## 3.1 INTORDUCTION

Research with ion-exchange resins is as fertile today as it was when it all first began. There is a renewed emphasis on water and wastewater treatment to remove both ions (cations and anions) and molecules. An important need is the ability to design ion-exchange resins a priori that are selective for targeted substrates. In this area amphoteric exchangers are making a huge impact. Although it was surmised long ago **[1]**, that simultaneous presence of anion and cation exchange groups may offer new interesting separation possibilities, very few attempts to exploit these possibilities in practice can be found in literature **[1,2]**. Oxides and hydrous oxides of Zr, Ti, Fe, Al, Nb, Cr, Th, etc. exhibit amphoteric behaviour, exchanging anions in acidic medium and cations in basic medium **[3,4]**. However the major drawback of oxides and hydrous oxides as amphoteric exchangers is their high solubility in acids or bases and poor performance in column operations. Some of these amphoteric ion exchangers are chelating resins with functional groups able to form complexes with several cations and are used for the preconcentration of trace elements, **[1, 3-7]** the sorptive effect of ions being based on the distribution of soluble ions between an aqueous solution and a reactive polymer/resin/material containing a selective ligand **[2,8-10]**, which requires a better understanding of substrate - ligand interactions and the influence of the polymer support on those interactions **[11,2]**. It was proposed that ion-exchange resins could be selective for targeted ions by incorporating chelating groups into their structure. The most important influence on sorption is the internal structure of the exchangers and coordinating ability of ligand end groups, which coordinate or chelate metal ions **[12-15]**. Resins with nitrogen atom containing ligands have been extensively reported **[15]**.

Very early reports reveal that amphoteric exchanger Thorium Triethanolamine was prepared by incorporation of triethanolamine group into the matrix of thorium oxide, wherein nitrogen atom present in the amine group offers chelating sites for metal ions. Zirconium-bis (triethylamine) exhibiting amphoteric character that exchanges anions and adsorbs cations through chelation action has also been reported **[16, 17]**. Polyethyleneimine is an important ligand. A composite has been prepared where the ligand is bonded to silica gel with intended applications of remediation of wastewater from mining operations and cooling water for power plants. In column studies, the composite had a high capacity for ions in the order Cu(II) > Co(II) ~

Ni(II). Succinylated mercerized cellulose modified with triethylenetetramine was used for adsorption of $Cu^{2+}$, $Cd^{2+}$ and $Pb^{2+}$ from aqueous single metal solutions which involves tedious synthesis strategies**[18]**.

## 3.2 AIM AND SCOPE OF THE PRESENT WORK

Ion exchange separation procedures are almost exclusively based on monofunctional ion exchangers. In contrast, amphoteric exchangers contain both cation and anion exchange sites and simultaneously exchange both cations and anions. In the present study new and novel, amphoteric ion exchangers have been synthesized by sol-gel routes using, inexpensive and easily available chemicals, $ZrOCl_2$ and polyamines (DETA = diethylene triamine and TETA = triethylene tetraamine) to yield zirconium diethylene triamine (ZrD) and zirconium triethlylene teraamine (ZrT).

ZrD and ZrT have been subjected to physical characteristics (appearance, percentage moisture content, particle size, apparent density, true density, nature of exchanger and chemical stability) ion exchange characteristics (ion exchange capacity, effect of calcination on IEC, void volume fraction, concentration of fixed ionogenic groups, volume capacity of the resin) and instrumental methods of characterization {elemental analysis, Spectral analysis (FTIR), thermal analysis (TGA), X-ray diffraction (XRD) studies Scanning electron microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX)}. To explore the applicability of ZrD and ZrT as amphoteric exchangers the following studies were undertaken.

- Anion exchange capacity (AEC) for $Cl^-$, $Br^-$, $Cr_2O_7^{2-}$, $F^-$ and $AsO_4^{3-}$ has been determined.
- Distribution coefficient $K_d$ for $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$ (transition metal ions) and $Cd^{2+}$, $Hg^{2+}$, $Pb^{2+}$ (heavy metal ions) has been evaluated by batch equilibration techniques in aqueous as well as various electrolyte media/concentrations.
- Elution behaviour of all the metal ions (under study) have been studied using $HNO_3$, citric acid and $HClO_4$ of 0.2 M and 0.02 M concentrations as eluants.
- Based on the separation factor (α), a few binary separations have been performed on a chromatographic column packed with ZrD and ZrT.
- The amphoteric behavior of ZrD and ZrT has been demonstrated using $CuCl_2$ and $HgCl_2$ and amount of cation and anion exchanged simultaneously determined.

- The practical applicability of ZrD and ZrT as amphoteric exchangers have been further highlighted by performing a case study.
- The performance ability, of ZrD and ZrT has also been assessed by regenerating and reusing the exchangers.

## 3.3 EXPERIMENTAL

***Materials:*** Zirconium oxychloride ($ZrOCl_2.8H_2O$), diethylene triamine (DETA) ($C_4H_{13}N_3$ M.WT=103.17 and Density = 0.955 gm/mL), triethylene tetraamine (TETA) ($C_6H_{18}N_4$ Mw = 146 and Density = 0.955 gm/mL) was procured from Loba Chemicals. Metal salts of AR grade were obtained from E Merck, India, Disodium salt of ethylenediaminetetracetic acid (EDTA) was procured from Fluka. Indicators and reagents used are of AR grade. Deionized water (DIW) was used for all the studies.

***Synthesis of ZrD and ZrT:*** The main objective was to prepare a material with maximum anion exchange capacity (AEC) and which is highly insoluble and chemically resistant to any media (where exchanger would be used). ZrD/ZrT were synthesized by sol-gel method varying several conditions/parameters such as mole ratio of reactants, temperature, mode of mixing [metal salt solution to DETA/TETA solution or vice versa], aging and rate of mixing and synthesis conditions optimized, in each case using AEC as the indicative tool. Each sample synthesized was assessed for chemical stability/resistivity as well as preparative reproducibility. For performing ion exchange studies (distribution, separations and case studies) the material was synthesized at optimized conditions. **Tables 3.1** and **3.2** describe optimization of reaction conditions for synthesis of ZrD (Entry No. 1) and ZrT (Entry No. 12).

***Synthesis of ZrD at optimized conditions:*** ZrD was prepared by mixing aqueous solutions of DETA (0.1 M, 50 mL) and $ZrOCl_2$ (0.1 M, 50 mL) at room temperature, dropwise and with continuous stirring. A gelatinous precipitate was obtained, and solution along with precipitate further stirred for 1 h. The resulting gelatinous precipitate was allowed to age for 15 h, and then filtered, washed with DIW till removal of adhering ions, followed by drying at room temperature. The material was then broken down to the desired particle size 30-60 mesh (ASTM) by grinding and sieving. This material was used for all studies.

**Table 3.1** ***Optimization of reaction conditions for synthesis of ZrD***

| No | Parameters | Mole ratio Metal: Anion (M) | Volume ratio Metal: Anion (mL) | Temp (°C) | Stirring time (h) | Aging time (h) | AEC (meq/g) for $Cl^-$ |
|---|---|---|---|---|---|---|---|
| **1** | Concentration | **0.1:0.1** | **50 : 50** | **25** | **1** | **15** | **1.91** |
| 2 | | 0.1:0.2 | 50 : 50 | 25 | 1 | 15 | 1.50 |
| 3 | | 0.2:0.1 | 50 : 50 | 25 | 1 | 15 | 1.00 |
| 4 | Volume | 0.2:0.1 | 100 : 25 | 25 | 1 | 15 | 1.82 |
| 5 | | 0.1:0.1 | 100 : 50 | 25 | 1 | 15 | 1.72 |
| 6 | | 0.1:0.1 | 100 : 75 | 25 | 1 | 15 | 1.20 |
| 7 | Temperature | 0.1:0.1 | 50 : 50 | 30 | 1 | 15 | 1.10 |
| 8 | | 0.1:0.1 | 50 : 50 | 50 | 1 | 15 | 1.16 |
| 9 | | 0.1:0.1 | 50 : 50 | 70 | 1 | 15 | 1.24 |
| 10 | Aging Time | 0.1:0.1 | 50 : 50 | 25 | 1 | 1 | 1.65 |
| 11 | | 0.1:0.1 | 50 : 50 | 25 | 1 | 3 | 1.57 |
| 12 | | 0.1:0.1 | 50 : 50 | 25 | 1 | 5 | 1.60 |
| 13 | | 0.1:0.1 | 50 : 50 | 25 | 1 | 7 | 1.52 |
| 14 | Stirring Time | 0.1:0.1 | 50 : 50 | 25 | 2 | 15 | 1.50 |
| 15 | | 0.1:0.1 | 50 : 50 | 25 | 3 | 15 | 1.72 |
| 16 | Mode of addition | 0.1:0.1 | 50 : 50 | 25 | 1 | 15 | 1.02* |

