



# Efficacy of Zirconium(IV) Tellurotungstate Encapsulated in The Matrix of Polyaniline for Heavy Metal Ion Separation

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## Abstract

A new heteropolyacid salt based composite cation exchanger, Zirconium(IV)tellurotungstate (ZrTeW), has been synthesized by co-precipitation method and it is incorporated into the matrix of polyaniline by simple method. The material was found to be granular and can be conveniently used in column operations. The material was characterized by various analytical techniques. The material showed higher ion exchange capacity (1.48 meq/g) than its inorganic counterpart (1.1meq/g). Effects of temperature and ionic radii on ion exchange capacity, chemical stability in various solvents, pH titration studies were also carried to understand the ion exchange capabilities. The distribution co-efficient studies of metal ions in various electrolytes on exchanger revealed that the material is highly selective for  $\text{Bi}^{3+}$  and  $\text{Th}^{4+}$ , which are toxic environmental pollutants. The selectivity of various metal ion was found to be in the order  $\text{Bi}^{3+} > \text{Th}^{4+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+} > \text{Al}^{3+} > \text{Hg}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Mg}^{2+} > \text{Cu}^{2+}$ . The analytical application has been explored by achieving some binary separation of heavy metal ions such as  $\text{Bi}^{3+}$ - $\text{Cu}^{2+}$ ,  $\text{Th}^{4+}$ - $\text{Cu}^{2+}$ , etc. Practical application of the material was tested by using various industrial wastewaters and was found to be used successfully in the separation of toxic/heavy metal ions.

**Keywords:** Cation exchanger, polyaniline, distribution coefficient, binary separation

## Introduction

In view of continuous worsening of ecological situation due to accumulation of toxic products of human activities the ecological problems including that of heavy metal removal from aqueous solutions are objects of permanent concern for scientist in many countries. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. It is essential to extend methods for the removal of metal ions to decrease the pollution load on the environment. Therefore, various competent technologies including membrane process, precipitation, adsorption on to the activated carbon and ion-exchange<sup>1-7</sup> were developed to remove the heavy toxic metal ions from the polluted water. From the literature survey it is evident that sorption by ion exchangers is a dominant and efficient process for purification and separation of metals ions from wastewater.

In the last few decades, synthetic organic resins or inorganic ion exchangers<sup>8-14</sup> are widely exploited for the removal and recovery of toxic metal ions from waste waters, but they suffer certain limitations. The main drawback existing with inorganic ion exchangers are low mechanical and chemical strength and the fact that they are obtained in powdered form, which is not suitable for column applications. The serious limitations of organic resins are their poor thermal and chemical stability (less stable in highly acidic and basic media). Ion exchange process for the sorption of metal ions greatly depends on the effectiveness of the material, organic-inorganic hybrid, a new

class of materials is attractive for creating high performance are expected to provide many possibilities. Due to the flexibility of the organic part these materials possess specific chemical reactivity and the presence of inorganic backbones make them thermally and mechanically more stable.

The present work describes the synthesis of novel heteropolyacid salt based ion exchanger Zirconium(IV) tellurotungstate (ZrTeW), and it is incorporated into the polymeric matrix of polyaniline by simple stirring method. Effectiveness of the synthesized material for the removal of heavy metal has been evaluated with the help of distribution coefficient studies.

## Methodology

**Reagents:** The main reagents used for the synthesis of the composite material were Zirconium oxychloride (E.Merck), Sodium tungstate (E.Merck), Sodium tellurite (Lobachemie), Aniline (E.Merck), Ammonium persulphate (E.Merck). All other reagents and chemicals used were of analytical grade.

**Apparatus and instruments:** A glass column was used for column operations. ELICO LI613 pH meter was used for pH measurements. FT-IR Spectrometer model Thermo-Nicolet Avtar 370 were taken by KBr disc method at room temperature for IR studies, X-ray Diffractometer Bruker AXS D8 Advance for X-ray diffraction studies with Cu K $\alpha$  radiations, TG Perkin Elmer Diamond TG/DTA Analysis System for thermogravimetric/ derivative thermogravimetric analysis were

used at a rate of 10°C in nitrogen atmosphere. UV-Visible Spectrophotometer model JASCO V660 was used for spectrophotometric measurements. Magnetic stirrer (Remi Equipments) was used for stirring purposes.

