Titanium-embedded nanocomposite material stimulates ion-exchange characteristics to deal with pollutants in aquatic environment

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Abstract

Nano-sized composite ion-exchanger can be applied as an electrochemically switchable ion-exchanger for waste water treatment, especially pollutants removal process. Advanced polyaniline/Ti(IV) iodomolybdate nanocomposite ion-exchanger have been synthesized by in-situ chemical oxidation polymerization shows better ion-exchange capacity than individual inorganic counterpart. The physico-chemical characterization was done by FT-IR, XRD, simultaneous TGA-DTA, SEM, HR-TEM and electrochemical impedance studies. According to impedance/dielectrical study, it has high resistivity in the low frequency region. The distribution studies and binary separation revealed that the ion-exchange material is highly selective for Pb\(^{2+}\), which is a most important environmental pollutant. Thus, PANI/TIM nanocomposite ion-exchanger can be used for Pb(II) ion-selective membrane for the treatment of aquatic pollutants in future.

Introduction

Environmental exposure to heavy metals has risen typically in the past decades, however, as a result of an exponential increase in the use of heavy metals in industrial processes and its products. The hazardous heavy metal ions that possess potential dangers to human lives from industrial effluents are present even in small concentrations. Metal toxicity studies have shown that the heavy metals which are present in the aquatic system can directly influence human functions by impairing mental and neurological functions. Removal of toxic heavy metals from the polluted aquatic system has special importance from the eco-toxicological point of view. Because of their significant impact on human health nanocomposite materials represent a rapidly growing research field.

The natural leading polymer polyaniline (PANI) is one of the foremost conducting polymers. It have been broadly utilized as a part of the different fields such as sensors, batteries, catalysis, supercapacitors, electronic devices and anticorrosion coatings due to its relatively low cost, easily synthesized, high conductivity, non-toxic, excellent chemical and environmental stability [1–4]. In the present study, we utilized the conducting polymer PANI which is synthesized and reported earlier [5].

Recently, conducting polymeric-inorganic composites has been considered a new class of materials for many optoelectronic and magnetic applications because many bulk properties can be improved after the combination of pure guest conducting polymers and host inorganic nanoparticles [6–10]. Numerous synthetic approaches have been performed for the preparation of organic-inorganic nanocomposites by using in-situ chemical polymerization, sol-gel technique, emulsion technology, unsymmetrical current wave methods, etc. [11, 12].

The introduction of inorganic material into PANI may lead to charge transfers, electronic interactions, morphological modifications, or a combination of these effects between the constituents of the polymeric-inorganic nanocomposite [13, 14]. Such interactions among the constituents of the polymeric-inorganic nanocomposite not only improve the existing properties but may also introduce interesting
novel features [15]. The polymeric-inorganic composite material can be used to modify organic polymeric parts or to modify inorganic parts that exhibit very different properties from their original components. The inorganic ion-exchange materials have more stable to high temperature and radiation fields than the organic material [16]. To obtain a combination of these advantages associated with polymeric and inorganic materials, attempts have been made to develop a polymeric-inorganic composite material [17].

The polymeric-inorganic composite material must be an interesting material, as it should possess the mechanical stability and selectivity for some important heavy metal ions [18–21]. It was therefore considered to synthesize transition metal decorated conducting polymeric-inorganic nanocomposite materials with a good ion-exchange capacity, high stability, reproducibility and selectivity for heavy metal ions, indicating its useful environmental application including polluted aquatic treatment [22].

In the present study, a new venture made to synthesize the nanocomposite with suitable molar proportions of reactants, study their physic-chemical, highlight the importance of ion-exchange studies, and interpreted their conducting behavior and also compared with individual counterparts.

Experimental Methods

1.2.1 Reagents and Instruments

The main reagents used for the synthesis of the PANI/TIM nanocomposite ion-exchanger were polyaniline, potassium perdisulfate (KPS), Ti(IV) chloride, ammonium molybdate dihydrate, and potassium iodate purchased from Merck (E-Merck Ltd, India). All the chemicals and reagents used were of analytical grade and were used without further purification.

FT-IR spectrum of the sample in the original and dried form was taken by KBr disc method at room temperature performed on Thermo Nicolet, Avatar 370 Fourier Transform Infra-Red Spectrometer. The powder X-ray diffraction technique has been employed on the present sample by a Bruker AXS D8 Advance Twin Twin Model using monochromatized Cu-\(K_{\alpha}\) (1.5406Å). JEOL/JSM-6390 LV Model was used for SEM at various magnifications. The HR-TEM images were obtained from a JEOL/JEM-2100 Model transmission electron microscope, using an accelerated voltage of 200KV with the magnification of 2000X–150000X. Simultaneous TGA-DTA studies were carried out by an automatic thermobalance on heating the material from 40 °C to 750 °C at a constant rate (10 °C min\(^{-1}\)) in the nitrogen gas atmosphere with Perkin Elmer STA 6000 instrument. AC electrical and dielectric studies were performed on the pressed samples by using an IM6 ZAHNER electrochemical impedance analyzer.

1.2.2 Preparation of Ti (IV) Iodomolybdate (TIM)

Ti(IV) chloride solution (0.05M) is added to the mixture of potassium iodate (0.05M) and ammonium molybdate dihydrate (0.1M) in the mixing volume ratio of 1:1:2. During the addition, the pH was maintained at 0.9. The mixing solution is heated to 60°C in a water bath for 2 hrs and then stirred
continuously for 1 hr by using a magnetic stirrer. The resultant solution is allowed to stand for overnight, then filtered and washed with water, and dried at room temperature. Finally, the white precipitate of TIM was obtained.

### 1.2.3 Preparation of PANI/Ti(IV) iodomolybdate (PANI/TIM) nanocomposite ion-exchanger

PANI/Ti(IV) iodomolybdate nanocomposite ion-exchanger was prepared by the sol-gel mixing of polyaniline into the Ti(IV) iodomolybdate inorganic ion-exchanger. Polyaniline was prepared by mixing 0.1 M aniline (prepared in 1 M HCl) and 0.1 M potassium persulfate at a 1:1 volume ratio and stirred for 1 hr with the help of the magnetic stirrer. The green colour precipitate of polyaniline was obtained. The dark green colour precipitate of polyaniline was added to the inorganic precipitate of TIM with constant stirring. The resultant product was kept in the refrigerator for 24 hrs, then filtered and washed with methanol and acetone and dried in an oven at 50 °C.