**Change in mode of addition-ZrOCl$_2$ to DETA, RT = Room Temperature (25 °C)*

**Table 3.2** ***Optimization of reaction conditions for synthesis of ZrT***

| No | Parameters | Mole ratio Metal: Anion (M) | Volume ratio Metal: Anion (mL) | Temp (°C) | Stirring time (h) | Aging time (h) | AEC (meq/g) for $Cl^-$ |
|---|---|---|---|---|---|---|---|
| 1 | Concentration | 0.1:0.1 | 50 : 50 | 25 | 1 | 15 | 0.86 |
| 2 | | 0.1:0.2 | 50 : 50 | 25 | 1 | 15 | 2.10 |
| 3 | | 0.2:0.1 | 50 : 50 | 25 | 1 | 15 | 0.61 |
| 4 | Volume | 0.2:0.1 | 100 : 25 | 25 | 1 | 15 | 1.92 |
| 5 | | 0.1:0.1 | 100 : 50 | 25 | 1 | 15 | 0.31 |
| 6 | | 0.1:0.1 | 100 : 75 | 25 | 1 | 15 | 2.68 |
| 7 | Temperature | 0.1:0.1 | 50 : 50 | 30 | 1 | 15 | 2.52 |
| 8 | | 0.1:0.1 | 50 : 50 | 50 | 1 | 15 | 2.13 |
| 9 | | 0.1:0.1 | 50 : 50 | 70 | 1 | 15 | 1.90 |
| 10 | Aging Time | 0.1:0.2 | 50 : 50 | 25 | 1 | 1 | 2.19 |
| 11 | | 0.1:0.2 | 50 : 50 | 25 | 1 | 3 | 2.34 |
| 12 | | **0.1:0.2** | **50 : 50** | **25** | **1** | **5** | **2.76** |
| 13 | | 0.1:0.2 | 50 : 50 | 25 | 1 | 7 | 2.01 |
| 14 | Stirring Time | 0.1:0.2 | 50 : 50 | 25 | 2 | 15 | 2.18 |
| 15 | | 0.1:0.2 | 50 : 50 | 25 | 3 | 15 | 2.10 |
| 16 | Mode of addition | 0.1:0.2 | 50 : 50 | 25 | 1 | 15 | 2.12* |

**Change in mode of addition-ZrOCl$_2$ to TETA, RT = Room Temperature (25 °C)*

***Synthesis of ZrT at optimized conditions:*** ZrT was prepared by mixing aqueous solutions of TETA (0.2 M, 50 mL) and $ZrOCl_2$ (0.1 M, 50 mL) at room temperature, dropwise and with continuous stirring. A gelatinous precipitate was obtained, and solution along with precipitate further stirred for 1 h. The resulting gelatinous precipitate was allowed to age for 5 h, then filtered, washed with DIW till removal of adhering ions, followed by drying at room temperature. The material was then broken down to the desired particle size 30-60 mesh (ASTM) by grinding and sieving. This material was used for all studies.

## 3.4 MATERIAL CHARACTERIZATION

Amphoteric exchangers ZrD and ZrT were subjected to physical, ion exchange and instrumental methods of characterization.

### 3.4.1 Physical Characteristics

Physical characteristics- appearance, percentage moisture content, particle size, apparent density, true density and chemical stability were performed using methods and equations as discussed in details in chapter-II section-2.7**.** Experimental details of studying the nature of exchanger (pH titration) is described below. Results are presented in **Tables 3.3** and **3.11.**

***Nature of exchanger*: ** The pH-titration of ZrD/ZrT was performed by Topp and Pepper method **[19-21]**. 500 mg of exchanger was treated with 50 mL 0.01M HCl solution with intermittent shaking. The solution along with exchanger was allowed to equilibrate and pH noted when the value was constant. This was the initial reading. This solution mixture was now titrated with 0.01 M NaCl solution. After addition of every 0.5 mL of titrant, sufficient time was provided for establishment of equilibrium between the ion exchanger and the solution. A *p*H titration curve was obtained by plotting *p*H versus volume of NaCl.

### 3.4.2 Ion Exchange Characteristics

Ion exchange characteristics- void volume fraction/porosity, concentration of fixed ionogenic groups and volume capacity of the resin have been performed using methods and equations as described in chapter-II section 2.7. Experimental details of determining anion exchange capacity and effect of calcination on AEC are described below. Results are presented in **Tables 3.3 and 3.11**.

## 3.5 ANION EXCHANGE PROPERTIES OF ZrD/ZrT

***Determination of Anion Exchange Capacity (AEC):*** 2g of the exchanger ZrD/ZrT was treated with NaCl/ KBr/ $K_2Cr_2O_7$ (0.2 M, 20 mL) for 30 min in a conical flask with continuous shaking and material then separated from solution by decantation. This process was repeated at least five times. The material was finally washed with DIW for removal of any adhering ions and dried at room temperature. 0.5g of this material [ZrD/ZrT exchanged ($Cl^-/Br^-/Cr_2O_7^{2-}$)] was placed in a glass column [30 cm × 1 cm (internal diameter)], DIW poured onto column, and flow rate adjusted to 0.5mL.min$^{-1}$ to wash the exchanger material. A 1.0 M, 250mL sodium nitrate solution was now passed through the column. The effluent containing (NaCl/KBr) was titrated against 0.1 M $AgNO_3$ for determination of chloride and bromide, while the effluent containing ($K_2Cr_2O_7$) was titrated against 0.1 M $FeSO_4.6H_2O$ solution for determination of dichromate. AEC for $Cl^-$ ,$Br^-$ and $Cr_2O_7^-$ was determined, using the formula *aV/W*, where *a* is molarity , *V* the amount of titrant used during titration, and *W* is the weight of the exchanger.

The AEC values for $F^-$ and $AsO_4^{3-}$ was determined by a colorimetric method. Fluoride concentration was determined using reagent zirconyl acid-SPANDS **[22]** while arsenic was determined, based on formation of molybdoarsenate with subsequent reduction to heteropoly blue **[23]**. In both cases concentration was determined using standard calibration curves. The concentration determined was converted to AEC.

***Effect of calcination on AEC:*** The effect of calcination on AEC (in case of $Cl^-$ ) was studied by calcining several 1 g portions of the material for 2 h in the temperature range 100–500 °C at 100 °C intervals in a muffle furnace, cooling them to room temperature, and determining AEC by column method as discussed above.

## 3.6 CATION EXCHANGE PROPERTIES OF ZrD/ ZrT

***Equilibrium time determination:*** This experiment was performed in case of copper. 10 mL (0.014 M) $Cu^{2+}$ solution was shaken with 0.1g of exchanger ZrD/ZrT in stoppered conical flasks at room temperature for different time intervals (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0, 6.0, 7.0 h). After every prescribed time interval, the metal ion concentration was evaluated by EDTA titration. From the plot of fractional attainment of equilibrium $U(t)$ versus time ($t$) , maximum equilibrium time was determined.

***Effect of metal ion concentration on distribution coefficient:*** Effect of metal ion concentration on distribution coefficient ($K_d$) for $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$(transition metals) and $Cd^{2+}$, $Hg^{2+}$ , $Pb^{2+}$ (heavy metals) was determined by batch method. 0.1g of ZrD/ZrT was equilibrated with 20 mL of varying metal ion concentration (0.002-0.02 M with interval of 0.002M) for 6 h (maximum equilibrium time) at room temperature. The metal ion concentration was determined by EDTA titrations. $K_d$ at each concentration was evaluated using the expression,

$$K_d = [(I-F)/F] \text{ X } V/W \text{ (mL.g}^{-1}) \quad \textbf{(Eq. 3.1)}$$

where, $I$ = total amount of the metal ion in the solution initially; $F$ = total amount of metal ions left in the solution after equilibrium; $V$ = volume of the metal ion solution; $W$ = weight of the exchanger in g.

***Effect of pH on adsorption of metal ions:*** To 0.1g of exchanger, ZrD/ZrT, 10 mL of 0.014 M metal ion solution $Co^{2+}$, $Ni^{2+}$ ,$Cu^{2+}$ ,$Zn^{2+}$ (transition metal ions) and $Cd^{2+}$ , $Hg^{2+}$ , $Pb^{2+}$ (heavy metal ions) was added and pH(1-7) adjusted using dilute $HNO_3$ /NaOH and the mixture shaken for 30 min, followed by determination of metal ion concentration by EDTA titrations. Uptake of metal ions (%) has been calculated using formula,

$$[(C_o - C_e)/C_o] \times 100 \quad \textbf{(Eq. 3.2)}$$

where, $C_o$ = initial concentration of metal ion in g. $L^{-1}$ and $C_e$ = final concentration of metal ion in g. $L^{-1}$.