**Synthesis of polyaniline:** Polyaniline gels were prepared by mixing of the acidic solutions of 0.05M aniline and 0.1 M ammonium persulfate in different volume ratios with continuous stirring by a magnetic stirrer keeping the temperature below 10 °C for half an hour. Green colored polyaniline gels obtained were kept overnight in a refrigerator.

**Synthesis of Zirconium(IV) tellurotungstate:** The salt was prepared by mixing boiling aqueous solutions of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O and NaTeO<sub>3</sub> upon vigorous stirring. pH was adjusted to acidic by adding 1M HNO<sub>3</sub> drop wise, the gelatinous precipitate locally formed disappears upon stirring. After boiling for a few minutes, the clear solution was precipitated by addition of an aqueous solution of Zirconium oxychloride. A white gelatinous precipitate was formed. The excess reagents were removed by filtration.

**Synthesis of Zirconium(IV) tellurotungstate incorporated polyaniline composite cation exchanger:** Zirconium(IV) tellurotungstate incorporated polyaniline was prepared by simple stirring method. The ex-situ polymerized gels of polyaniline were added to the white inorganic precipitate of Zirconium(IV) tellurotungstate and mixed thoroughly with constant stirring, the resultant mixture turned slowly into a green colored slurry. The green colored gel was kept for 24hours at room temperature (25 ± 2°C) for digestion. The supernatant liquid was decanted and the gel was filtered. The excess acid was removed by washing with DMW and the material was dried in an air oven at 30°C. The dried products were immersed in DMW to obtain small granules. They were converted to H<sup>+</sup> form by treating with 1M HNO<sub>3</sub> for 24hours with occasional shaking, intermittently replacing the supernatant liquid with fresh acid. The excess acid was removed after several washings with DMW and then dried at 30°C. The particles size of the range (125 µm) was obtained by sieving and was kept in desiccators.

**Physiochemical Properties: Chemical dissolution:** About 250mg portion of the composite cation exchanger (H<sup>+</sup> form) was treated with 20mL of different common acids (HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>), bases (NaOH, KOH, NH<sub>4</sub>OH), sodium nitrate solution, and few organic solvents (DMSO, DMF, acetone, THF, CHCl<sub>3</sub>, CCl<sub>4</sub>) and also with demineralized water for 24hours with occasional shaking. Changes in color, nature and weight of the sample were noted.

**Ion-exchange capacity (IEC):** The ion exchange capacity of the material was determined by column method. 1g of the exchanger in H<sup>+</sup> form was taken in a glass column of 1.1cm diameter. The H<sup>+</sup> ions were eluted by percolating 100 ml of 1M NaCl solution. The effluent was collected and titrated against

standard sodium hydroxide solution. The ion exchange capacity in meqg<sup>-1</sup> was calculated using the formula,

$$IEC = \frac{av}{w}$$

Where, *a* is the molarity, *v* is the volume of alkali used during titration and, *w* is the weight of the exchanger taken<sup>15</sup>.

**Thermal effect on ion exchange capacity:** The effect of temperature on ion exchange capacity was studied by heating the material at different temperature for 3hours and the Na<sup>+</sup> ion exchange capacity was determined by column process after cooling them at room temperature.

**Effect of ionic radii on IEC:** The effect of the size and charge of the exchanging ions on the ion-exchange capacity was determined as described above, by using other alkali and alkaline earth metal solution as eluent in addition to NaCl.

**pH-titration:** A pH-titration study of polyaniline-zirconium tellurotungstate was performed by the method of Topp and Pepper<sup>16</sup>. 500mg portions of the cation-exchanger in the H<sup>+</sup> form were placed in several 250 ml conical flasks, followed by the addition of equimolar solutions of alkali metal chlorides and their hydroxides in different volume ratio. The final volume is kept 50 ml to maintain the ionic strength constant. The pH of each solution was recorded<sup>17-19</sup> after every 24hours until equilibrium was attained, which needed ~5 days and pH at equilibrium was plotted against the milli equivalents of OH<sup>-</sup> ions added.