The as-synthesized PANI/TIM ion-exchanger were splintered into small granules which was dark bluish green in colour and it was converted into H\(^+\) form by treating with 0.1 M HNO\(_3\) for 24 hrs with occasional shaking and washed numerous times with de-ionized water in order to take off excess of acid and finally dried at 50°C.

### 1.2.4 Characterization

The various morphological features of the newly synthesized PANI/TIM nanocomposite ion-exchanger were characterized by FTIR, XRD, simultaneous TGA-DTA, SEM and HR-TEM studies and also physical parameters like water content and swelling nature were predicted.

### 1.3 AC Conductivity/Dielectric Studies

The AC electrical conductivity studies were performed on solid pellets form of PANI/TIM nanocomposite ion-exchanger by using IM6 ZAHNER electrochemical impedance analyzer and AC electrical conductivity values can be calculated using the following equation as given below.

\[
\sigma_{a.c} = 2\pi f \varepsilon_0 \varepsilon' \tan\delta \quad \text{Eq. (1)}
\]

Where \(\sigma_{a.c}\) is AC electrical conductivity; \(\varepsilon_0\) is permittivity in free space (8.85x10\(^{-12}\) f/m); \(\varepsilon'\) is dielectric constant; \(f\) is the frequency (Hz); \(\tan\delta\) is dielectric loss factor.

The value of dielectric constant \(\varepsilon'\) is calculated by using following the formula.

\[
\varepsilon' = \frac{C_p x t}{\varepsilon_0 A} \quad \text{Eq. (2)}
\]
Where, $C_p$ is the capacitance of the specimen (F); $t$ is thickness of pellet; $A$ is area of cross section of the flat surface of the pellet.

The dielectric loss factor (tan $\delta$) which is expressed is the ratio of the imaginary part of the dielectric constant to the real part calculated as below.

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad \text{Eq.(3)}$$

1.5 Ion-Exchange Properties and Their Effects

1.5.1 Ion-Exchange Capacity (IEC)

For the determination of ion-exchange capacity, 1.0 g of the dry cation-exchanger ($H^+$ form) was taken into a glass column. The bed length was approximately 1.5 cm; alkali nitrate (0.025M) solution was used to elute the $H^+$ ions completely from the cation-exchange column maintaining a very slow flow rate of $\sim$ 0.5 mL min$^{-1}$. The liberated $H^+$ ion was determined titrimetrically against 0.1M NaOH solution for the determination of IEC by using phenolphthalein as an indicator.

1.5.2 Effect of Eluent Concentration on IEC

The effect of eluent concentration was studied to find out the maximum volume of eluent required for complete elution of $H^+$ ion from the glass column containing 1.0 g of $H^+$ form of nanocomposite ion-exchanger. 1.0 M solution of alkali nitrate was used as an eluent. The effluent was collected in 10 mL fractions and titrated against the standard alkali solution by using phenolphthalein as an indicator.

1.5.3 Elution Behavior

To find out the optimum concentration of eluent required for the complete elution of alkali metal ion, 1.0 g of the nanocomposite ion-exchanger in its $H^+$ form was eluted with alkali metal nitrate solution of various concentrations in different 20 mL fractions at a flow rate of $\sim$ 0.5 mL/min and each fraction of 20 mL effluent was titrated against a standard alkali NaOH solution for the $H^+$ ions eluted out.

1.5.4 Thermal Effect on IEC

Thermal effect on the ion-exchange capacity was studied at different temperatures with the help of a muffle furnace. $H^+$ form of the composite ion-exchanger (1 g) was heated for 1 hr, cooled to room temperature, and then IEC of each sample was determined by column process.

1.5.5 Selectivity Studies

The distribution behavior of metal ions plays a key role in the material’s selectivity determination. The determination of metal ions (before and after equilibrium) was carried out volumetrically using EDTA as titrant. 200 mg of the dry nanocomposite ion-exchanger in the $H^+$ form were equilibrated with 20 mL of
different metal ion solutions in the required medium and kept for 24 hrs with intermittent shaking. The distribution coefficient ($K_d$) values were calculated by using the following relation.

\[
K_d = \frac{A_{metal ions in exchange phase}}{A_{metal ions in solution phase}}
\]  
\[
K_d = \frac{(I - F) / F}{V / M} (mLg^{-1})
\]

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

### 1.5.6 Quantitative Separations of Metal Ions in Synthetic Binary Mixtures

Quantitative separations of some important metal ions were attained with 1.0 g of PANI/TIM nanocomposite ion-exchanger in H$^+$ form taken in the glass column. The binary mixture of metal ions was loaded and allowed to pass at a constant flow rate of ~ 0.5 mL/min through the column until the level reached above the surface of the material and was eluted with a suitable solvent [23]. The effluent from the glass column was collected in 10 mL fractions each time at a constant flow rate of ~ 0.5 mL/min. The metal ions in the effluent were titrated using the standard solution of 0.01 M of EDTA.

### 1.5.7 Selective Separation of Metal Ions

The selective separation of ions was carried from a mixture of Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$, Fe$^{3+}$, Hg$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$ in an aqueous solution containing Pb$^{2+}$ ions in variable amounts. This was achieved by pouring the mixture onto the top of the glass column containing 1g of nanocomposite ion-exchanger (H$^+$ form) and stand for 1 hr and allowed to pass at a constant flow rate of ~ 0.5 mL/min through the column until the level reached above the surface of the material. Finally, the metal ions in the effluent were determined quantitatively by the standard solution of EDTA titration.

### Results and Discussion

The inorganic material, Ti(IV) iodomolybdate obtained as white amorphous in nature. The conditions used for the preparation have shown a considerable effect on the ion-exchange property of the as-synthesized material. To determine the optimum IEC value of Ti(IV) iodomolybdate, different TIM samples were prepared by varying the mixing volume ratio of the reactants (Table 1). Among these, the 1:1:2 mixing volume ratio (comprising Ti(IV) chloride, potassium iodate, and ammonium molybdate dihydrate) of the reactants exhibited a relatively higher IEC and this was employed for the subsequent synthesis work. This is because ammonium molybdate dihydrate is the precursor for the anionic part where the replaceable H$^+$ attaches. Increasing the anionic part has a positive result in lifting the IEC of exchangers to a certain extent. This is because as the anionic part inside the cation exchanger increases, there is also an increase in IEC.
Table 1