***Distribution studies ($K_d$):*** $K_d$ has also been evaluated at optimum condition, (optimum metal ion concentration, pH of maximum adsorption and maximum equilibrium time) by batch method, using 0.1g of the exchanger in aqueous as well as various electrolyte media like $HNO_3$, citric acid and $HClO_4$ of 0.02 and 0.2 M concentration at room temperature. In each case the metal ion concentration was determined by EDTA titrations. $K_d$ was evaluated using the expression mentioned above **(Eq. 3.1)**.

***Column Preparation:*** For elution and separation studies, the column was prepared as follows. A dry glass column [30 cm (length) × 1 cm (internal diameter)] was filled with glass-wool at bottom (height = ~1 cm) and washed thoroughly with DIW. 0.5g of the ion exchanger ZrD/ZrT, was now introduced into the column (bed height = 1.3 cm), and packed with glass-wool (height = ~1 cm) at the top and washed thoroughly with deionized water to remove air bubbles from the column and flow rate adjusted to 0.5 $mL \cdot min^{-1}$ for all studies.

***Elution and separation studies:*** For elution studies (single metal), 0.5 g ZrD/ZrT was packed in a glass column (prepared as above). The metal ion solution (0.014 M, 10 mL) was loaded onto the column. The metal ion loaded was eluted with reagents like $HNO_3$, citric acid and $HClO_4$, of 0.02 and 0.2M concentration.

For binary separations, the mixture of metal ions (0.014 M, 10mL of each metal ion) to be separated was loaded on column. The separations were achieved by passing suitable eluent through the column. In all cases, the metal ion concentration was determined quantitatively by EDTA titration. For every experimental point in graphs, two identical sets are prepared to compare/verify the obtained values. Reproducibility in values for same experimental point was assessed by again preparing two identical sets. The percentage metal recovered (metal eluted) was calculated in terms of % elution expressed as,

$$\% E = (C_e/C_o) \times 100 \qquad \textbf{(Eq. 3.3)}$$

where, $C_e$ is the concentration of the metal ion in the eluted solution and $C_o$ is the concentration of metal ion loaded onto the column.

## 3.7 AMPHOTERIC BEHAVIOR OF THE MATERIAL

Amphoteric behaviour of ZrD/ZrT was studied by batch method. 0.1g of ZrD/ZrT was treated with $CuCl_2$ /$HgCl_2$ and allowed to stand for 6 hrs. In both cases, metal ion concentration ($Cu^{2+}$, $Hg^{2+}$) before and after exchange was determined quantitatively by EDTA titration while $Cl^-$ was determined by argentometric titration. After exchange, ZrD/ZrT was collected for EDX analysis for confirming the adsorption of cations and anions on exchanger surface.

## 3.8 CASE STUDY

The practical applicability of ZrD/ZrT has been demonstrated in a case study using tap water sample from our institute. The tap water sample was passed through a column packed with 0.5g ZrD/ZrT (prepared as above) in 10 mL fractions. Tap water was analyzed by EDX for a qualitative idea of presence of cations and anions in the sample. The initial sample as well as eluent collected were analyzed for the presence of respective cations ($Ca^{2+}$, $Mg^{2+}$) before and after exchange by EDTA titration. Anion ($Cl^{-}$) was determined by argentometric titration. After exchange, ZrT was collected for EDX analysis for confirming the adsorption of cations and anions on exchanger surface.

## 3.9 REGENERATION AND REUSABILITY OF ION EXCHANGER

Regeneration and reuse of ion exchanger ZrD/ZrT was performed in the case of copper ion by batch method. 0.014M (Optimum concentration) $Cu^{2+}$ solution was treated with 0.1g of ZrD/ZrT and kept for 6 h (maximum equilibrium time) after which metal ion concentration was determined by EDTA titration and $K_d$ value determined. The $Cu^{2+}$ exchanged ZrD/ZrT was treated with $HNO_3$ (1 M, 50 mL) for 30 min with occasional shaking. The sample ZrD/ZrT was separated from acid by decantation and treated with DIW to remove adhering acid. This process was repeated at least five times to ensure complete removal of $Cu^{2+}$ from exchanger. $K_d$ values were determined using this regenerated ZrD/ZrT. This process was repeated till wide variation in $K_d$ values was observed. % retention in $K_d$ values $K_{d(R)}$ was determined using the expression, $K_{d(R)} = K_{d(C)}/K_d \times 100$ where $K_d$ = Initial value obtained, $K_{d(C)}$ = $K_d$ determined in each subsequent cycle.

## 3.10 INSTRUMENTAL METHODS OF CHARACTERIZATION

Following instrumental methods were used for of characterization of ZrD and ZrT. ICP-AES was performed on (Labtam, 8440 Plasmalab). C, H, N analysis was performed on Perkin Elmer-2400. TGA was performed on a thermal analyzer Shimadzu (model TGA-50) at a heating rate of 10 °C/min. FTIR spectra was obtained using KBr pellet on a Shimadzu (model 8400S). $^1$H-NMR spectra was obtained using NMR spectrometer (Bruker 500 MHz) in $D_2O$ solvent. UV-DRS was obtained using Shimadzu (Model UV-DRS 2450).X-ray diffractogram was obtained on X-ray diffractometer (Brucker AXS D8) with Cu-$K_\alpha$ radiation with nickel filter. SEM and EDX of the material were obtained on Jeol JSM-5610-SLV scanning electron microscope.

## 3.11 RESULTS AND DISCUSSION-PART-I

### *Structural studies of ZrD*

Physical and ion exchange characteristics of ZrD are presented in (**Table 3.3**). ZrD was obtained as hard glassy transparent granules. A gel is formed when an aqueous solution of DETA is added to an aqueous solution of $ZrOCl_2$ (pH=1). The solution first turns neutral (pH=7) and then basic (pH=9). The gel formed is entirely different as compared to addition of an inorganic base to $ZrOCl_2$. The gel formation probably takes place in two steps: (a) Formation of hydrous $ZrO_2$ gel **[24, 25]** followed by (b) Surface interaction and polymerization of amine molecules involving weak and strong bonding, resulting in the formation of a macro-particle **[24, 25]** which can be formulated as $[(ZrO)_n(DETA)_n](OH)_n$ **(Figure 3.1)**.

Elemental analysis for ZrD shows % Zr = 60.80, % C = 9.52, % N = 8.18 which matches well with formula $[(ZrO)_6(C_8H_{18}N_6)](OH)_4$. Further, the presence of Zr and N is confirmed by EDX **(Figure 3.2)**.

In FTIR spectrum of ZrD, sharp bands are expected in the region ~3300cm$^{-1}$ (–NH stretching frequency) and at ~3400cm$^{-1}$ (-OH stretching frequency), indicating presence of free -$NH_2$ groups and -OH in ZrD. However, the FTIR (**Figure 3.3**), spectrum of ZrD shows a broad band in the region ~3400-3200 cm$^{-1}$ which is probably due to merging of -OH and -NH stretching frequency. Band at~1580 cm$^{-1}$ is attributed to C-C stretching vibration, while, band at ~1360 cm$^{-1}$ is attributed to C-N bending.

Since the unit Zr-DETA in ZrD is positively charged, it therefore behaves as an anion exchanger where –OH part of ZrD behaves as the anion exchange unit. The pH titration curve **(Figure 3.4)** of ZrD exhibits mono functional behavior **[16, 17, 24]**. When ZrD was kept in contact with a solution of sodium nitrate, no release of $H^+$ was observed. However, the presence of NaOH was tested by phenolphthalein indicator (which turns the solution pink) confirming -OH as anion exchange sites.

