Chapter 2

Chapter 2

2.1 Introduction

Ion exchange is considered as a time honored analytical tool for the analysis of complex mixtures in diverse fields. It is now a well established technique in many industrial processes and is widely employed in chemical lab. Since the classical work of Amphlett, numerous inorganic ion exchangers have been synthesized under different conditions of synthesis and their properties were also studied [1]. The different types of ion exchanger and their applications in diverse fields are documented in a book by Clearfield [2].

Organic polymers showed the properties of chemical stability through synthetic methods [3]. Due to presence of both Bronsted and Lewis acid sites on their surfaces, synthetic ion exchangers have greater ion exchange capacity than commercial organic ion exchangers. The inorganic ion-exchange materials based on polyvalent metals have been established now with an excellent recognition in various disciplines, i.e. metal ion separation, catalysis, environmental studies, medical science (kidney dialysis), ion-selective electrodes preparation, heterogeneous solid state membrane formation, ion-exchange fibers preparation, etc. Besides other advantages, these materials are important in being more stable to high temperature radiation field than the organic one [4]. 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 [5]. In order to obtain associated organic and inorganic materials as ion-exchangers, attempts have been made to develop a new class of composite ion-exchangers also known as ‘polymeric-inorganic’ hybrid composite [6-9] with enhance physical properties and possessing good selectivity for heavy metals indicating its usefulness in environmental application [10,11].

Now a days, nano-composites lead to unexpected new properties exhibiting a vast application potential [12] which are often not exhibited by individual compounds and thus open a new avenue for chemists, physicists and materials scientists [13]. 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 present 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 [14,15]. The growing interest of this subject matter has been reflected in two symposia organized recently by the Materials Research Society [16,17].

Many ‘organic-inorganic’ composite ion-exchangers have been developed earlier by incorporation of organic monomers in to inorganic matrix, by way of pillaring or non-pillaring methods [18-21]. Few such excellent ion-exchange materials have been developed in our laboratory and successfully being used in environmental analysis [22-28].

An effort has been done to improvise and use the properties of advanced bimetallic tetravalent metal acid (TMA) salts as inorganic ion exchanger by incorporating the highly conducting polymers, polypyrrole and polyaniline, into the matrix of inorganic precipitate of Zirconium Titanium phosphate (ZTP) and Zirconium Tungstioiodophosphate (ZWIP) under varying conditions. In order to determine the composition, size, structural and thermal properties of these material, several physico-chemical investigations were carried out by elemental analysis, atomic absorption spectrophotometry (AAS), Transmission electron microscopy (TEM), scanning electron microscopy (SEM), spectral analysis (FTIR), thermal analysis (simultaneous TGA-DTA) and X-Ray analysis. This chapter represents the preparative conditions and physico-chemical properties of the above said composite cation-exchange materials.

2.2 Experimental

2.2.1 Chemicals and reagents

The main reagents used for the synthesis were:

Zirconium Oxychloride (ZrOCl₂·8H₂O), Di-sodium hydrogen ortho phosphate [Na₂HPO₄ (88-93%)], Pyrrole [C₄H₅NH (99%)], Ammonium per sulphate [(NH₄)₂S₂O₈ (95%)], Hydrochloric acid [HCl (35%)], Nitric acid (HNO₃), Toluene [C₆H₅CH₃ (95%)], Aniline[C₆H₅NH₂ (95%)], Titanium tetrachloride (TiCl₄), Ferric Chloride (Anhydrous), [FeCl₃ (95%)], Sulphuric Acid (H₂SO₄), Sodium tungstate (NaHWO₃), Potassium iodate (KIO₃). All the reagent and chemicals were of analytical grade.
2.2.2 Instrumentation

The following instruments were used for chemical analysis and characterization of the composite materials:

- A digital pH meter-Elico (India), model LI-10, UV/VIS spectrophotometer - Elico (India), model EI 301E;
- Double Beam Atomic Absorption Spectrophotometer (AAS) - GBC 902 (Australia) with air-acetylene flame, scanning electron microscope with EDAX -LEO 435 VP (Australia), FTIR spectrometer - Perkin Elmer (U.S.A.), model Spectrum BX, Elemental analyzer - Elementary Vario EL III, Carlo-Erba, model 1108; used for C, H and N analyses, thermal analyzer - V2.2A DuPont 9900, X-ray diffractometer - Phillips (Holland), model PW 1148/89 with Cu Kα radiations, Transmission electron microscope -TEM Philips EM 400, an automatic temperature controlled water bath incubator shaker - Elcon (India), digital muffle furnace, an air oven - Lab quip (India), an electronic balance (digital) - Sartorius (Japan), model 21 OS and a magnetic stirrer.