**Partition Coefficients (sorption) studies:** The distribution coefficient (K<sub>d</sub>) of various metal ions on polyaniline-zirconium tellurotungstate was determined by a batch method in various solvent systems. In this method, 0.1g of the exchanger (60-100 mesh) was equilibrated with 20ml of the metal ion solution for 24hours at room temperature. The metal ion concentrations before and after sorption were determined spectrophotometrically/ complexometric titration against standard EDTA solution. In the complexometric method, the K<sub>d</sub> values were calculated using the formula,

$$K_d = \frac{(I - F)}{F} \times \frac{V}{W}$$

where, *I* is the initial volume of EDTA used, *F* is the final volume of EDTA used, *V* is the volume of the metal ion solution (ml) and *W* is the weight of the exchanger.

**Binary Separations: Quantitative Separation of Metal Ions in Binary Synthetic Mixtures:** Quantitative binary separation of some metal ions of analytical utility was achieved on the column of polyaniline-zirconium (IV) tellurotungstate. The column on which the separations were to be carried out was filled uniformly with the exchanger in the H<sup>+</sup> form. First of all

distilled water was added to pack the granules so that no air bubbles get stuck. Binary mixture of the metal ions to be separated was poured on to the column and allow to flow at a rate of 0.3-0.5 mL min<sup>-1</sup>. The process was repeated for maximum sorption. Individual metal ions were eluted using appropriate eluting reagents. The flow rate of the eluent was maintained (0.3 - 0.5 mL·min<sup>-1</sup>) throughout the elution process. The effluent was collected and was titrated against the standard solution of di-sodium salt of EDTA.

**Quantitative separation of metal ions from industrial waste water:** Different samples of waste water were collected from phosphate fertilizer plant. The samples were filtered first to remove suspended particle and then neutralised. The solution was decolourised using charcoal. The samples thus obtained were analysed to detect heavy metal present in it. The granular ion exchanger having greater selectivity towards heavy metals were packed in a column, 100 ml of the sample was passed through the column. The flow rate was maintained at 0.3-0.5 mL/min. Finally the ions were separated using eluents and determined quantitatively.

## Results and Discussion

Zirconium(IV) tellurotungstate samples of different composition were synthesized and its ion exchange capacity was determined (table-1). It is evident from table-1 that the ion exchange capacity of the material greatly depends upon the concentration of reactants, mixing volume ratio and pH of mother liquor. Among these the sample, ZrTeW-1, having maximum IEC (1.1 meqg<sup>-1</sup>) was selected and was tried to incorporate in to the polymeric matrix of polyaniline. Analysis of IEC of composite material reveals that it shows higher IEC than its inorganic counterpart, may be due to more number of freely movable H<sup>+</sup> ions and H<sub>2</sub>O molecules situated in the cavities of the polymeric matrix.

The material was found to be quite stable in different concentrations of mineral acids such as 10 M HNO<sub>3</sub>, 5.0M H<sub>2</sub>SO<sub>4</sub> and 12 M HCl, 0.05M solutions of bases and organic solvents like ethanol, acetone, CCl<sub>4</sub>, DMSO, DMF etc.

Thermal effect on IEC (table-2) shows a gradual decrease in ion exchange capacity with increase in temperature for both ZrTeW-1 and PANI-ZrTeW. It is evident from the data that composite material retains 80% of its IEC up to 250°C. After this temperature the decrease in IEC may be due to decomposition of organic moieties from the exchanger.