Synthetic conditions of inorganic ion-exchanger Ti (IV) iodomolybdate

<table>
<thead>
<tr>
<th>Ti(IV) chloride (M)</th>
<th>Potassium iodate (M)</th>
<th>Ammonium molybdate dihydrate (M)</th>
<th>Mixing volume ratio</th>
<th>pH</th>
<th>Colour</th>
<th>Ion-Exchange Capacity (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>1:1:1</td>
<td>1.00</td>
<td>White</td>
<td>1.49</td>
</tr>
<tr>
<td>0.10</td>
<td>0.05</td>
<td>0.05</td>
<td>2:1:1</td>
<td>0.95</td>
<td>Yellow</td>
<td>1.83</td>
</tr>
<tr>
<td>0.05</td>
<td>0.10</td>
<td>0.05</td>
<td>1:2:1</td>
<td>1.10</td>
<td>Pale Yellow</td>
<td>1.35</td>
</tr>
<tr>
<td>0.05</td>
<td>0.05</td>
<td>0.10</td>
<td>1:1:2</td>
<td>0.90</td>
<td>White</td>
<td>1.89</td>
</tr>
<tr>
<td>0.10</td>
<td>0.10</td>
<td>0.05</td>
<td>2:2:1</td>
<td>1.00</td>
<td>Yellow</td>
<td>1.48</td>
</tr>
<tr>
<td>0.10</td>
<td>0.05</td>
<td>0.10</td>
<td>2:1:2</td>
<td>0.10</td>
<td>White</td>
<td>1.52</td>
</tr>
<tr>
<td>0.05</td>
<td>0.10</td>
<td>0.10</td>
<td>1:2:2</td>
<td>0.95</td>
<td>White</td>
<td>1.76</td>
</tr>
</tbody>
</table>

Various samples of PANI/TIM nanocomposite ion-exchanger material have been developed by incorporation of electrically conducting polyaniline into inorganic matrices of Ti(IV) iodomolybdate and its IEC values are also listed below (Table 2). Due to better ion-exchange capacity, electrical conductivity, and thermal stability, a 1:1:1:2 mixing volume ratio comprising aniline, Ti(IV) chloride, potassium iodate, and ammonium molybdate dihydrate was selected for subsequent studies. An effort has been made to synthesize PANI/TIM nanocomposite ion-exchanger material, which provided a good electrical and ion-exchange capacity (2.82 meq/g) as compared to the inorganic counterpart TIM (1.89 meq/g) (Table 4).

Table 2

Preparation of various PANI/TIM nanocomposite ion-exchanger materials and its IEC

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Polyaniline (M)</th>
<th>Ti(IV) chloride (M)</th>
<th>Potassium iodate (M)</th>
<th>Ammonium molybdate dihydrate (M)</th>
<th>Mixing volume ratio</th>
<th>Ion-Exchange Capacity (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.025</td>
<td>0.05</td>
<td>0.05</td>
<td>0.10</td>
<td>0.5:1:1:2</td>
<td>2.63</td>
</tr>
<tr>
<td>2</td>
<td>0.050</td>
<td>0.05</td>
<td>0.05</td>
<td>0.10</td>
<td>1:1:1:2</td>
<td>2.82</td>
</tr>
<tr>
<td>3</td>
<td>0.100</td>
<td>0.05</td>
<td>0.05</td>
<td>0.10</td>
<td>2:1:1:2</td>
<td>2.69</td>
</tr>
<tr>
<td>4</td>
<td>0.150</td>
<td>0.05</td>
<td>0.05</td>
<td>0.10</td>
<td>3:1:1:2</td>
<td>2.54</td>
</tr>
<tr>
<td>5</td>
<td>0.200</td>
<td>0.05</td>
<td>0.05</td>
<td>0.10</td>
<td>4:1:1:2</td>
<td>2.37</td>
</tr>
</tbody>
</table>

FT-IR spectrum of TIM in Fig. 1 shows the peaks at 1690, 3190, and 3430 cm$^{-1}$ may be attributed to lattice water [24]. The peaks at 3710 cm$^{-1}$ in the spectra are due to the stretching and bending vibration of the $–\text{OH}$ group. A small band between 989 and 1075 cm$^{-1}$ corresponds to the metal-oxygen bonds in the molybdate ion [25]. The peak observed at the 904 cm$^{-1}$ region is due to symmetric and asymmetric...
stretching of the M–O–H bond which revealed that the presence of Mo–O–H bond in the TIM inorganic ion-exchanger [26]. In the FT-IR spectrum of PANI-TIM nanocomposite ion-exchanger (Fig. 1), the very weak characteristic peak at 3430 cm$^{-1}$ is assigned to the O–H stretching vibration of water molecules, due to the presence of moisture in the sample. A broad band around 3000 cm$^{-1}$ indicates the symmetric and asymmetric stretching vibration of the H$_2$O molecule due to the presence of moisture in the sample. Also, a broad band in the region 2420 cm$^{-1}$ was characteristic of N–H bending vibration. An assembly of bands in the region 1400–1600 cm$^{-1}$ may be ascribed to the stretching vibration frequency of C–N bonds. A peak observed at 1300 cm$^{-1}$ was attributed to stretching vibration of C–H in the benzenoid ring, and that observed at 1470 cm$^{-1}$ was attributed to C$=$N stretching vibration of the quinoid ring [27]. A band at 1560 cm$^{-1}$ indicates the C–C stretching vibration of the quinoid ring [28]. A sharp band at 800 cm$^{-1}$ shows the presence of $\rho$-substituted aromatic rings, indicating polymer formation. In addition to that, in the case of PANI/TIM nanocomposite ion-exchanger, a strong band in the region of 800 – 500 cm$^{-1}$ indicates the presence of iodate and metal oxide. The peaks at 617 cm$^{-1}$ and 650 cm$^{-1}$ are attributed to C–H out-of-plane bending vibration. Other characteristic bands associated with the individual parts of the inorganic precipitate TIM and PANI [5] were reflected with a noticeable shift in the PANI/TIM nanocomposite ion-exchange material. It gives evidence for the encapsulation TIM in the polymeric matrix of polyaniline and forms PANI-TIM nanocomposite material.

X-ray diffraction (XRD) was carried out in the Bragg Brentano configuration, on a Bruker Discover 8 diffractometer operating at 40 kV and 40 mA, with Cu-K$_{\alpha}$ radiation. Furthermore, the average crystallites size of the material was determined mathematically using the well-known Debye-Scherer equation as follows.

\[
D = \frac{K \lambda}{\beta \cos \theta} \tag{6}
\]

Where $K$ is the constant (0.96), $\lambda$ is the wavelength of the X-ray (1.54 $\times$ 10$^{-10}$), $\beta$ is the full-width half maximum (FWHM) of the peak, and $\theta$ is the diffracted angle of the X-ray.