2.2.3 Synthesis of ‘organic-inorganic’ composite cation-exchange material

2.2.3.1 Preparation of reagent solutions

- 0.1M solution of titanium tetrachloride, TiCl₄ and a 0.1M solution of zirconium oxychloride, ZrOCl₂·8H₂O were prepared in demineralized water (DMW) with different concentrations of H₂SO₄ and Na₂HPO₄. Solution of 0.5M of sodium tungstate and 0.1M of potassium iodate (KIO₃) were prepared only in demineralized water.

- Aniline and 0.1M ammonium persulphate solution of different percentage concentration (v/v) were prepared in 1M HCl. Pyrrole solutions were prepared in toluene at different percentage concentrations (v/v) and 0.1M FeCl₃ was prepared in demineralized water (DMW).

2.2.3.2 Synthesis of polymer

2.2.3.2.1 Synthesis of polyaniline (PANI)

Polyaniline gel was prepared by oxidative coupling using ammonium persulphate in acidic aqueous medium [29]. Various samples of polyaniline gel were prepared by mixing 0.1%-1.0% of aniline and 0.1M (NH₄)₂S₂O₈ (in 1M HCl) with
continuous stirring by a magnetic stirrer. Dark purplish green color gels were obtained by keeping the samples below 10° C for an hour.

2.2.3.2.2 Synthesis of polypyrrole (PPy)

Polypyrrole samples were prepared by chemical oxidative polymerization [30-31] by adding solutions of pyrrole (in toluene, at concentrations up to 33% by weight) dropwise to the 0.1M FeCl₃ solutions (in DMW) in different volume ratios at room temperature with continuous magnetic stirring for 2hrs. The black slurries obtained were kept for 24 hrs.

2.2.3.3 Synthesis of inorganic precipitate
2.2.3.3.1 Synthesis of zirconium titanium phosphate (ZTP)

The method of preparation of the precipitated zirconium titanium phosphate ion-exchanger was very similar to that of Alberti and Constantino [32], with a slight modification [33] by mixing a solution containing 0.1M TiCl₄ and 0.1M ZrOCl₂.8H₂O in H₂SO₄ at a flow rate of 0.5 ml min⁻¹ with the aqueous solution of Na₂HPO₄ of different molarities. Constant stirring was maintained using a magnetic stirrer at room temperature (25±2°C) for 3hrs. The white gel obtained was left for 24hrs at room temperature for digestion.

2.2.3.3.2 Synthesis of zirconium tungstoiodophosphate (ZWIP)

Inorganic gels of zirconium tungstoiodophosphate was prepared by adding 0.1M ZrOCl₂.8H₂O solution to a mixture of 0.5M sodium tungstate, 0.1M potassium iodate and 1M orthophosphoric acid, in different volume ratios with intermittent shaking of the mixture and maintaining the pH at 1.

2.2.3.4 Preparation of ‘organic-inorganic’ composites
2.2.3.4.1 Preparation of polyaniline zirconium titanium phosphate (PANI-ZTP)

The composite 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 precipitate of polyaniline (PANI) was added into the white inorganic gel of ZTP with a constant stirring. Black colored precipitate obtained was allowed to settle overnight which was filtered off and washed
thoroughly with DMW to remove excess acid and any adhering ions (chloride and sulphate). The washed gel was dried over P₂O₅ at 30°C in an oven. The dried product was immersed in 1M HNO₃ solution for complete replacement of counter ions by H⁺ form. The excess acid was removed after several washing with DMW then dried at 40°C and sieved to obtain shiny black granules of PANI-ZTP. Sample PA-7 was selected, on the basis of Na⁺ ion-exchange capacity, yield and physical appearance, for further studies.

2.2.3.4.2 Preparation of polypyrrole zirconium titanium phosphate (PPy-ZTP) composite

In this process, 0.1M ferric chloride (FeCl₃) 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 1hr. The resultant mixture turned first to green and then slowly into black slurries, which was kept for 24 hrs at room temperature (25±2°C). The dried products were protonated and sieved to obtain shiny black granules of polypyrrole zirconium titanium phosphate (PPy-ZTP).