The effect of size and charge on ion exchange capacity for ZrTeW-1 and PANI-ZrTeW were studied for alkali metals and alkaline earth metal ions. The order was found to be Li<sup>+</sup> < Na<sup>+</sup> < K<sup>+</sup>; Mg<sup>2+</sup> < Ca<sup>2+</sup> < Ba<sup>2+</sup> (table-3). This sequence is in accordance with the hydrated radii of the exchanging ions<sup>20</sup>. The ions with smaller hydrated radii easily enter the pores of the exchanger, resulting in higher sorption<sup>21</sup>.

pH titration studies (figure-1) using NaCl/NaOH, KCl/KOH systems show nearly bifunctional behavior for both of the exchanger, indicating the presence of two ionizing groups. The exchange capacity obtained from the curve is in agreement with that obtained by the column method.

FTIR spectra of a) ZrTeW-1 b) PANI-ZrTeW are represented in (figure-2). FTIR spectrum of ZrTeW-1 (figure-2(a)), shows a broad band in the region 3200–3500 cm<sup>-1</sup> and a sharp peak in the region 1600cm<sup>-1</sup><sup>23</sup>. These bands justify the presence of – OH stretching and bending mode. A sharp peak at 1387cm<sup>-1</sup> is attributed to W-O bond. The band observed in the 650-967 cm<sup>-1</sup> region is due to the symmetric and asymmetric stretching of M-O-H bond. In the IR spectrum of PANI-ZrTeW (figure-2(b)), an assembly of bands in the region 1400–1600 cm<sup>-1</sup> may be ascribed to the stretching vibration frequency of C–N bonds<sup>24</sup> and a band around 3100 cm<sup>-1</sup> may be related to the stretching of NH bonds of benzenic and quinonic rings<sup>25</sup> present in the material. Other characteristic band associated with inorganic precipitate is reflected with slight shift in the composite material. It gives an evidence for the encapsulation ZrTeW in the polymeric matrix of polyaniline and forms PANI-ZrTeW composite material.

Figure-3a and b shows the thermogram of ZrTeW-1 and PANI-ZrTeW respectively. Figure-3a shows 16% loss of weight at around 102°C due to the evaporation of external water molecules and condensation of structural hydroxyl groups. Above this, heat energy changes without any appreciable weight loss. This may be due to phase changes of the material. As the temperature increases, it shows a gradual weight loss and about 77% of the weight is lost when the temperature reaches 900°C. From the figure-3b) it is evident that the composite material also show the same decomposition pattern as its inorganic counterpart up to 500°C, after increasing heat energy up to 900°C the thermogram shows that 46% of the material is retained. This clearly reveals that the composite material is quite stable at high temperatures than ZrTeW and can be used in high temperature applications.

X-ray diffraction pattern of both materials show number of low intensity peaks (figure-4) which confirms the amorphous nature of the material.

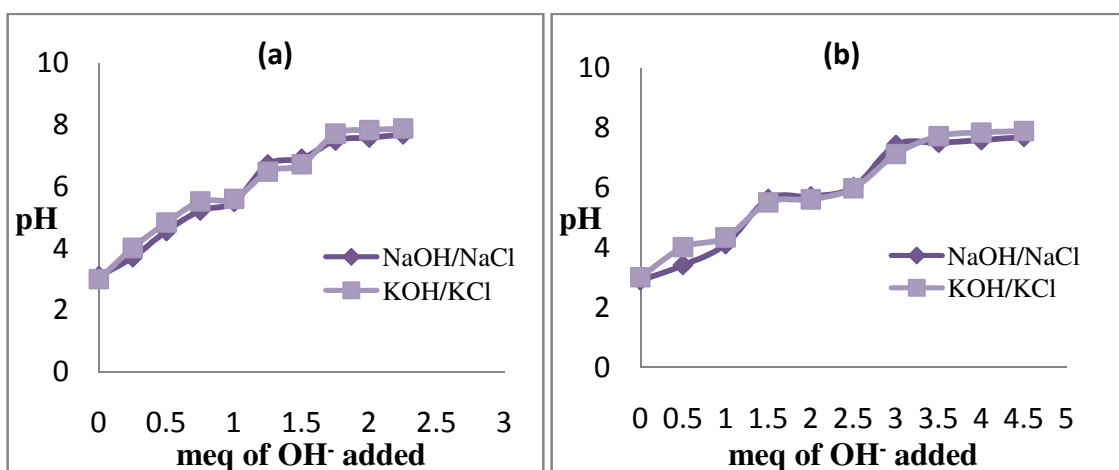
**Partition Coefficients (sorption) studies:** The distribution studies of metal ions in water and various other electrolytes (Table-4) shows that the composite ion exchanger has very high affinity towards Bi<sup>3+</sup> and Th<sup>4+</sup> ions in comparison to other metal ions studied. The selectivity was found to be in the order Bi<sup>3+</sup>> Th<sup>4+</sup>> Pb<sup>2+</sup>> Zn<sup>2+</sup>> Mn<sup>2+</sup>> Ca<sup>2+</sup>> Al<sup>3+</sup>> Hg<sup>2+</sup>> Co<sup>2+</sup>> Ni<sup>2+</sup>> Cd<sup>2+</sup>> Mg<sup>2+</sup>> Cu<sup>2+</sup>. The effect of electrolyte concentrations on distribution coefficients shows that the value decreases with increase in electrolyte concentrations.