From the XRD analysis (Fig. 2), inorganic ion-exchanger TIM has broad peaks indicating that amorphous in nature. The average crystallite size of TIM is found to be in the range of ~39 nm. From the XRD analysis, the PANI/TIM nanocomposite ion-exchanger exhibits high intensity peaks at 2$\theta$ values of 11.7 and 13.2 and a broad peak at 2$\theta$ value of 25.1 shown in Fig. 2 indicated that the nanocomposite was amorphous in nature. From these values, the calculated average particle size of PANI/TIM is found to be in the range of ~27 nm. Hence, XRD studies clearly depict that the formation of PANI/TIM nanocomposite ion-exchanger leads to decrease in size compared to the conducting polymer PANI [5] and inorganic counterpart.

As evident from Fig. 3, the thermogram of the TIM ion-exchanger proved that the 9.7% weight loss up to 115°C is due to the removal of external water molecules. The decreased weight loss (6.3%) up to 300°C, owing to the elimination of interstitial water molecules present in the sample. Furthermore, major weight
loss was predicted (7.5%) up to 560°C, which can be explained as due to the condensation of hydroxyl
groups, and the volatilization of the iodate (IO$_3^-$) group [29] present in the structure. This loss is supported
by an endothermic peak at 487 ºC. The weight becomes almost constant above 560 ºC (only 3.0%) owing
to the formation of metal oxides as a final product (73.5%). From the TGA curve of PANI/TIM
nanocomposite ion-exchanger in Fig. 4, the continuous weight loss (8%) up to 123°C may be accounted
for by the evaporation of internal water molecules as the result of condensation of –OH groups [30]. Then
the weight loss (9%) up to 325°C may be due to the removal of the dopant molecule. Further weight loss
(8%) up to 530°C may be due to the slight decomposition of the organic part of the material. Above
530°C, a sharp weight loss up to 720°C (5%) is observed, which indicates the complete conversion of the
nanocomposite material into metal oxide (70%) as final product. Finally, the concurrent curve of TGA-DTG
studies inferred that PANI/TIM nanocomposite ion-exchanger was slightly less stable than TIM but more
stable than organic counterpart PANI [5].

The scanning electron microphotographs (SEM) of TIM and PANI/TIM at different enlargements are
represented in Fig. 4. It is clear from the photographs that, there are large granules aggregates on the
PANI/Ti(IV) iodomolybdate nanonanocomposite ion-exchanger. The organic conducting polymer is tightly
binding to the inorganic precipitate, providing mechanical stability and preventing the leaching out of the
inorganic precipitate. The possible reason for the formation of the large granules aggregates is that the
TIM (Fig. 4b) acted as templates to allow PANI to be polymerized surrounding them [8]. So the surface
morphology of PANI/TIM nanocomposite ion-exchanger (Fig. 4a) became rougher. As a result of SEM
studies, the surface morphology in ×3,500 magnified image of the PANI/TIM nanocomposite ion-
exchanger exhibits the schistose structure.

Due to the short magnification of the sample in SEM micrographs, it is troublesome to notice TIM in the
nanocomposite ion-exchanger matrix; thus a felicitous way of observing TIM in PANI/TIM
nanocomposite ion-exchanger matrix was the utilization of HR-TEM. The microstructure of the PANI/TIM
nanocomposite ion-exchanger was examined by HR-TEM with selected area electron diffraction (SAED)
images at different magnifications as shown in Fig. 5. According to the HR-TEM micrographs, the TIM
nanoparticles were seen as dark spots dispersed in PANI polymer matrix. It is obvious that TIM was
uniformly coated by PANI and the nanocomposite ion-exchanger was found to be in the range of 20–33
nm and hence the above-prepared material can be considered a nanocomposite material.

To determine water content in TIM and PANI/TIM nanocomposite ion-exchanger, 1 g of freshly prepared
samples were dissolved in de-ionized water for 2 hrs and then filtered the sample and wrapped in filter
paper to remove the surface water molecule and weighed the sample carefully. The water uptake in
percentage was calculated as below.

\[
Wateruptake (\%) = \frac{W_W - W_D}{W_D} \times 100 \quad \text{Eq. (7)}
\]

Where, $W_W$ and $W_D$ are weight of sample in wet and weight of sample in dry respectively.
To predict the percentage of swelling nature of TIM and PANI/TIM nanocomposite ion-exchanger, the dried samples (1 g) was dissolved in de-ionized water for 24 hrs at room temperature. It could be filtered through previously weighed sintered glass crucible and the final mass of was calculated. The percentage of swelling nature samples were determined by using the following relation.

\[
Swelling\ nature = \left(\frac{S_{\text{Wet}} - S_{\text{Dry}}}{S_{\text{Wet}}}\right) \times 100
\]

Eq.(8)

Where, \(S_{\text{Wet}}\) and \(S_{\text{Dry}}\) are weight of sample in wet and weight of sample in dry respectively. The percentages of water content and swelling nature are represented in Table 3 was given below: Data’s from Table 3 clearly identified that PANI/TIM nanocomposite ion-exchanger have high external water content as well as swelling nature compared to TIM. The calculated percentage of water content was in good deals with TGA data. The greater percentage of swelling nature reveals that PANI/TIM nanocomposite ion-exchanger was a suitable material column packing for the ion-exchange studies compared to TIM.

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight of the sample (g)</th>
<th>Water uptake (%)</th>
<th>Swelling nature (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIM</td>
<td>1.0</td>
<td>0.0022</td>
<td>0.0056</td>
</tr>
<tr>
<td>PANI/TIM</td>
<td>1.0</td>
<td>0.1036</td>
<td>0.3574</td>
</tr>
</tbody>
</table>

According to above data’s (including selective molar ratio for further studies) of TIM and PANI/TIM, a feasible reluctant mechanism for the formation of PANI/Ti(IV) iodomolybdate composite ion-exchanger (Scheme 1) may be proposed as follows.

The prepared nanocomposite ion-exchange material shows reasonably good chemical stability in HCl, \(H_2SO_4\), acetic acid and acetone, whereas it is partially soluble in DMSO, ammonia and \(HNO_3\). The chemical stability of PANI/TIM nanocomposite ion-exchanger may be due to the presence of metal-metal strong bonding in the non-aqueous medium.

The comparative AC electrical conductivity study was an easily automatized technique to investigate the electrical properties of a great variety of materials. The conductivity values for PANI/TIM nanocomposite ion-exchanger (\(H^+\) form) lies between the semiconductor region \([31]\) which exhibited the nanocomposite ion-exchanger has semiconductor behavior. The conductivity of the polymer matrix also depends on the dopant nature and the concentration of inorganic materials, which have a major role in the conductivity of the nanocomposite \([32]\).

