthesized by using an advanced inorganic ZTP, shows good I.E.C. (3.68) as compared to ZTP (3.36). TEM study proved the material as nano-composite. This composite material acts as an electroactive component for the preparation of ion-selective membrane electrode for the determination of Th(IV) ions in the working concentration range 10^{-1}–10^{-7} M with a pH range of 4.0–9.0 and a response time ~15 s. It showed good reproducibility, detection limit, lifetime of 6 weeks, and high selectivity for Th(IV) ions in the presence of different cations. The practical utility can be determined by using this electrode as a potentiometric sensor for the titration of thorium ions.

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