**Table-1**  
**Synthesis and properties of various samples of Zirconium tellurotungstate cation-exchange material**

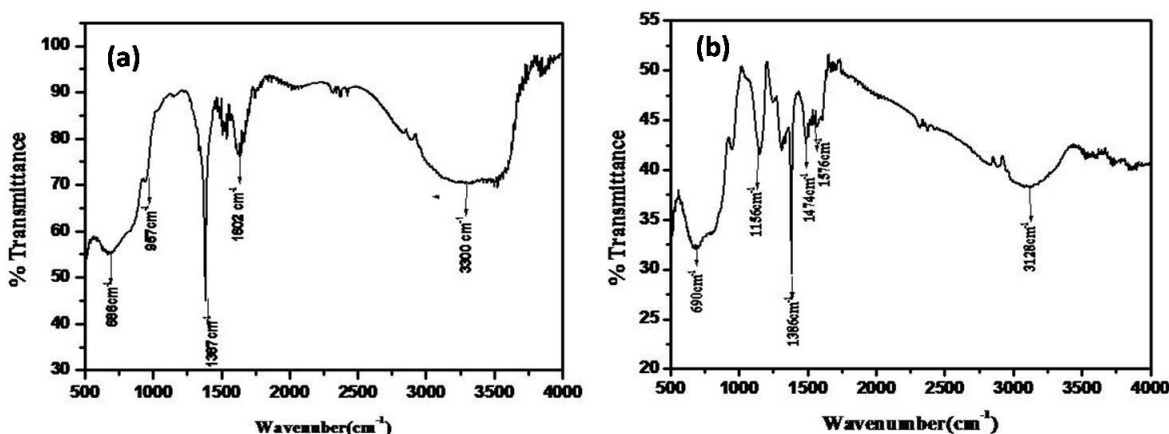
| Sample  | Volume ratio | pH | Appearance (colour) | Ion exchange capacity for Na <sup>+</sup> (meq/g) |
|---------|--------------|----|---------------------|---|
| ZrTeW-1 | 1:1:1        | 1  | White granular      | 1.1   |
| ZrTeW-2 | 1:1:2        | 1  | White granular      | 1.02  |
| ZrTeW-3 | 1:2:3        | 1  | White granular      | 0.95  |
| ZrTeW-4 | 1:2:4        | 1  | White granular      | 0.81  |
| ZrTeW-4 | 2:1:4        | 1  | White granular      | 0.98  |

**Table-2**  
**Thermal effect on ion-exchange capacity**

| Temperature<br>oC | Duration<br>(hrs) | Na <sup>+</sup> -IEC(meq/g) |            |
|-------------------|-------------------|-----------------------------|------------|
|                   |                   | ZrTeW                       | PANI-ZrTeW |
| 50                | 3                 | 1.1                         | 1.48       |
| 100               | 3                 | 1.09                        | 1.43       |
| 200               | 3                 | 0.81                        | 1.22       |
| 300               | 3                 | 0.73                        | 0.87       |
| 400               | 3                 | 0.57                        | 0.83       |
| 500               | 3                 | 0.46                        | 0.64       |