It is quite clear that the component [Zr(DETA)] contains free amino groups, offering chelating sites to metal ions and behaves as the cation exchange unit. Due to lone pair of electrons present on the nitrogen atom of amine groups (**Figure 3.1**), ZrD can act as chelating exchanger. The chelating property of ZrD was studied by a batch process. When ZrD was treated with $Cu^{2+}$ salt solution it turns to a deep blue color confirming the chelation of $Cu^{2+}$ with ZrD. Accordingly, $Cu^{2+}$ chelated ZrD could be depicted as proposed **(Figure 3.5).**

The presence of $Cu^{2+}$ on exchanger was confirmed by scanning an FTIR spectrum of $Cu^{2+}$ exchanged ZrD, in which the ~1360 $cm^{-1}$ band shifts to ~1410 $cm^{-1}$ due to coordination of $Cu^{2+}$ with nitrogen atom of amine group **(Figure 3.3)**. From UV-DRS spectrum for ZrD (**Figure 3.6**), it is evident that $Cu^{2+}$ chelated ZrD exhibits peak around 500 nm which could be attributed to d–d transition band of a $Cu^{2+}$ ion centered in pseudo-octahedral environment **[26]**. EDX **(Figure 3.7)** is also supportive to $Cu^{2+}$ exchanged ZrD. NMR spectra of ZrD (**Figure 3.8)** exhibits a peak at $\delta$3.04 and $\delta$2.42 which corresponds to (multiplet methylene group –Zr-N-$CH_2$-) and (multiplet methylene group $CH_2$-N-$CH_2$) respectively which shift to $\delta$4.02 and $\delta$3.05 respectively (**Figure 3.9**) attributed to $Cu^{2+}$ chelated ZrD.

Anion exchange capacity was determined for $Cl^-$, $Br^-$, $Cr_2O_7^{2-}$, $F^-$ and $As_2O_4^{3-}$. The AEC values in $meq.g^{-1}$ are presented in (**Table 3.3**).

TGA (**Figure 3.10**) of ZrD exhibits two regions of weight loss. The first weight loss in the temperature range 30-150°C could be attributed to loss of moisture/hydrated water. A second weight loss in the temperature range 150-500 ºC, is attributed to dehydoxylation, and decomposition of the organic moiety. The thermal behavior of the materials is further supported by the effect of calcination on AEC. As observed from **(Table 3.3)**, AEC values decrease as calcination temperature increases. Decrease in AEC with increasing temperature could be attributed to dehydroxylation and decomposition of organic moiety.

The absence of sharp peaks in XRD (**Figure 3.11**) of ZrD indicates amorphous nature of the materials. SEM image of ZrD **(Figure 3.12)** shows irregular morphology of the material. When using ion exchangers, it has to be subjected to various environments and chemical media. A study on the chemical stability of ZrD shows that it is stable in acids, bases and organic solvent media. No transmetalation or zirconium metal washout is observed, confirming the ZrD moiety to be the rigid framework.

## *Cation exchange properties of ZrD*

A plot of the fractional attainment of equilibrium $U(^{2}=)$ versus time (*t*) (**Figure 3.13**) in case of $Cu^{2+}$ shows that the exchange equilibrium for ZrD appears to have attained within 6 h. For all studies therefore a maximum equilibrium time of 6h was allowed.

The effect of pH on the sorption behaviour of metal ions (under study) have been presented in (**Table 3.4).** It is observed that at pH values less than ~3, very less sorption has been observed for all metal ions. The lack of sorption at low pH could be attributed to high concentration of hydrogen ions competing with the metal ions for sorption/exchange sites. The observed order for % uptake of metal ion at optimum pH, is $Cu^{2+} > Co^{2+} > Zn^{2+} > Ni^{2+}$ (amongst transition metal ions) and $Pb^{2+} > Hg^{2+} > Cd^{2+}$ (amongst heavy metal ions).

It is observed that with increase in metal ion concentration, $K_d$ values increase. Above a particular concentration $K_d$ values are constant attributed to the fact that at lower concentrations, almost all the ions are exchanged due to availability of exchangeable sites, which are not available at higher concentrations. $K_d$ values evaluated by varying metal ion concentration are presented in (**Table 3.5).**

The distribution coefficient ($K_d$) values evaluated at optimum conditions using ZrD have been presented in **(Table 3.6)**. $K_d$ values in aqueous medium follows the order: $Cu^{2+} > Co^{2+} > Ni^{2+} > Zn^{2+}$ amongst the transition metal ions and $Hg^{2+} > Pb^{2+} > Cd^{2+}$ amongst the heavy metal ions.

## *Elution and Separation Studies using ZrD*

The elution behaviour of transition metal ions and heavy metal ions (under study) have been carried out using different electrolytes such as $HNO_3$, citric acid and $HClO_4$, of 0.02 and 0.2M concentration and results presented in **(Table 3.7)**. The % metal eluted in all cases is in the range 78 to 99 %. Good elution is observed due to presence of single metal ion and non interference of elements. Higher concentration of eluant and acids in general, are better eluents. Further, all elution curves {**Figure 3.14(a-g)}** are symmetrical bell shaped indicating elution efficiency. Using 0.2M $HNO_3$, order of % metal eluted amongst transition metal ions is $Zn^{2+}$ (99%) > $Ni^{2+}$ (96 %) > $Co^{2+}$ (93 %) > $Cu^{2+}$ (88 %) and amongst heavy metal ions is $Cd^{2+}$ (96%) >$Pb^{2+}$ (89%) > $Hg^{2+}$ (88%). This observation is in keeping with the fact that metal ions with high $K_d$ values are less eluted and vice-versa.

Binary separations for following metal ion pairs (under study) $Zn^{2+}$- $Co^{2+}$ , $Zn^{2+}$- $Cu^{2+}$, $Ni^{2+}$-$Cu^{2+}$, $Co^{2+}$-$Cu^{2+}$, $Cd^{2+}$-$Hg^{2+}$, $Cd^{2+}$- $Pb^{2+}$ have been performed using concept of high separation factor in a particular medium. In binary separations **{Figure 3.15(a-f)}**, separation efficiency is in the range 68–97 % amongst transition metal ions and 64-90% amongst heavy metal ions **(Table 3.8)**. In all cases of binary separation, irrespective of metal ion pair, maximum % metal eluted is $Zn^{2+}$ (97%), $Ni^{2+}$ (96%), $Co^{2+}$ (82%), $Cu^{2+}$(68%) (amongst transition metal ions) and $Cd^{2+}$ (90%), $Pb^{2+}$ (74%), $Hg^{2+}$ (64%), (amongst heavy metal ions). This observation is in keeping with separation factor (α) and $K_d$ values of metal ions. % metal eluted decreases with decreasing separation factor and increases with increasing separation factor and as explained earlier, metal ions with high $K_d$ values are less eluted and vice-versa.

### *Amphoteric Behaviour of ZrD*

On treating a ZrD packed column with $CuCl_2$/$HgCl_2$ simultaneous exchange of cations and anions occurred. Respective cations and anions present before and after exchange are presented in **(Table 3.9)**. Further, the presence of exchanged $Cu^{2+}$, $Hg^{2+}$ and $Cl^-$ on ZrD is confirmed by EDX. **(Figure 3.16 & 3.17)**.

### *Case study*

Practical utility of ZrD has been demonstrated in a case study. Simultaneous exchange of cations and anions occurred on treating a ZrD packed column using tap water sample from our institute region. Analysis of water sample by EDX (**Figure 3.18**) in wt. % is $Mg^{2+}$=1.93, $Ca^{2+}$ = 26.76, $Cu^{2+}$ = 1.09 and $Cl^-$ = 18.85. Since, concentration of $Cu^{2+}$ and $Mg^{2+}$ is very less, we have focused towards $Ca^{2+}$ and $Cl^-$ in the present study. The initial concentration of $Ca^{2+}$ and $Cl^-$ in tap water sample was found to be 300 mg.$L^{-1}$ and 289 mg.$L^{-1}$ respectively, whereas eluent (after passing through column containing ZrD) contains 151 mg.$L^{-1}$ and 94 mg.$L^{-1}$ of $Ca^{2+}$ and $Cl^-$ respectively.The water samples were analyzed for $Ca^{2+}$ and $Cl^-$ by EDTA titration and argentometric titration respectively before and after passing through the column containing ZrD. The presence of $Ca^{2+}$, $Mg^{2+}$ $Cu^{2+}$ and $Cl^-$ on ZrD column (after passing water samples) is confirmed by EDX **(Figure 3.19)**. The amount of cations and anions removed from water sample is presented in (**Table 3.10).**

### *Regeneration and reusability of Ion exchanger ZrD*

A study on regeneration and reuse of exchanger ZrD was performed as described in experimental section 3.10. It is observed that the exchanger, once used, can be converted back to its original form by desorption of the metal ions with concentrated nitric acid. A plot of % retention in $K_d$ values *vs* No of cycles is presented in **(Figure 3.20)** which shows that % retention in $K_d$ values is almost the same upto 4 cycles, indicating that ZrD could be regenerated and reused without much decline in performance.