The charge carriers i.e., polaron and bipolaron present in the nanocomposite ion-exchanger are responsible for the enhanced electrical conductivity. The magnitude of the conductivity was determined by the number of charge carriers available for conduction and their mobility rate. The observed high AC electrical conductivity value of the PANI/TIM nanocomposite ion-exchanger (\(H^+\) form) compared to TIM,
also proposes a large number of charge diffusion within the semicrystalline region and this indicates the presence of isolated polarons and bipolarons in this region. Thus, we can conclude that H⁺ form of PANI/TIM nanocomposite ion-exchanger material shows enhanced electrical conductivity due to the better transport of charge carries within and between the PANI component of the PANI/TIM nanocomposite ion-exchanger material and inorganic precipitate TIM.

Impedance plots for TIM and PANI/TIM nanocomposite ion-exchanger (H⁺ form) samples were demonstrated in Fig. 6. The electrical behavior of PANI/TIM nanocomposite ion-exchanger is exhibited by the formation of semicircular arcs in Nyquist plot [33]. The Nyquist plot of TIM has only the semicircular portion and has high charge transfer resistance. But the Nyquist plot of PANI/TIM nanocomposite ion-exchanger (H⁺ form) consisted of two different portions. One is a semicircle in the high-frequency region corresponds to the charge transfer resistance and another one is an oblique line in the low-frequency region denotes to the diffusion limited reaction takes place. From the nature of arcs, a significant difference was noticed. The decrease in charge transfer resistance obtained in H⁺ form of PANI/TIM nanocomposite ion-exchanger when compared to inorganic part TIM, leads to electron transfer in PANI/TIM nanocomposite ion-exchanger was very fast i.e. low charge transfer resistance proved a significant enhancement in the impedance or conductance supported that PANI/TIM nanocomposite ion-exchanger has higher conductivity nature than TIM.

Figure 7 shows the variation of impedance as a function of frequency [Fig. 7(a)] and the variation of phase angle as a function of frequency (Fig. 7(b)) of PANI/TIM nanocomposite ion-exchanger (H⁺ form). It has been found that impedance decreases with the increase in frequency. This is due to increase in conductivity H⁺ form of PANI/TIM nanocomposite ion-exchanger as a function of frequency. It can also be seen that, at lower frequency region the impedance value has strong frequency dependence behavior and strongly frequency independent behavior in the higher frequency region. The effectiveness of resistive grain boundaries of PANI/TIM nanocomposite ion-exchanger (H⁺ form) material in the low frequency region leads to high resistivity of PANI/TIM nanocomposite ion-exchanger (H⁺ form) material but the resistivity sharply decreases in the higher frequency region. Figure 7(b) also reveals that phase of impedance increases with increasing frequency. Initially in the low frequency region, the phase of impedance value decreases. The phase value of impedance obtained maximum value when the frequency region higher. In both Fig. 7(a) and (b), PANI/TIM is quite better than TIM.

In the case of real and imaginary part of the dielectric constant of PANI/TIM nanocomposite ion-exchanger exhibited a steep decrease at lower frequency and become almost constant at higher frequency shown in Fig. 8 (a) and (b). The decrease in the dielectric constant with increasing frequency is due to by dielectric relaxation i.e., electron hopping mechanism enhanced with a frequency that gives lower dielectric constant. Initially, high dielectric constant value was observed at low frequency in the PANI/TIM nanocomposite ion-exchanger (H⁺ form), which was due to the small conductivity of the grain boundary. The dielectric constant achieved high value by the interfacial/space charge polarization into the heterogeneous nature i.e., porosity and grain structure of PANI/TIM nanocomposite ion-exchanger (H⁺
The magnitude of polarization effect decreases with increasing frequency and then reaches a constant value due to the fact that beyond a particular frequency of applied external field, the flow of electrons between metal ions present in TIM and PANI that cannot follow the changing field. AC electrical conductivity of PANI/TIM nanocomposite ion-exchanger (H⁺ form) slowly increases with an increase in frequency in lower region and there is an abrupt increase of AC conductivity in the higher frequency region due to electron tunneling and reaches maximum (Fig. 8 (c)) which demonstrated to the enhanced electron hopping phenomenon [34].

The AC impedance as well as conductivity data of PANI/TIM nanocomposite ion-exchanger (H⁺ form) at various frequencies was also represented in Table 4. The conductivity value of the PANI/TIM nanocomposite ion-exchanger (7.98 x 10⁻⁵ Scm⁻¹) was quite better compared to TIM inorganic ion-exchanger (6.74 x 10⁻⁶ Scm⁻¹) when the incorporation of TIM into the matrix of conducting organic polymer i.e. PANI/TIM nanocomposite ion-exchanger is a semiconducting material.
Table 4
The AC impedance and conductivity data of (H⁺ form) PANI/TIM nanocomposite ion-exchanger at various frequencies