**Figure-1**  
 pH titration curve of a) ZrTeW-1 b) PANI- ZrTeW



**Figure-2**  
 FTIR spectra of a) ZrTeW-1 b) PANI-ZrTeW

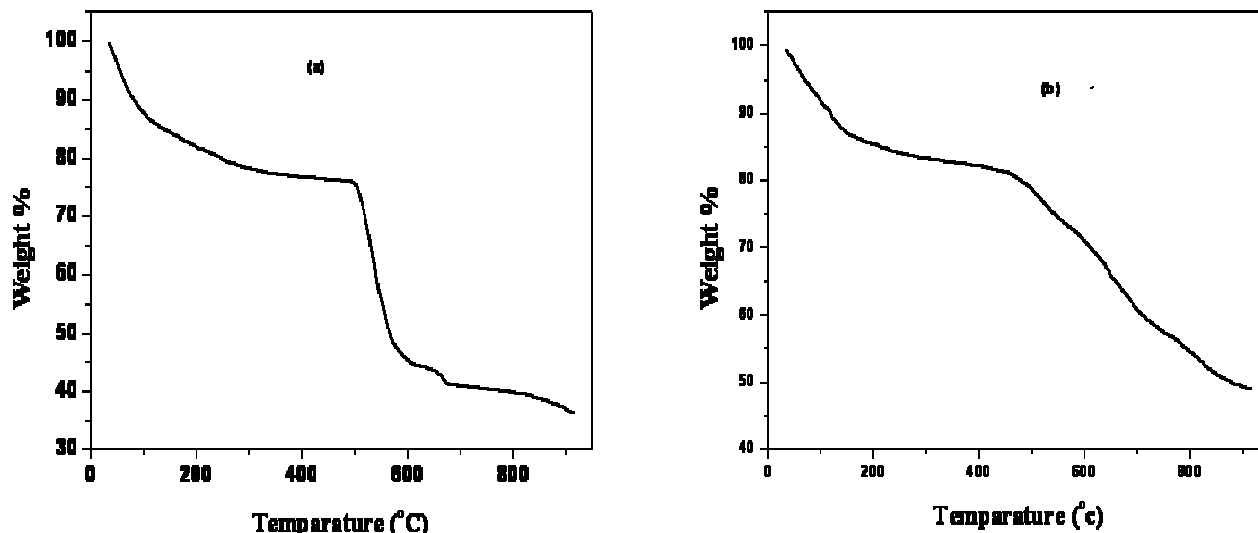


Figure-3  
 TGA of a)ZrTeW-1 b) PANI-ZrTeW

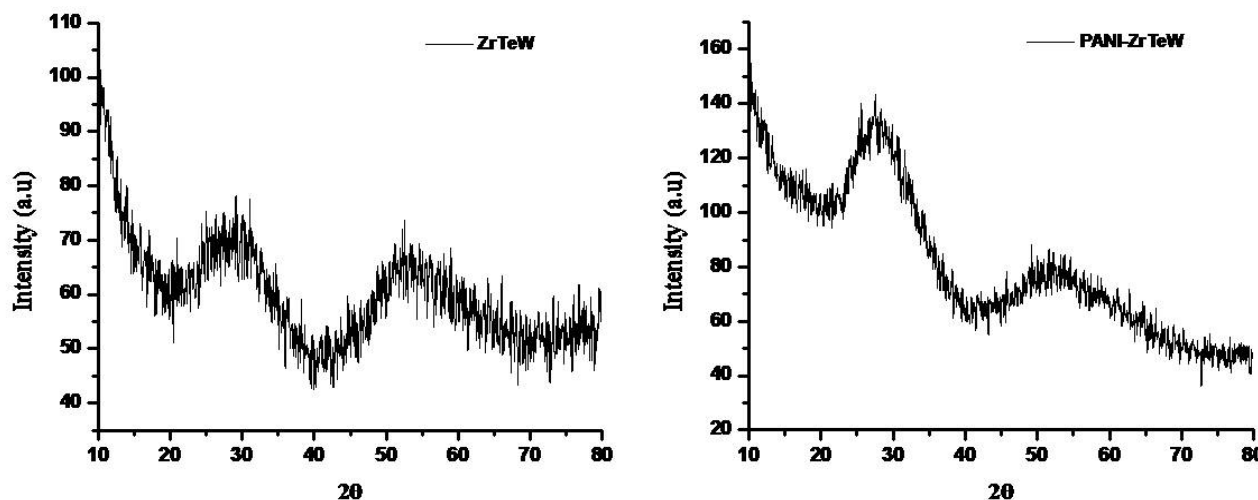


Figure-4  
 XRD pattern of a)ZrTeW-1 b) PANI-ZrTeW

**Binary Separations, Quantitative separation of metal ions from binary synthetic mixtures:** The potentiality of the composite exchanger, PANI-ZrTeW, to adsorb various heavy metal ions in different extent has been utilized to explore the binary separation of metal ion mixtures. Some binary separation achieved on the column of the composite cation exchange material is shown in table-4 Bi(III)-Cu(II), Th(IV)-Cu(II), Bi(III)-Mg(II) etc. mixtures were successfully (above 96%) separated using different concentration of eluting agents such as  $\text{NH}_4\text{NO}_3$  and  $\text{HNO}_3$  in a sequential order.

**Quantitative separation of metal ions from industrial waste water:** Waste water effluent collected from phosphate fertilizer plant was analysed qualitatively, confirmed the presence of Th(IV) and Cd(II). The separation factor of Cd(II) with Th(IV) on the exchange is higher than 5 and can be separated easily

using suitable eluent (table-6). The analysis shows that 100ml of the effluent contains 1.5-4 mg of ions.

Table-3  
 Effect of hydrated ionic radii on IEC

| Metal Ion        | Hydrated ionic radii( $\text{Å}^\circ$ )[22] | I.E.C(meq/g) |            |
|------------------|--|--------------|------------|
|                  |  | ZrTeW        | PANI-ZrTeW |
| $\text{Li}^+$    | 3.40   | 0.98         | 1.21       |
| $\text{Na}^+$    | 2.76   | 1.1          | 1.48       |
| $\text{K}^+$     | 2.32   | 1.19         | 1.52       |
| $\text{Mg}^{2+}$ | 7.00   | 1.23         | 1.63       |
| $\text{Ca}^{2+}$ | 6.30   | 1.31         | 1.68       |
| $\text{Ba}^{2+}$ | 5.90   | 1.35         | 1.74       |

**Table-4**  
**Distribution coefficients in water and other Electrolytes**

| Cations | Distribution coefficients ( $K_d$ ) |                  |        |       |                                 |        |       |