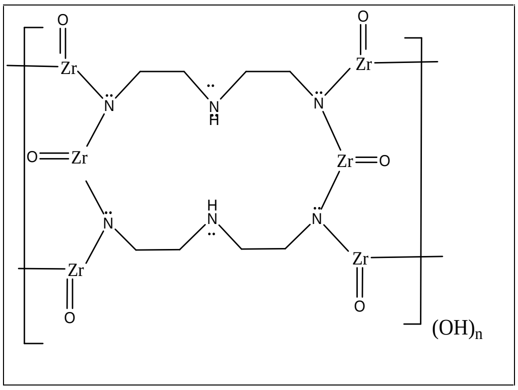
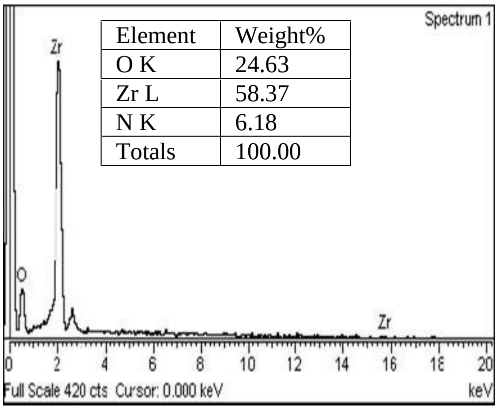


**Figure 3.1** ***Proposed Structure of ZrD Gel***



| Element | Weight% |
|---|---|
| O K | 24.63 |
| Zr L | 58.37 |
| N K | 6.18 |
| Totals | 100.00 |

**Figure 3.2** ***EDX of ZrD***

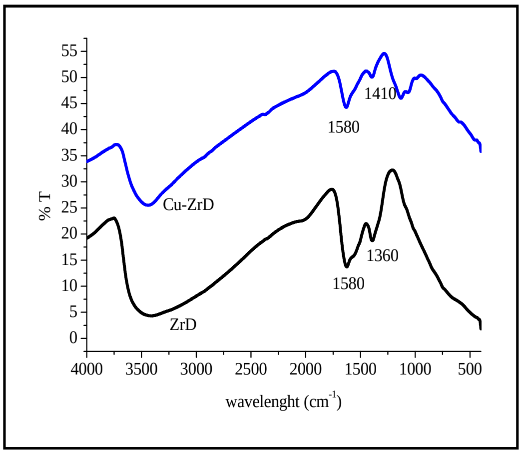


**Figure 3.3** ***FTIR spectrum of ZrD and $Cu^{2+}$ chelated ZrD***

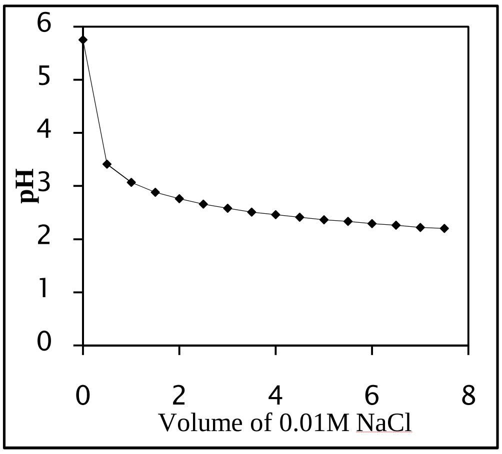


**Figure 3.4** ***pH titration curve for ZrD***

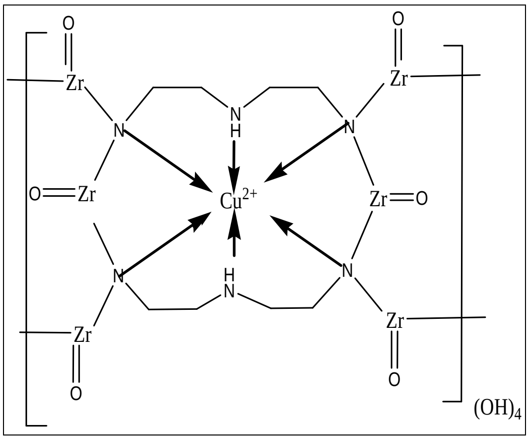


**Figure 3.5** ***Proposed Structure of $Cu^{2+}$ chelated ZrD***

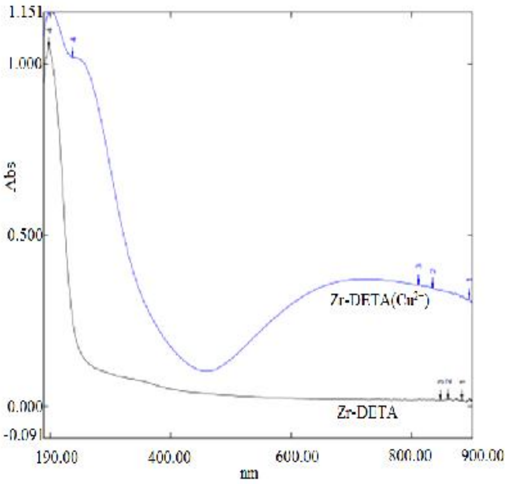
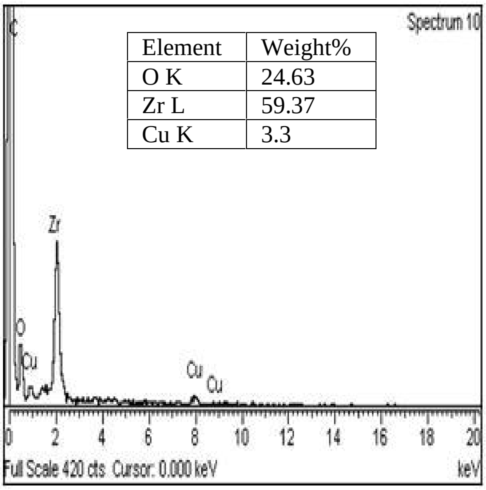


**Figure 3.6** ***UV-DRS Spectrum of ZrD and $Cu^{2+}$ chelated ZrD***



| Element | Weight% |
|---|---|
| O K | 24.63 |
| Zr L | 59.37 |
| Cu K | 3.3 |

**Figure 3.7** ***EDX of $Cu^{2+}$ chelated ZrD***

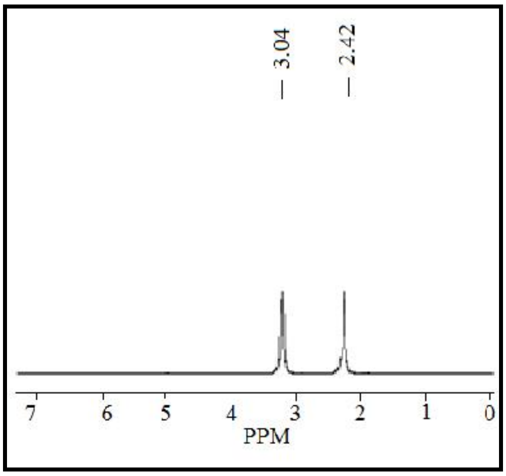


**Figure 3.8** ***NMR Spectra of ZrD***

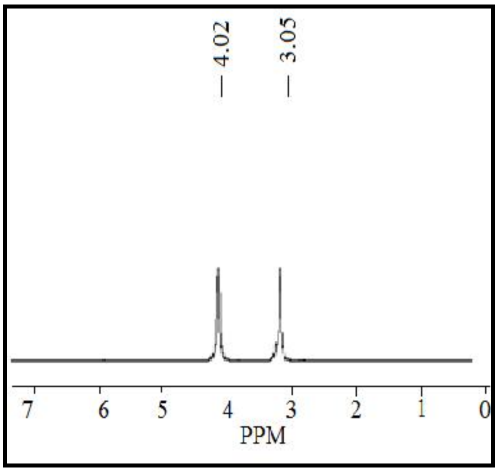


**Figure 3.9** ***NMR Spectra of $Cu^{2+}$ chelated ZrD***

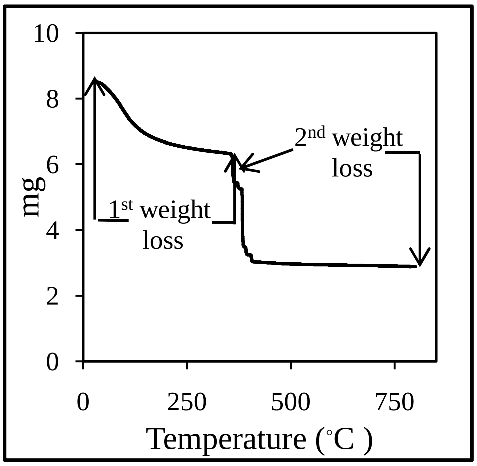
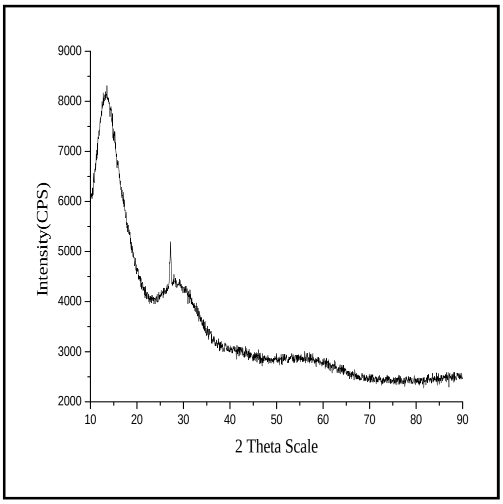