2.2.3.4.3 Preparation of polyaniline zirconium tungstooiodophosphate (PANI-ZWIP) composite

The preparation method is same as of PANI-ZTP composite, only the inorganic precipitate is different. The precipitate of polyaniline was added into the white inorganic gel of zirconium tungstooiodophosphate with constant stirring. The resultant material was dried, sieved and protonated according to above mentioned method. Shiny black granules of polyaniline zirconium tungstophosphate (PANI-ZWIP) were obtained.

2.2.4. Physico-chemical properties of ‘organic-inorganic’ composite cation-exchange materials

2.2.4.1 Chemical stability

The chemical stability also plays an important role in the elucidation of properties of the ion-exchangers. Portions of 250 mg of prepared composites (PANI-ZTP, PPy-ZTP and PANI-ZWIP) in H⁺ form were treated with 20 ml of varying
concentration of acids, bases, organic solvents and also with DMW for 24h with occasional shaking.

2.2.4.2 Thermal stability

To study the effect of drying temperature, 1g samples of the composite cation-exchange material (PA-7, PP-9 and PW-6) were heated at various temperatures in a muffle furnace for 1hr each; physical appearance and the percentage of weight losses were determined after cooling them at room temperature.

2.2.4.3 Chemical composition

The chemical composition also plays an important role in the elucidation of molecular structure of the ion-exchangers. The composition of the material can be determined either by gravimetrically or spectrophotometrically. With the help of these methods, we can determine the percentage of metals or groups present in the ion-exchangers.

To determine the chemical composition of prepared composites, 200 mg of each sample was dissolved in 20 ml of concentrate H₂SO₄. The material was analysed for zirconium and titanium by ICP-MS and phosphate by the phosphomolybdate method. Carbon, hydrogen and nitrogen contents of the cation-exchanger were determined by elemental analysis.

2.2.4.4. Characterization of ‘organic-inorganic’ composite materials

2.2.4.4.1 Transmission electron microscopy (TEM) studies

Fine particle dispersion method was used for sample preparation in which the prepared sample materials (PANI-ZTP, PPy-ZTP and PANI-ZWIP) were grinded into fine powder by using mortar pastel. A dilution step is required to obtain very low concentrations of the material, so that the particles on the support film remain isolated. Sonication of the samples was done for half an hour which separated the agglomerated particles and ensured a homogenous suspension. The samples were inaugurated on copper coated grid. Adhere it for 3-5 minutes, later blot dried. Then the samples were put in transmission electron microscope for taking image of particle size of the sample materials.
2.2.4.4.2 Scanning electron microscopy (SEM) studies

To examine the difference in surface morphology between the parent materials and the prepared composites, micrographs of the organic polymers (polyaniline and polypyrrole), inorganic precipitates (ZTP and ZWIP) and organic-inorganic composite materials (PANI-ZTP, PPy-ZTP and PANI-ZWIP) were obtained by the scanning electron microscope at various magnifications.

2.2.4.4.3 X-ray analysis

Powder X-ray diffraction (XRD) pattern was obtained in an aluminum sample holder for the prepared composite materials (PANI-ZTP, PPy-ZTP and PANI-ZWIP) in the original form using a PW 1148/89 based diffractometer with Cu Kα radiations.

2.2.4.4.4 Fourier transform infrared (FTIR) spectroscopic studies

The FTIR spectrum of organic polymers (polyaniline and polypyrrole), inorganic precipitates (ZTP and ZWIP) and organic-inorganic composite materials (PANI-ZTP, PPy-ZTP and PANI-ZWIP) in the original form dried at 40°C were taken by KBr disc method at room temperature.

2.2.4.4.5 Thermogravimetric analysis-differential thermal analysis (TGA-DTA) studies

Simultaneous TGA and DTA studies of the composite cation-exchange materials (PANI-ZTP, PPy-ZTP and PANI-ZWIP) in original form were carried out by an automatic thermo balance on heating the material from 10°C to 1000°C at a constant rate (10°C per minute) in the air atmosphere (air flow rate of 400 ml min⁻¹).