|---------|-------------------------------------|------------------|--------|-------|---------------------------------|--------|-------|
|         | DMW                                 | HNO <sub>3</sub> |        |       | NH <sub>4</sub> NO <sub>3</sub> |        |       |
|         |                                     | 0.001 M          | 0.01 M | 0.1 M | 0.001 M                         | 0.01 M | 0.1 M |
| Al(III) | 52.16                               | 23.14            | 5.76   | NS    | 26.76                           | 3.27   | NS    |
| Bi(III) | 366.24                              | 261.87           | 94.55  | 53.85 | 268.23                          | 97.85  | 58.34 |
| Ca(II)  | 75.28                               | 53.78            | 12.43  | 6.12  | 58.61                           | 15.67  | 625   |
| Cd(II)  | 25.08                               | 9.87             | NS     | NS    | 11.34                           | 2.12   | NS    |
| Co(II)  | 32.36                               | 18.64            | 7.89   | NS    | 20.03                           | 9.12   | 1.26  |
| Cu(II)  | 19.12                               | 8.13             | 1.36   | NS    | 9.24                            | 1.89   | NS    |
| Hg(II)  | 40.8                                | 22.54            | 8.42   | 4.31  | 25.22                           | 9.45   | 5.14  |
| Mg(II)  | 20.72                               | 6.34             | NS     | NS    | 7.21                            | 1.08   | NS    |
| Mn(II)  | 75.6                                | 38.40            | 17.45  | 9.52  | 41.58                           | 23.53  | 10.32 |
| Ni(II)  | 24.36                               | 11.56            | 3.87   | NS    | 12.32                           | 4.21   | 1.21  |
| Pb(II)  | 110.32                              | 71.54            | 46.89  | 23.45 | 75.31                           | 51.94  | 24.13 |
| Zn(II)  | 91.8                                | 68.64            | 26.30  | 4.43  | 72.09                           | 31.43  | 5.89  |
| Th(IV)  | 249.24                              | 169.01           | 78.54  | 29.74 | 175.84                          | 82.42  | 34.31 |