**Figure 3.10** ***TGA of ZrD***



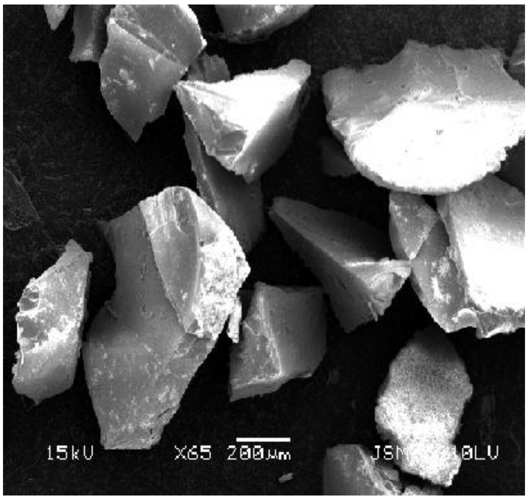


**Figure 3.11** ***XRD of ZrD***

**Figure 3.12** ***SEM of ZrD***

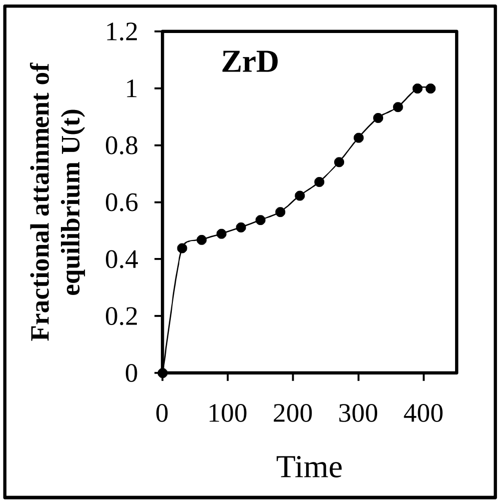
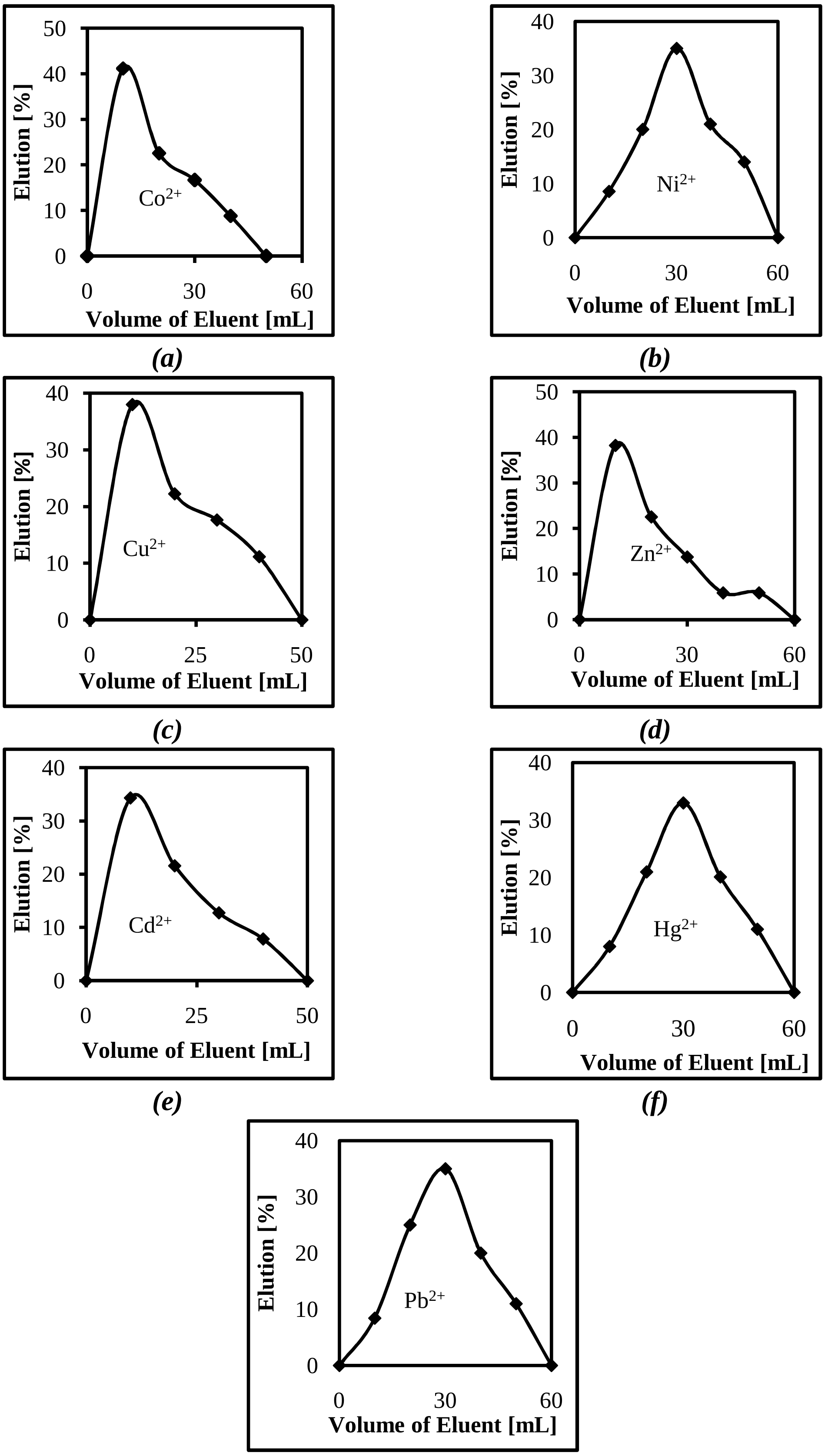
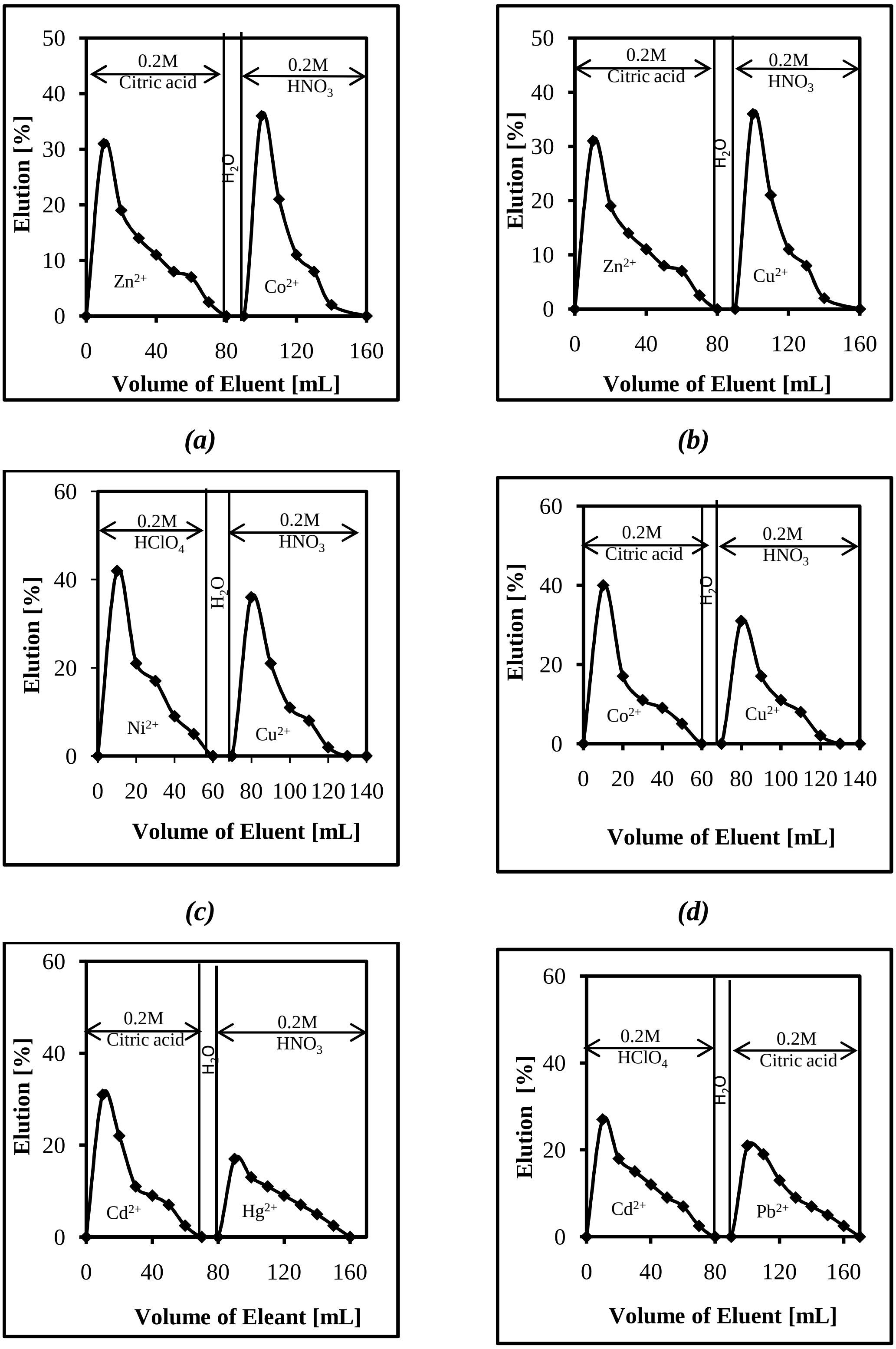