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>Capacitance C (F)</th>
<th>Impedance</th>
<th>Dissipation Factor (tanδ)</th>
<th>Conductivity $\sigma_{ac}$ (S/m)</th>
<th>Permittivity (F/m)</th>
<th>Phase angle ($\theta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00 x 10⁵</td>
<td>3.04 x 10⁻¹⁰</td>
<td>6.91 x 10³</td>
<td>1.16 x 10⁰</td>
<td>1.08 x 10⁻¹</td>
<td>2.55 x 10⁴</td>
<td>6.22 x 10¹</td>
</tr>
<tr>
<td>5.62 x 10⁴</td>
<td>7.78 x 10⁻¹⁰</td>
<td>8.46 x 10³</td>
<td>4.76 x 10⁻¹</td>
<td>8.80 x 10⁻²</td>
<td>6.54 x 10⁴</td>
<td>4.42 x 10¹</td>
</tr>
<tr>
<td>3.16 x 10⁴</td>
<td>2.82 x 10⁻⁹</td>
<td>8.49 x 10³</td>
<td>2.15 x 10⁻¹</td>
<td>8.77 x 10⁻²</td>
<td>2.37 x 10⁵</td>
<td>1.21 x 10¹</td>
</tr>
<tr>
<td>1.78 x 10⁴</td>
<td>9.33 x 10⁻⁹</td>
<td>8.34 x 10³</td>
<td>1.16 x 10⁻¹</td>
<td>8.92 x 10⁻²</td>
<td>7.84 x 10⁵</td>
<td>6.60 x 10⁰</td>
</tr>
<tr>
<td>1.00 x 10⁴</td>
<td>2.78 x 10⁻⁸</td>
<td>8.28 x 10³</td>
<td>6.93 x 10⁻²</td>
<td>8.98 x 10⁻²</td>
<td>2.34 x 10⁶</td>
<td>3.96 x 10⁰</td>
</tr>
<tr>
<td>5.62 x 10³</td>
<td>8.39 x 10⁻⁸</td>
<td>8.31 x 10³</td>
<td>4.06 x 10⁻²</td>
<td>8.95 x 10⁻²</td>
<td>7.05 x 10⁶</td>
<td>2.33 x 10⁰</td>
</tr>
<tr>
<td>3.16 x 10³</td>
<td>1.88 x 10⁻⁷</td>
<td>8.36 x 10³</td>
<td>3.21 x 10⁻²</td>
<td>8.91 x 10⁻²</td>
<td>1.58 x 10⁷</td>
<td>1.84 x 10⁰</td>
</tr>
<tr>
<td>1.78 x 10³</td>
<td>3.50 x 10⁻⁷</td>
<td>8.37 x 10³</td>
<td>3.06 x 10⁻²</td>
<td>8.89 x 10⁻²</td>
<td>2.94 x 10⁷</td>
<td>1.75 x 10⁰</td>
</tr>
<tr>
<td>1.00 x 10³</td>
<td>5.93 x 10⁻⁷</td>
<td>8.42 x 10³</td>
<td>3.19 x 10⁻²</td>
<td>8.84 x 10⁻²</td>
<td>4.98 x 10⁷</td>
<td>1.83 x 10⁰</td>
</tr>
<tr>
<td>5.62 x 10²</td>
<td>8.30 x 10⁻⁷</td>
<td>8.48 x 10³</td>
<td>4.03 x 10⁻²</td>
<td>8.78 x 10⁻²</td>
<td>6.97 x 10⁷</td>
<td>2.31 x 10⁰</td>
</tr>
<tr>
<td>3.16 x 10²</td>
<td>1.10 x 10⁻⁶</td>
<td>8.57 x 10³</td>
<td>5.34 x 10⁻²</td>
<td>8.69 x 10⁻²</td>
<td>9.25 x 10⁷</td>
<td>3.06 x 10⁰</td>
</tr>
<tr>
<td>1.78 x 10²</td>
<td>1.41 x 10⁻⁶</td>
<td>8.72 x 10³</td>
<td>7.31 x 10⁻²</td>
<td>8.54 x 10⁻²</td>
<td>1.18 x 10⁸</td>
<td>4.18 x 10⁰</td>
</tr>
<tr>
<td>1.00 x 10²</td>
<td>1.89 x 10⁻⁶</td>
<td>8.89 x 10³</td>
<td>9.50 x 10⁻²</td>
<td>8.37 x 10⁻²</td>
<td>1.59 x 10⁸</td>
<td>5.43 x 10⁰</td>
</tr>
<tr>
<td>5.62 x 10¹</td>
<td>2.31 x 10⁻⁶</td>
<td>9.11 x 10³</td>
<td>1.35 x 10⁻¹</td>
<td>8.16 x 10⁻²</td>
<td>1.94 x 10⁸</td>
<td>7.71 x 10⁰</td>
</tr>
<tr>
<td>3.16 x 10¹</td>
<td>3.02 x 10⁻⁶</td>
<td>9.50 x 10³</td>
<td>1.78 x 10⁻¹</td>
<td>7.83 x 10⁻²</td>
<td>2.54 x 10⁸</td>
<td>1.01 x 10¹</td>
</tr>
</tbody>
</table>
The ion-exchange capacity of the PANI/TIM nanocomposite ion-exchanger for alkali metal ions increases with a decrease in the hydrated ionic radii as shown in Table 5. The higher sorption behavior of K$^+$ is due to the ions having smaller hydrated ionic radii entering the pores of the nanocomposite ion-exchanger more easily than others [35]. The IEC values from Table 5 revealed the presence of exchangeable protons in PANI/TIM nanocomposite ion-exchanger than TIM. The incorporation of conducting polymer (PANI) into the inorganic counterpart (TIM) leads to enhancing the ion-exchange capacity of the nanocomposite ion-exchanger material. The IEC values of TIM and PANI/TIM nanocomposite ion-exchanger are represented in Fig. 9.

The elution behavior of the PANI/TIM nanocomposite ion-exchanger indicated that the exchange is quite better. It has been noticed that 260 mL LiNO$_3$ (Fig. 10a), 240 mL NaNO$_3$ (Fig. 10b), and 220 mL KNO$_3$
(Fig. 10c) solutions were sufficient to release the total H\(^+\) ions from 1.0 g of the nanocomposite ion-exchanger which indicates better column efficiency.

Thermal effect on the IEC of PANI/TIM nanocomposite ion-exchanger (Table 6) demonstrated that the as-synthesized nanocomposite ion-exchanger material retained its ion-exchange capacity (100%) up to 100°C. On heating up to 250°C, the PANI/TIM nanocomposite ion-exchanger material keeps back 84.40% of its initial ion exchange capacity. The reported values implied that ion-exchange capacity slowly decreases and colour also changes from bluish green to grayish black upon increasing the temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Appearance</th>
<th>Weight loss (%)</th>
<th>IEC for Na(^+) ions (meq/g)</th>
<th>% Retention of IEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>Dark bluish green</td>
<td>2.3</td>
<td>2.82</td>
<td>100.00</td>
</tr>
<tr>
<td>100</td>
<td>Dark bluish green</td>
<td>9.1</td>
<td>2.82</td>
<td>100.00</td>
</tr>
<tr>
<td>150</td>
<td>Bluish green</td>
<td>10.5</td>
<td>2.71</td>
<td>96.10</td>
</tr>
<tr>
<td>200</td>
<td>Bluish black</td>
<td>11.4</td>
<td>2.50</td>
<td>88.65</td>
</tr>
<tr>
<td>250</td>
<td>Grayish black</td>
<td>15.8</td>
<td>2.38</td>
<td>84.40</td>
</tr>
</tbody>
</table>