NS:No sorption

**Table-5**  
**Binary separation of metal ions on Pani-ZrTeW**

| Separations Achieved | Separation factor | Eluent   | Metal ion(mg) |        | % efficiency |
|----------------------|-------------------|--|---------------|--------|--------------|
|                      |                   |  | Loaded        | Eluted |              |
| Cu(II)<br>Bi(III)    | 19.15             | 0.1M HNO <sub>3</sub>  | 2.14          | 2.08   | 98.1         |
|                      |                   | 1.0M HNO <sub>3</sub> + 0.5M NH <sub>4</sub> NO <sub>3</sub> | 2.62          | 2.54   | 96.9         |
| Cu(II)<br>Th(IV)     | 13.03             | 0.1M HNO <sub>3</sub>  | 2.14          | 2.09   | 97.7         |
|                      |                   | 0.5M HNO <sub>3</sub> + 0.5M NH <sub>4</sub> NO <sub>3</sub> | 3.65          | 3.53   | 96.7         |
| Mg(II)<br>Bi(III)    | 17.67             | 0.01M HNO <sub>3</sub>                                       | 2.41          | 2.38   | 98.7         |
|                      |                   | 1M HNO <sub>3</sub> + 0.5M NH <sub>4</sub> NO <sub>3</sub>   | 2.62          | 2.56   | 97.7         |
| Mg(II)<br>Th(IV)     | 12.03             | 0.01M HNO <sub>3</sub>                                       | 2.41          | 2.39   | 99.1         |
|                      |                   | 0.5M HNO <sub>3</sub> + 0.5M NH <sub>4</sub> NO <sub>3</sub> | 3.65          | 3.60   | 98.6         |
| Cd(II)<br>Bi(III)    | 14.60             | 0.01M HNO <sub>3</sub>                                       | 1.44          | 1.39   | 96.5         |
|                      |                   | 1M HNO <sub>3</sub> + 0.5M NH <sub>4</sub> NO <sub>3</sub>   | 2.62          | 2.54   | 96.9         |

**Table-6**  
**Waste water treatment on Pani-ZrTeW**

| Sample | Metal ions       | Eluents  | Amount in mg/100ml |
|--------|------------------|--|--------------------|
| 1      | Cd(II)<br>Th(IV) | 0.01M HNO <sub>3</sub>                                       | 2.8                |
|        |                  | 0.5M HNO <sub>3</sub> + 0.5M NH <sub>4</sub> NO <sub>3</sub> | 1.9                |
| 2      | Cd(II)<br>Th(IV) | 0.01M HNO <sub>3</sub>                                       | 3.8                |
|        |                  | 0.5M HNO <sub>3</sub> + 0.5M NH <sub>4</sub> NO <sub>3</sub> | 1.3                |
| 3      | Cd(II)<br>Th(IV) | 0.01M HNO <sub>3</sub>                                       | 2.1                |
|        |                  | 0.5M HNO <sub>3</sub> + 0.5M NH <sub>4</sub> NO <sub>3</sub> | 1.5                |

### Conclusion

Zirconium(IV) tellurotungstate incorporated into the polyaniline matrix shows high ion exchange capacity than its inorganic counterparts. The newly synthesized material is highly selective for Bi(III) and Th(IV). The practical utility of the hybrid material was explored by the quantitative separation of metal ions in binary synthetic mixtures as well as from the waste water effluent collected from phosphate fertilizer plant.

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