2.3 Results and Discussion

2.3.1 Synthesis of ‘organic-inorganic’ nanocomposite cation-exchangers

2.3.1.1 Preparation of polyaniline and polypyrrole zirconium titanium phosphate nanocomposite cation-exchanger

The inorganic material zirconium titanium phosphate is a mixed material of the class of tetravalent bimetallic acid salts containing two cation and an anion with improved ion-exchange properties and selectivity as compared to single salts. Literature survey shows that extensive work has been carried out on zirconium and titanium phosphates and their oxides [34]. The ion exchange behavior of crystalline
ZTP has already been studied [35-42], but its hybrid composites are not yet reported. So, effort has been done to synthesize ‘organic-inorganic’ composite using this advanced class of inorganic ion exchanger, by incorporation of polyaniline and polypyrrole into the inorganic matrices of zirconium titanium phosphate (ZTP) respectively, which provided extraordinary Na$^+$ exchange capacity to the synthesized composite material (PANI-ZTP - 4.52 meq g$^{-1}$ and PPy-ZTP - 3.68 meq g$^{-1}$) as compare to inorganic ion-exchanger ZTP (3.36 meq dry g$^{-1}$) as given in Table 2.1 and 2.2.

Polyaniline can be easily synthesized either chemically or electrochemically from acidic aqueous solution. In this study, polyaniline gel was prepared by oxidative coupling using (NH$_4$)$_2$S$_2$O$_8$ in acidic aqueous medium as given below [43]:

![Polyaniline synthesis diagram]

The binding of polymer into the inorganic matrix can be explained as:

![Polyaniline binding diagram]

Pyrrole is one of the most easily oxidized monomer and hence a variety of oxidizing agents are available for preparing polypyrrole. Commonly used oxidants for pyrrole polymerization are oxidative transition metal ions. In this study, ferric salts are used as oxidizing agents for the synthesis of highly conducting polymer PPy, scheme for which is given below:
Among the various samples prepared, sample **PA-7** (Table 2.1) of PANI-ZTP and **PP-9** (Table 2.2) of PPy-ZTP possessed best Na\(^+\) ion-exchange capacity, thus selected for carrying out further studies.