**Figure 3.13** ***Plot of fractional attainment of equilibrium for $Cu^{2+}$-$H^{+}$ exchange vs. time using ZrD***



*(a)* *(b)* *(c)* *(d)* *(e)* *(f)* *(g)*

**Figure 3.14(a-g)** *Elution behaviour of transition and heavy metal ions using 0.2 M $HNO_3$ as eluent (a) $Co^{2+}$;(b) $Ni^{2+}$; (c) $Cu^{2+}$; (d)$Zn^{2+}$; (e) $Cd^{2+}$; (f) $Hg^{2+}$; (g) $Pb^{2+}$ using ZrD*

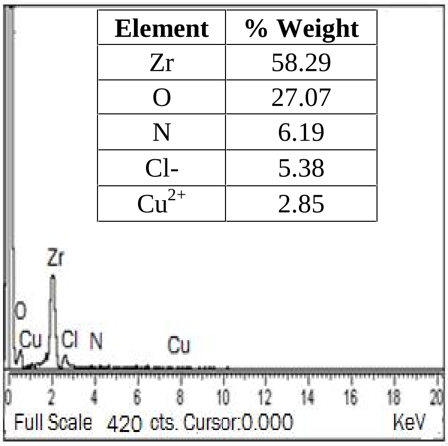


*(a)* *(b)*

*(c)* *(d)*

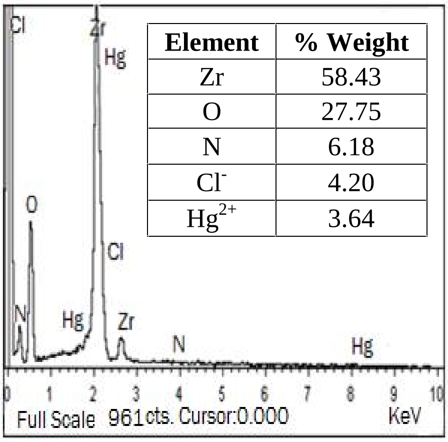
*(e)* *(f)*

**Figure 3.15 (a-f)** *Binary separations of transition and heavy metal ions using ZrD (a) $Zn^{2+}$-$Co^{2+}$ (b) $Zn^{2+}$-$Cu^{2+}$ (c) $Ni^{2+}$-$Cu^{2+}$ (d) $Co^{2+}$-$Cu^{2+}$ (e) $Cd^{2+}$-$Hg^{2+}$ (f) $Cd^{2+}$-$Pb^{2+}$*



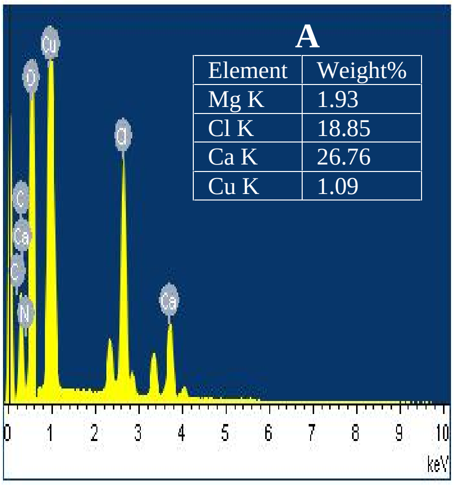
| Element | % Weight |
|---|---|
| Zr | 58.29 |
| O | 27.07 |
| N | 6.19 |
| Cl- | 5.38 |
| $Cu^{2+}$ | 2.85 |

**Figure 3.16** ***EDX of ZrD treated with $CuCl_2$***



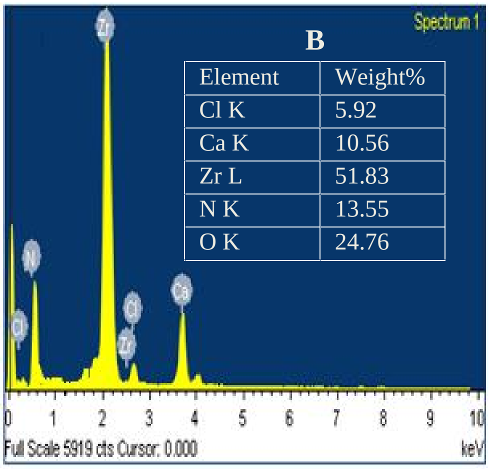
| Element | % Weight |
|---|---|
| Zr | 58.43 |
| O | 27.75 |
| N | 6.18 |
| $Cl^-$ | 4.20 |
| $Hg^{2+}$ | 3.64 |

**Figure 3.17** ***EDX of ZrD treated with $HgCl_2$***



| Element | Weight% |
|---|---|
| Mg K | 1.93 |
| Cl K | 18.85 |
| Ca K | 26.76 |
| Cu K | 1.09 |

**Figure 3.18** ***EDX of tap water sample***



| Element | Weight% |
|---|---|
| Cl K | 5.92 |
| Ca K | 10.56 |
| Zr L | 51.83 |
| N K | 13.55 |
| O K | 24.76 |

**Figure 3.19** ***EDX of ZrD treated with tap water sample***

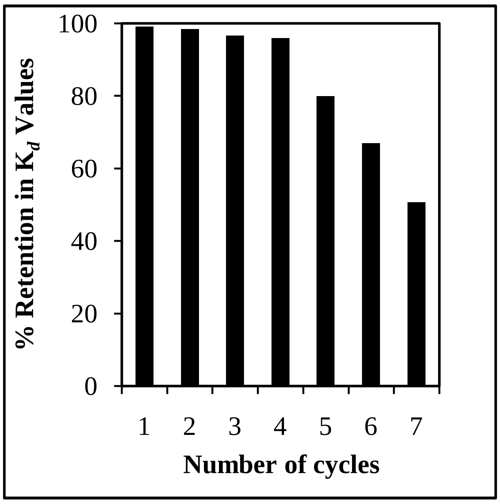


**Figure 3.20** ***Plot of % retention in $K_d$ values versus number of cycles using ZrD***

**Table 3.3** *Physical and ion exchange characteristics of ZrD*

| **Characteristics** | **ZrD** |
|---|---|
| Appearance | Glassy transparent granules |
| Particle size(range) | 250-590 µm |
| % Moisture content | 16.49 % |
| True density | 1.46 $g.mL^{-1}$ |
| Apparent density | 0.53 $g.mL^{-1}$ |
| Void volume fraction | 0.65 |
| Concentration of fixed ionogenic groups | 3.13 $mmol.g^{-1}$ |
| Volume capacity of resin | 1.07 $mL.g^{-1}$ |
| **Anion Exchange Capacity (AEC) ($meq.g^{-1}$)** | |
| Br- | 0.96 |
| $Cr_2O_7^{2-}$ | 0.92 |
| $F^-$ | 0.94 |
| $AsO_4^{3-}$ | 2.10 |
| **Effect of calcination on AEC for $Cl^-$ ($meq.g^{-1}$)** | |
| AEC (RT) | 1.91 |
| 100°C | 1.15 |
| 200°C | 1.09 |
| 300°C | 0.98 |
| 400°C | 0.90 |
| 500°C | 0.84 |
| Chemical stability | Maximum tolerable limits |
| i) Acids | 18 N $H_2SO_4$, 8 N $HNO_3$, 5.6 N HCl |
| ii) Bases | 2 N NaOH, 5 N KOH |
| iii) Organic solvents | Ethanol, Benzene, Acetone, Acetic acid |