The practical applicability of thermal effect on the IEC of PANI/TIM nanocomposite ion-exchanger with Pb\(^{2+}\) ions was also conducted. Table 7 revealed that IEC of PANI/TIM nanocomposite ion-exchanger material for Pb\(^{2+}\) ions decreased with increasing temperature. This is due to the loss of water (external/interstitial) and dopant molecule when thermal effect applied on the PANI/TIM nanocomposite ion-exchanger material. At 250°C, the PANI/TIM nanocomposite ion-exchanger material retained 86.60% of its initial ion exchange capacity.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>IEC for Pb(^{2+}) ions (meq/g)</th>
<th>% Retention of IEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2.91</td>
<td>100.00</td>
</tr>
<tr>
<td>100</td>
<td>2.91</td>
<td>100.00</td>
</tr>
<tr>
<td>150</td>
<td>2.83</td>
<td>97.25</td>
</tr>
<tr>
<td>200</td>
<td>2.64</td>
<td>90.72</td>
</tr>
<tr>
<td>250</td>
<td>2.52</td>
<td>86.60</td>
</tr>
</tbody>
</table>
To demonstrate the analytical utility of this PANI/TIM nanocomposite ion-exchanger, distribution studies were carried out by batch method in four different solvent systems under study. The distribution behavior of metal ions plays an important role in the material’s selectivity determination. 200 mg of the nanocomposite cation-exchanger in the H\(^+\) form were taken in three different flasks with 20 mL of Pb(NO\(_3\))\(_2\), Cd(NO\(_3\))\(_2\), and Hg(NO\(_3\))\(_2\) in the required medium, respectively, and kept aside for 24 hrs with occasional shaking by using the magnetic stirrer. The concentrations of metal ions (before and after equilibrium) in the solution were determined by titrating against the standard 0.005M solution of EDTA. In order to find out the potentiality of PANI/TIM nanocomposite ion-exchanger in the separation of metal ions, distribution studies for three different metal ions were performed in different solvent media with different concentrations. The PANI/TIM nanocomposite ion-exchanger had significant K\(_d\) values for Pb\(^{2+}\) metal ions, indicating that these metal ions are strongly adsorbed on the material, whereas the remaining metal ions are partially adsorbed (Fig. 11). It was also apparent from data (Table 8) that the K\(_d\) values depended upon the nature and composition of the contacting of the solvents studied. The adsorption was maximum in demineralized water whereas less in 0.1 N nitric acid. The difference in the adsorption behavior of the PANI/TIM nanocomposite ion-exchanger in different solvents was based on the difference in the stability constant of metal ion-exchanger complexes in different solvents.

Table 8: K\(_d\) values of some metal ions on H\(^+\) form of PANI/TIM nanocomposite ion-exchanger in different solvent systems

<table>
<thead>
<tr>
<th>Heavy metal ions</th>
<th>Pb(^{2+})</th>
<th>Cd(^{2+})</th>
<th>Hg(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvents</td>
<td>Pb(^{2+})</td>
<td>Cd(^{2+})</td>
<td>Hg(^{2+})</td>
</tr>
<tr>
<td>DMW</td>
<td>882.16</td>
<td>612.68</td>
<td>192.63</td>
</tr>
<tr>
<td>25% C(_2)H(_5)OH</td>
<td>553.67</td>
<td>358.12</td>
<td>121.91</td>
</tr>
<tr>
<td>50% C(_2)H(_5)OH</td>
<td>516.59</td>
<td>323.82</td>
<td>109.47</td>
</tr>
<tr>
<td>0.1 M CH(_3)COOH</td>
<td>482.40</td>
<td>269.47</td>
<td>98.01</td>
</tr>
<tr>
<td>0.5 M CH(_3)COOH</td>
<td>435.56</td>
<td>239.11</td>
<td>71.72</td>
</tr>
<tr>
<td>0.1 M HNO(_3)</td>
<td>308.76</td>
<td>175.43</td>
<td>84.50</td>
</tr>
<tr>
<td>0.5 M HNO(_3)</td>
<td>338.82</td>
<td>200.89</td>
<td>91.38</td>
</tr>
<tr>
<td>0.1 M HCl</td>
<td>268.71</td>
<td>152.88</td>
<td>60.25</td>
</tr>
<tr>
<td>0.5 M HCl</td>
<td>232.64</td>
<td>135.64</td>
<td>51.46</td>
</tr>
</tbody>
</table>

The separation proficiency of this PANI/TIM nanocomposite ion-exchanger was also manifested by performing some important binary separations of different synthetic metal mixtures such as Cd\(^{2+}\)-Pb\(^{2+}\), Cu\(^{2+}\)-Pb\(^{2+}\), Fe\(^{2+}\)-Pb\(^{2+}\), Hg\(^{2+}\)-Pb\(^{2+}\), Ni\(^{2+}\)-Pb\(^{2+}\), and Zn\(^{2+}\)-Pb\(^{2+}\). The detailed results are outlined in Table 9.
The binary separation chromatograms were sketched in Fig. 12. It is clear from the results that the sequential elution of the metal ions occurred from the column of the ion-exchanger material, which depended upon the metal-eluting ligand stability. It was revealed that Pb$^{2+}$ were strongly adsorbed onto the PANI/TIM nanocomposite ion-exchanger material and thus eluted at last in every separation. The separations were quite fast and reproducible in each quantitative separation.

The quantitative separation of metal ion in the synthetic binary mixtures by using PANI/TIM nanocomposite ion-exchanger (Table 10) depicted that the Pb$^{2+}$ ions were selectively separated from the synthetic binary mixtures containing Cd$^{2+}$-Pb$^{2+}$, Cu$^{2+}$-Pb$^{2+}$, Fe$^{2+}$-Pb$^{2+}$, Hg$^{2+}$-Pb$^{2+}$, Ni$^{2+}$-Pb$^{2+}$, Zn$^{2+}$-Pb$^{2+}$ respectively.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Binary system</th>
<th>Amount loaded (mg)</th>
<th>Amount found (mg)</th>
<th>% recovery</th>
<th>% Error</th>
<th>Volume of eluent used (mL) Eluent used</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cd$^{2+}$-Pb$^{2+}$</td>
<td>9.2541</td>
<td>9.2289</td>
<td>99.73</td>
<td>-0.27</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>Hg$^{2+}$-Pb$^{2+}$</td>
<td>10.2786</td>
<td>10.2501</td>
<td>99.72</td>
<td>-0.28</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>Cu$^{2+}$-Pb$^{2+}$</td>
<td>7.4906</td>
<td>7.4725</td>
<td>99.76</td>
<td>-0.24</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>Zn$^{2+}$-Pb$^{2+}$</td>
<td>8.6265</td>
<td>8.6078</td>
<td>99.78</td>
<td>-1.87</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>Ni$^{2+}$-Pb$^{2+}$</td>
<td>10.3520</td>
<td>10.3118</td>
<td>99.61</td>
<td>-0.39</td>
<td>70</td>
</tr>
<tr>
<td>6</td>
<td>Fe$^{2+}$-Pb$^{2+}$</td>
<td>11.9964</td>
<td>11.9742</td>
<td>99.81</td>
<td>-0.18</td>
<td>40</td>
</tr>
</tbody>
</table>