### 2.3.1.2 Preparation of polyaniline zirconium tungstoiodophosphate (PANI-ZWIP)

Various samples of PANI-ZWIP composite cation exchange material was developed by incorporation of polyaniline into inorganic matrices of zirconium tungstoiodophosphate (ZWIP) using same mechanism as mention above for polyaniline composite. On the basis of better Na\(^+\) ion-exchange capacity (2.86 meq dry g\(^{-1}\)) as compared to inorganic precipitate zirconium tungstoiodophosphate (2.20 meq dry g\(^{-1}\)), sample **PW-6** was selected for detailed studies (Table 2.3).
Table 2.1
Conditions of preparation and the ion-exchange capacity of polyaniline zirconium titanium phosphate (PANI-ZTP)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mixing volume ratio (v/v) of inorganic TiCl₄ in H₂SO₄ ZrOCl₂ in H₂SO₄ Na₂HPO₄ in DMW</th>
<th>Mixing volume ratio (v/v) of Organic 0.1M Aniline S₂O₈ in 1M HCl (NH₄)₂S₂O₈ in 1M HCl</th>
<th>Appearance of the sample</th>
<th>I.E.C. (meq/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA-1</td>
<td>1(1M)</td>
<td>1(1M)</td>
<td>1(2M)</td>
<td>1</td>
</tr>
<tr>
<td>PA-2</td>
<td>1(0.1M)</td>
<td>1(4M)</td>
<td>2(1M)</td>
<td>2</td>
</tr>
<tr>
<td>PA-3</td>
<td>1(0.1M)</td>
<td>1(2M)</td>
<td>2(0.2M)</td>
<td>1</td>
</tr>
<tr>
<td>PA-4</td>
<td>1(1M)</td>
<td>1(1M)</td>
<td>2(1M)</td>
<td>1</td>
</tr>
<tr>
<td>PA-5</td>
<td>1(0.2M)</td>
<td>1(0.1M)</td>
<td>2(0.2M)</td>
<td>1</td>
</tr>
<tr>
<td>PA-6</td>
<td>1(0.1M)</td>
<td>1(0.1M)</td>
<td>2(0.2M)</td>
<td>1</td>
</tr>
<tr>
<td>PA-7</td>
<td>1(0.2M)</td>
<td>1(0.1M)</td>
<td>2(0.2M)</td>
<td>1</td>
</tr>
<tr>
<td>PA-8</td>
<td>1(0.2M)</td>
<td>1(0.1M)</td>
<td>2(0.2M)</td>
<td>0.25</td>
</tr>
<tr>
<td>PA-9</td>
<td>1(0.1M)</td>
<td>1(0.1M)</td>
<td>2(0.2M)</td>
<td>1</td>
</tr>
<tr>
<td>PA-10</td>
<td>1(0.2M)</td>
<td>1(0.1M)</td>
<td>2(0.2M)</td>
<td>-</td>
</tr>
<tr>
<td>PA-11</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
</tbody>
</table>
Table 2.2 Conditions of preparation and the ion-exchange capacity of polypyrrole zirconium titanium phosphate (PPy-ZTP)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mixing volume ratio (v/v) of inorganic</th>
<th>Mixing volume ratio (v/v) of organic</th>
<th>Appearance of the sample</th>
<th>I.E.C. (meq/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-1</td>
<td>1(1M) 1(1M) 1(2M)</td>
<td>0.5 1</td>
<td>Grey</td>
<td>1.02</td>
</tr>
<tr>
<td>PP-2</td>
<td>1(0.2M) 1(0.1M) 2(0.2M)</td>
<td>- -</td>
<td>White</td>
<td>3.36</td>
</tr>
<tr>
<td>PP-3</td>
<td>1(0.1M) 2(2M) 1(0.2M)</td>
<td>20 1</td>
<td>Black</td>
<td>2.15</td>
</tr>
<tr>
<td>PP-4</td>
<td>- -</td>
<td>33 2</td>
<td>Black</td>
<td>0.72</td>
</tr>
<tr>
<td>PP-5</td>
<td>1(1M) 1(1M) 1(0.2M)</td>
<td>33 1</td>
<td>Black</td>
<td>1.28</td>
</tr>
<tr>
<td>PP-6</td>
<td>1(1M) 1(2M) 2(0.2M)</td>
<td>33 1</td>
<td>Black</td>
<td>2.5</td>
</tr>
<tr>
<td>PP-7</td>
<td>1(0.2M) 1(0.1M) 2(0.2M)</td>
<td>33 2</td>
<td>Shiny Black</td>
<td>3.1</td>
</tr>
<tr>
<td>PP-8</td>
<td>1(0.2M) 1(0.1M) 2(0.2M)</td>
<td>33 2</td>
<td>Shiny Black</td>
<td>3.34</td>
</tr>
<tr>
<td>PP-9</td>
<td>1(0.2M) 1(0.1M) 2(0.2M)</td>
<td>33 2</td>
<td>Blackish purple</td>
<td>3.68</td>
</tr>
</tbody>
</table>
Table 2.3
Conditions of preparation and the ion-exchange capacity of polyaniline zirconium tungstoadiphosphate phosphate (PANI-ZWIP)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mixing volume ratio (v/v) of inorganic</th>
<th>Mixing volume ratio (v/v) of organic</th>
<th>Appearance of the sample</th>
<th>L.E.C. (meq/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1M ZrOCl₂ in H₂SO₄</td>
<td>0.5M NaHWO₄ in DMW</td>
<td>0.5M KIO₃ in DMW</td>
<td>1M H₃PO₄ in DMW</td>
</tr>
<tr>
<td>PW-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>PW-2</td>
<td>2</td>
<td>.2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>PW-3</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>PW-4</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>PW-5</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PW-6</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>PW-7</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>PW-8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

2.3.2 Chemical stability
The chemical stability depends on the structure of ion exchanger, the degree of cross-linking in the matrix and on the nature and number of the fixed ionic groups. The solubility experiment of PANI-ZTP composite shows that the material was resistant to 8M H₂SO₄, 6.5M HNO₃ and 6M HCl, only slight decomposition of phosphate group was observed. Similarly, PPy-ZTP and PANI-ZWIP were fairly stable in different chemicals. The composite PPy-ZTP was resistant to 2M H₂SO₄, 2.5M HNO₃, 2M HCl. PANI-ZWIP was resistant to 2M H₂SO₄, 2.5M HNO₃ and 3M HCl. The results of the extent of dissolution of the above said cation exchanger composites are summed up in Table 2.4.

It is apparent from the results that the synthesized composite cation exchangers are quite stable in mineral acids and organic solvents. Chemical dissolution in alkaline media and DMW is almost negligible. The chemical stability may be due to the presence of binding polymer, which can prevent the dissolution of heteropolyacids sols or leaching of any constituent element into the solution.

### 2.3.3 Thermal stability

The synthesized composite materials were found to possess higher thermal stability. On heating at different temperatures for 1h, the mass and physical appearance of the dried sample materials (PA-7, PP-9 and PW-6) were changed as the temperature increased as shown in Table 2.5. The synthesized composite materials are found to be stable up to 150°C with respect to the ion-exchange capacity and appearance.

The composite PANI-ZTP (PA-7) maintained about 56% whereas composite PPy-ZTP (PP-9) and PANI-ZWIP (PW-6) retained about 76% and 62% of the initial mass by heating up to 600 °C. The results support the TGA studies. It can be concluded from the result given in Table 2.5 that PPy-ZTP is thermally more stable followed by PANI-ZWIP and PANI-ZTP.
Table 2.4
Chemical stability of PANI-ZTP, PPy-ZTP and PANI-ZWIP in various solvent systems

<table>
<thead>
<tr>
<th>Solvent used</th>
<th>PANI-ZTP Amount dissolved (mg/20 ml)</th>
<th>PPy-ZTP</th>
<th>PANI-ZWIP Amount dissolved (mg/20 ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr (IV)</td>
<td>Ti (IV)</td>
<td>P (III)</td>
<td>Zr (IV)</td>
</tr>
<tr>
<td>DMW</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2M HCl</td>
<td>0.08</td>
<td>0.05</td>
<td>0.40</td>
</tr>
<tr>
<td>3M HCl</td>
<td>0.20</td>
<td>0.14</td>
<td>0.98</td>
</tr>
<tr>
<td>6M HCl</td>
<td>0.57</td>
<td>0.32</td>
<td>1.69</td>
</tr>
<tr>
<td>1.5 M HNO₃</td>
<td>0.12</td>
<td>0.16</td>
<td>0.46</td>
</tr>
<tr>
<td>2.5 M HNO₃</td>
<td>0.22</td>
<td>0.19</td>
<td>0.47</td>
</tr>
<tr>
<td>6.5M HNO₃</td>
<td>0.86</td>
<td>0.73</td>
<td>1.78</td>
</tr>
<tr>
<td>2M H₂SO₄</td>
<td>0.20</td>
<td>0.12</td>
<td>0.58</td>
</tr>
<tr>
<td>4M H₂SO₄</td>
<td>0.33</td>
<td>0.19</td>
<td>1.12</td>
</tr>
<tr>
<td>8M H₂SO₄</td>
<td>1.02</td>
<td>0.74</td>
<td>2.01</td>
</tr>
<tr>
<td>3 M HClO₄</td>
<td>0.40</td>
<td>0.74</td>
<td>0.42</td>
</tr>
<tr>
<td>1M NaOH</td>
<td>0.48</td>
<td>0.36</td>
<td>0.76</td>
</tr>
<tr>
<td>10% Acetone</td>
<td>0.00</td>
<td>0.00</td>
<td>0.11</td>
</tr>
<tr>
<td>1M CH₃COOH</td>
<td>0.00</td>
<td>0.00</td>
<td>0.16</td>
</tr>
<tr>
<td>10% Dimethyl sulphoxide</td>
<td>0.02</td>
<td>0.00</td>
<td>0.31</td>
</tr>
</tbody>
</table>
Table 2.5
Thermal stability of PANI-ZTP, PPy-ZTP and PANI-ZWIP cation-exchanger after heating to various temperatures for one hour

<table>
<thead>
<tr>
<th>Heating Temperature (°C)</th>
<th>PANI-ZTP</th>
<th>PPy-ZTP</th>
<th>PANI-ZWIP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Appearance (color)</td>
<td>% Weight loss</td>
<td>Appearance (color)</td>
</tr>
<tr>
<td>50</td>
<td>Black</td>
<td>-</td>
<td>Black</td>
</tr>
<tr>
<td>100</td>
<td>Black</td>
<td>1.65</td>
<td>Black</td>
</tr>
<tr>
<td>150</td>
<td>Black</td>
<td>2.8</td>
<td>Black</td>
</tr>
<tr>
<td>200</td>
<td>Black</td>
<td>5.4</td>
<td>Black</td>
</tr>
<tr>
<td>250</td>
<td>Grey</td>
<td>10</td>
<td>Grey</td>
</tr>
<tr>
<td>300</td>
<td>Grey</td>
<td>17.4</td>
<td>Grey</td>
</tr>
<tr>
<td>400</td>
<td>Grey</td>
<td>26.12</td>
<td>Grey</td>
</tr>
<tr>
<td>500</td>
<td>Grey</td>
<td>30.2</td>
<td>Grey</td>
</tr>
<tr>
<td>600</td>
<td>Buff color</td>
<td>44</td>
<td>Buff color</td>
</tr>
<tr>
<td>650</td>
<td>Silvery white</td>
<td>50</td>
<td>Dirty white</td>
</tr>
<tr>
<td>700</td>
<td>Dirty White</td>
<td>60</td>
<td>White</td>
</tr>
</tbody>
</table>