The practical applicability of selective separations of PANI/TIM nanocomposite ion-exchanger were also determined by separating metal ions quantitatively from a synthetic analytes of Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$, Fe$^{3+}$, Hg$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$ were also demonstrated in Table 10. From the selectivity studies, it was cleared that polyaniline/TIM nanocomposite ion-exchanger can have better potential to make Pb(II) ion-selective membrane for the treatment of industrial effluents in future.
Table 10
Selective separation of Pb\(^{2+}\) from a synthetic mixture\(^{x}\) using PANI/TIM nanocomposite ion-exchanger.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Amount of Pb(^{2+}) loaded (mg)</th>
<th>Amount of Pb(^{2+}) found (mg)</th>
<th>% Recovery</th>
<th>% Error</th>
<th>Volume of eluent used (mL)</th>
<th>Eluent used</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.25</td>
<td>6.15</td>
<td>98.40</td>
<td>-1.60</td>
<td>50</td>
<td>0.1M HNO(_3)</td>
</tr>
<tr>
<td>2</td>
<td>6.62</td>
<td>6.59</td>
<td>99.55</td>
<td>-0.45</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>7.10</td>
<td>7.01</td>
<td>98.73</td>
<td>-1.27</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>7.65</td>
<td>7.59</td>
<td>99.22</td>
<td>-0.78</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>8.15</td>
<td>8.03</td>
<td>98.53</td>
<td>-1.47</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>8.57</td>
<td>8.48</td>
<td>98.95</td>
<td>-1.05</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>8.93</td>
<td>8.88</td>
<td>99.44</td>
<td>-0.56</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

X = Pb\(^{2+}\) (6.25–10.50 mg), Cd\(^{2+}\) (9.25 mg), Cu\(^{2+}\) (7.49 mg), Fe\(^{3+}\) (12.00 mg), Hg\(^{2+}\) (10.28 mg), Ni\(^{2+}\) (10.35 mg) and Zn\(^{2+}\) (8.63 mg)

Conclusion

The conducting nature containing nano-sized PANI/TIM nanocomposite ion-exchanger was prepared successfully by using the in-situ electrochemical oxidative polymerization method. FT-IR and SEM studies confirmed that the inorganic ion exchanger TIM incorporated into the polyaniline matrix. XRD spectral studies proved that the composite ion-exchanger is in the nano-size range and semi-crystalline in nature. As shown in XRD, the average crystallite size of PANI/TIM nanocomposite ion-exchanger was \(~ 27\) nm. From SEM morphology studies, PANI/TIM nanocomposite ion-exchanger depicts that the material has dispersed network structure of the inorganic part TIM and the polymer matrix PANI. HR-TEM studies obviously predicted that TIM was uniformly coated by PANI and that the PANI/TIM composite ion-exchanger consider as a nano-material. Concurrent TGA-DTA studies reveal that the nanocomposite ion-exchanger has better stability compared to PANI. Improved AC electrical conductivity value was attributed to the presence of a large number of charge carriers in PANI/TIM nanocomposite ion-exchanger compared to TIM. The electrical characteristics have shown intimate relationship between TIM and PANI/TIM nanocomposite ion-exchanger. The impedance study revealed that PANI/TIM nanocomposite ion-exchanger material has high conductivity in the higher frequency region. From the electrochemical impedance studies, PANI/TIM nanocomposite ion-exchanger could be applied in the various fields such as semiconductor, batteries etc. PANI/TIM (2.82 meq/g) nanocomposite cation exchanger has enhanced Na\(^+\) ion exchange capacity compared to TIM (1.89 meq/g) exposed that the nanocomposite ion-exchanger material act as a good ion-exchanger. The practical utility of thermal effect on the IEC of PANI/TIM nanocomposite ion-exchanger with Pb\(^{2+}\) ions decreased with increasing temperature. On the basis of its selectivity studies, the nanocomposite ion-exchanger was highly selective for Pb(II) ions, a highly hazardous toxic transition metal in the environment, particularly for the aquatic system. The binary
separation was carried out for the different synthetic binary mixtures and their selective separations from synthetic mixture were also determined. Notably, the present study suggested that as-synthesized, PANI/TIM nanocomposite ion-exchanger material has tunable electrical and ion-exchange properties. Thus, it was concluded that PANI/TIM nanocomposite ion-exchanger believed to be a kind of promising Pb(II) ion-selective membrane for the treatment of industrial effluents containing hazardous heavy metal ions in analytical applications.

Declarations

Acknowledgments

The authors are thankful to the Research Department of Chemistry, Aditanar College of Arts and Science, Tiruchendur and STIC, Cochin University, Cochi, for providing all necessary research facilities for conducting these research investigations.

References


**Scheme 1**

Scheme 1 is available in the Supplementary Files section.

**Figures**
Figure 1

FT-IR spectrum of TIM and PANI/TIM nanocomposite ion-exchanger
Figure 2

XRD pattern of TIM and PANI/TIM nanocomposite ion-exchanger
Figure 3

Combined TGA-DTG curves of TIM and PANI/TIM nanocomposite ion-exchanger

Figure 4
SEM images of PANI/TIM nanocomposite ion-exchanger (a) and TIM (b) at same (×3,500) magnifications

Figure 5

HR-TEM images with SAED images of PANI/TIM nanocomposite ion-exchanger
Figure 6

Combined Nyquist plots for TIM and PANI/TIM nanocomposite ion-exchanger (H$^+$ form)

Figure 7

Variation of frequency against impedance (a) and its phase angle (b)
Figure 8

Variation of real part of dielectric constant ($\varepsilon'$) with frequency (a); Variation of imaginary part of dielectric constant ($\varepsilon''$) with frequency (b); Variation of $\sigma_{a.c}$ with frequency (c).
Figure 9

Combined IEC of various exchanging ions on TIM and H⁺ form of PANI/TIM nanocomposite ion-exchanger

Figure 10

(a)  (b)  (c)
Elution behavior of H⁺ form of PANI/TIM nanocomposite ion-exchanger using LiNO₃ (a), NaNO₃ (b) and KNO₃ (c) as eluent

Figure 11

Kₐ values for different metal ions in different solvent media
Figure 12

Binary separation chromatograms of PANI/TIM nanocomposite ion-exchanger with different metal ions mixtures.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Scheme1.png