2.3.4 Chemical composition
By performing chemical composition studies, the molar ratio of different elements of respective composites were noted which can suggest the tentative formula of the prepared composite materials. For PANI-ZTP nanocomposite material, the molar ratio of Zr, Ti, P, C, H, O and N was found to be 1:1.12:1.88:6.53:17.35:17.47:1, thus the tentative formula is:

\[ [(\text{ZrO}_2) (\text{TiO}_2)(\text{H}_3\text{PO}_4)_2 (-\text{C}_6\text{H}_6\text{NH}-)] \cdot n\text{H}_2\text{O} \]

For PPy-ZTP nanocomposite material, the molar ratio of Zr, Ti, P, C, H, O and N was noted to be 1:1.34:2.34:11.77:25.36:15.21:2.73, thus the suggested tentative formula:

\[ [(\text{ZrO}_2) (\text{TiO}_2)(\text{H}_3\text{PO}_4)_2 (-\text{C}_6\text{H}_6\text{NH}-)_3] \cdot n\text{H}_2\text{O} \]

The molar ratio of Zr, W, I, P, C, H, O and N in the PANI-ZWIP composite cation exchanger material was estimated to be 2.02:1.03:1.06:2:6.2:19.34:21.27:1.05 which suggest the following tentative formula of the material:

\[ [(\text{ZrO})_2(\text{WO}_3)(\text{IO}_3)(\text{H}_3\text{PO}_4)_2 (-\text{C}_6\text{H}_6\text{NH}-)] \cdot n\text{H}_2\text{O}. \]

Assuming that only the external water molecules are lost, the percentage weight loss of mass represented by TGA curve must be due to the loss of n\text{H}_2\text{O}. From the above structure the value of ‘n’ the external water molecules can be calculated using Alberti’s equation [44]:

\[
\% \text{ Weight loss} = \frac{18n}{M + 18n} \times 100
\]

where X is the percent weight loss (~11%) the exchanger and (M +18n) is the molecular weight of the material. From TGA curve, ~11% weight loss of mass for PANI-ZTP, ~12% for PPy-ZTP and ~6% weight loss for PANI-ZWIP has been observed by heating up to 250ºC. The calculations give ~ 4 external water molecule (n) for PANI-ZTP, ~5 for PPy-ZTP and ~3 for PANI-ZWIP per molecule of the cation-exchangers.

2.3.5 TEM (Transmission Electron Microscopy) studies
TEM micrographs shows that the particle size of synthesized composite materials (PANI-ZTP, PPy-ZTP and PANI-ZWIP) lies in nanorange (Fig. 2.1). They are observed to be in the range of 25-52 nm for PANI-ZTP, 31-77 nm for PPy-ZTP and 20-28 nm for PANI-ZWIP, which proves that all the proposed cation exchangers are nano-composites.

Fig.2.1 Transmission electron microphotographs (TEM) of (a) PANI-ZTP (b) PPy-ZTP and (c) PANI-ZWIP showing different particle size.

2.3.6 SEM (Scanning Electron Microscopy) studies
SEM study was performed to examine the difference in surface morphology between the parent materials and their composites. The SEM images of organic polymers PANI and PPy, inorganic precipitate ZTP and ZWIP and composites PANI-ZTP, PPy-ZTP and PANI-ZWIP at different magnification are represented in Fig. 2.2, 2.3 and 2.4. The SEM image shows the difference in the surface morphology after incorporation of the organic polymer into the inorganic precipitate, which indicates the binding of the inorganic ion exchange material to the organic polymer, thus the formation of a composite material was observed.

2.3.7 X-ray studies

The X-ray diffraction studies of the composite cation-exchangers (as prepared) was carried out using the range of 5° ≤ 2θ ≤ 80° at 30KV. Fig. 2.5 shows the typical XRD pattern of PANI-ZTP, PPy-ZTP and PANI-ZWIP nanocomposites at room temperature. The XRD pattern exhibited small sharp peaks in the spectrum that suggest semi-crystalline nature of the nanocomposite materials.

2.3.8 FTIR studies

The FTIR spectra of the composite cation-exchangers are represented in Fig 2.6. In the spectrum of PANI-ZTP (Fig. 2.6) a strong broad band around 3500 cm⁻¹ was found which could be attributed to –OH stretching frequency. Peaks at 1620 cm⁻¹ was observed, may be due to interstitial water present in the composite material. The assemblies of peaks at 950-1100 cm⁻¹ are due to the presence of ionic phosphate group [45] and peaks at 800 cm⁻¹ attributed to M-O bonding. The additional band at about 1400 cm⁻¹ in PANI-ZTP can be ascribed to stretching vibration of C–N [46] indicating the presence of aniline in good amount and a band around 3000 cm⁻¹ may be related to the stretching of NH bonds of benzenic and quinonic rings [47] present in the material [Fig. 2.6A(c)]. Further, these vibration frequencies in Fig. 2.6A(c) resemble the stretching vibration frequencies for C–N and NH bonds found in polyaniline [Fig. 2.6A(a)]. The FTIR spectrum of PPy(ZTP) [Fig. 2.6.B(c)] 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.
Fig. 2.2 Scanning electron microphotographs (SEM) of chemically prepared (a) PANI (b) ZTP and (c) PANI-ZTP composite system.

Fig. 2.3 Scanning electron microphotographs (SEM) of chemically prepared (a) PPy (b) ZTP and (c) PPy-ZTP composite system.
Fig. 2.4 Scanning electron microphotographs (SEM) of chemically prepared (a) PANI (b) ZWIP and (c) PANI-ZWIP composite system.
Fig.2.5 Powder X-ray diffraction pattern of (a) PANI-ZTP (b)PPy-ZTP and (c)PANI-ZWIP nano-composite (as prepared)
Fig. 2.6 FTIR spectra of as prepared
(A) (a) polyaniline (b) ZTP and (c) PANI-ZTP
(B) (a) polypyrrole (b) ZTP and (c) PPy-ZTP
(C) (a) polyaniline (b) ZWIP and (c) PANI-ZWIP
A sharp peak at 1700 cm\(^{-1}\) can be ascribed to the H–O–H bending band. The assembly of peaks in the region of 950-1100 cm\(^{-1}\) is due to the presence of an ionic phosphate group 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 [46].

In the spectrum of PANI-ZWIP [Fig. 2.6 C(e)] the broad band in the region 3600-3000 cm\(^{-1}\) assigned to –OH stretching frequency. Another strong and sharp peak with a maximum of 1635 cm\(^{-1}\) may be due to H–O–H bonding. The assemblies of peaks at 950-1100 cm\(^{-1}\) are due to ionic phosphate group and peaks at 830–500 cm\(^{-1}\) indicating the presence of iodate and metal oxide. The additional band at about 1400 cm\(^{-1}\) can be ascribed to stretching vibration of C–N indicating the presence of organic part aniline in good amount.

The characteristic stretching frequencies as shown in FTIR spectra of the synthesized cation exchanger (PANI-ZTP, PPy-ZTP and PANI-ZWIP) are in close resemblance with the spectra of inorganic precipitate and organic polymer indicating the binding of organic polymer in inorganic matrix confirming the formation of ‘organic-inorganic’ nanocomposite.

2.3.9 TGA-DTA (Thermogravimetric Analysis-Differential Thermal Analysis) studies

The TGA curve of the nanocomposites shows that upto 250°C only 11% weight loss was observed in PANI-ZTP [Fig. 2.7(a)], 12% in PPy-ZTP [Fig.2.7 (b)] and 6% in PANI-ZWIP [Fig.2.7(c)] which may be due to the removal of external H\(_2\)O molecules present at the surface of the composite materials [48]. A steep weight loss was observed between 250°C to 350°C in the nanocomposites are due to conversion of inorganic phosphate into pyrophosphate. Further slow weight loss of mass, about 6% of PANI-ZTP and 8% of PPy-ZTP was observed in between 300-750°C but in PANI-ZWIP major weight loss of about 33% takes place in between 300-700°C. This may be due to the decomposition of organic material. A smooth horizontal line in the TGA curve of respective material represents the complete formation of the oxide form of the nanocomposites. A broad peak in the DTA curves of respective nanocomposites shows that the reaction is exothermic during the change of phase of material.
Fig. 2.7 Simultaneous TGA-DTA curves of (a) PANI-ZTP (b) PPy-ZTP (c) PANI-ZWIP (as prepared)

References
1. C.B. Amphlet, Inorganic ion exchanger; Elsevier Amsterdam, 1964.