**Table 3.4** *Effect of pH on adsorption of metal ions using ZrD*

| **pH** | **Percentage Uptake of metal ions** | | | | | | |
|---|---|---|---|---|---|---|---|
| | **$Co^{2+}$** | **$Ni^{2+}$** | **$Cu^{2+}$** | **$Zn^{2+}$** | **$Cd^{2+}$** | **$Hg^{2+}$** | **$Pb^{2+}$** |
| 1 | 17.78 | 11.76 | 16.67 | 17.17 | 18.00 | 16.67 | 13.41 |
| 2 | 55.77 | 25.45 | 37.62 | 26.73 | 28.26 | 34.29 | 22.00 |
| 3 | 65.45 | 37.74 | 41.35 | 41.35 | 47.87 | 49.49 | **94.55** |
| 4 | 70.00 | **73.58** | 72.94 | **78.82** | **64.40** | **89.69** | 63.7 |
| 5 | **82.11** | 39.00 | **94.76** | 46.08 | 42.00 | 69.80 | 40.43 |

*After 6 pH = precipitation take place.*

**Table 3.5** ***Distribution coefficient ($K_d$) values ($mL{\cdot}g^{-1}$) evaluated varying metal ion concentration in aqueous medium using ZrD***

| **Concentration (M)** | **Distribution Coefficient ($K_d$)** | | | | | | |
|---|---|---|---|---|---|---|---|
| | **$Co^{2+}$** | **$Ni^{2+}$** | **$Cu^{2+}$** | **$Zn^{2+}$** | **$Cd^{2+}$** | **$Hg^{2+}$** | **$Pb^{2+}$** |
| 0.002 | 180 | NS | 1120 | NS | NS | 180 | 40 |
| 0.004 | 1140 | NS | 1290 | NS | NS | 1160 | 190 |
| 0.006 | 1160 | 40 | 1560 | 29 | 45 | 1220 | 360 |
| 0.008 | 1240 | 140 | 1920 | 120 | 130 | 1260 | 660 |
| 0.01 | 1360 | 260 | 2360 | 230 | 280 | 1340 | 870 |
| 0.012 | 1440 | **390** | 2500 | **288** | 300 | 1420 | 970 |
| **0.014** | **1590** | 390 | **2876** | 288 | **369** | **1940** | **1005** |
| 0.016 | 1590 | - | 2876 | - | 365 | 1930 | 1003 |

*NS = No Sorption, Maximum deviation in $K_d$ values = ± 3*

**Table 3.6** ***Distribution coefficient ($K_d$) ($mL{\cdot}g^{-1}$) evaluated at optimum conditions in aqueous and various electrolyte media/concentration using ZrD***

| **Metal Ions** | **OC** | **DIW** | **0.02M $HNO_3$** | **0.2 M $HNO_3$** | **0.02M Citric acid** | **0.2M Citric acid** | **0.02 M $HClO_4$** | **0.2 M $HClO_4$** |
|---|---|---|---|---|---|---|---|---|
| $Co^{2+}$ | 0.014 | 1647 | 317 | 256 | 231 | 212 | 446 | 354 |
| $Ni^{2+}$ | 0.012 | 402 | 204 | 115 | 232 | 163 | 59 | 30 |
| $Cu^{2+}$ | 0.014 | 2876 | 306 | 94 | 616 | 584 | 911 | 434 |
| $Zn^{2+}$ | 0.012 | 301 | 397 | 298 | 32 | 18 | 56 | 41 |
| $Cd^{2+}$ | 0.014 | 374 | 265 | 200 | 151 | 70 | 306 | 249 |
| $Hg^{2+}$ | 0.014 | 1980 | 609 | 536 | 754 | 657 | 446 | 256 |
| $Pb^{2+}$ | 0.014 | 1019 | 551 | 540 | 319 | 238 | 466 | 325 |

*$K_d$*Values obtained at optimum condition (Optimum metal ion concentration[OC], Optimum pH of solution and maximum equilibrium time); DIW = Deionized water, Maximum deviation in $K_d$ values = ± 3.*

**Table 3.7** ***Percentage elution (% E) of metal ions in different electrolyte media using ZrD***

| **Metal Ions** | **0.02M $HNO_3$** | **0.2 M $HNO_3$** | **0.02M Citric acid** | **0.2M Citric acid** | **0.02 M $HClO_4$** | **0.2 M $HClO_4$** |
|---|---|---|---|---|---|---|
| $Co^{2+}$ | 91 | 93 | 78 | 86 | 89 | 92 |
| $Ni^{2+}$ | 83 | 96 | 88 | 89 | 95 | 96 |
| $Cu^{2+}$ | 85 | 88 | 84 | 85 | 86 | 89 |
| $Zn^{2+}$ | 91 | 99 | 88 | 90 | 90 | 92 |
| $Cd^{2+}$ | 91 | 96 | 85 | 89 | 85 | 86 |
| $Hg^{2+}$ | 86 | 88 | 82 | 82 | 83 | 87 |
| $Pb^{2+}$ | 84 | 89 | 92 | 93 | 89 | 92 |

*Eluent volume = 60 mL and 50 mL for 0.02 M and 0.2 M electrolytes respectively*
*Maximum deviation in % elution of metal ions = ±2*

### Table 3.8 *Binary separations of transition and heavy metal ions using ZrD*

| **Metal ion pairs** | **Separation factor(~)** | **Eluent** | **Metal ion loaded [mg]** | **Metal ion Eluted [mg]** | **Elution [%]** |
|---|---|---|---|---|---|
| $Zn^{2+}$-$Co^{2+}$ | 5.47 | a) 0.2 M Citric acid ($Zn^{2+}$)<br>b) 0.2 M $HNO_3$ ($Co^{2+}$) | 9.15<br>8.25 | 8.21<br>6.55 | 89<br>82 |
| $Zn^{2+}$-$Cu^{2+}$ | 9.55 | a) 0.2 M Citric acid ($Zn^{2+}$)<br>b) 0.2 M $HNO_3$ ($Cu^{2+}$) | 9.15<br>8.89 | 8.89<br>6.13 | 97<br>68 |
| $Ni^{2+}$-$Cu^{2+}$ | 7.15 | a) 0.2 M $HClO_4$ ($Ni^{2+}$)<br>b) 0.2 M $HNO_3$ ($Cu^{2+}$) | 8.21<br>8.89 | 7.88<br>6.19 | 96<br>69 |
| $Co^{2+}$-$Cu^{2+}$ | 1.76 | a) 0.2 M Citric acid ($Co^{2+}$)<br>b) 0.2 M $HNO_3$ ($Cu^{2+}$) | 8.25<br>8.89 | 6.60<br>6.05 | 80<br>68 |
| $Cd^{2+}$-$Hg^{2+}$ | 5.29 | a) 0.2 M Citric acid ($Cd^{2+}$)<br>b) 0.2 M $HNO_3$ ($Hg^{2+}$) | 17.36<br>28.00 | 14.32<br>18.06 | 82<br>64 |
| $Cd^{2+}$-$Pb^{2+}$ | 2.72 | a) 0.2 M $HClO_4$ ($Cd^{2+}$)<br>b) 0.2 M Citric acid ($Pb^{2+}$) | 17.36<br>29.00 | 15.71<br>22.18 | 90<br>74 |

*Maximum deviation in % Elution = ± 2 %.*

### Table 3.9 *Simultaneous uptake of $Cu^{2+}$, $Hg^{2+}$ and $Cl^-$ using ZrD*

| **Cations and Anions** | **$Cu^{2+}$** | **$Cl^-$** | **$Hg^{2+}$** | **$Cl^-$** |
|---|---|---|---|---|
| Amount of cation/anion in solution | 1.27 | 1.41 | 1.28 | 1.41 |
| Amount of cation/anion after exchange in solution | 0.99 | 0.07 | 4.00 | 0.09 |
| Amount of cation/anion on exchange | 0.28 | 1.34 | 1.28 | 1.31 |
| Percentage uptake of cation/anion | 22 | 95 | 32 | 92 |

*Maximum deviation in Percentage uptake of cation and anion = $\underline{+}$1 %*

### Table 3.10 *Simultaneous removal of cations and anions in tap water samples using ZrD*

| **Amount of Water samples* loaded on ZrD column in (mL)** | **Cations** | **Anions** |
|---|---|---|
| | **$Ca^{2+}$** | **$Cl^-$** |
| 10 | 50 | 70 |
| 10 | 37 | 40 |
| 10 | 28 | 32 |
| 10 | 15 | 23 |
| 10 | 12 | 19 |
| 10 | 7 | 11 |
| 10 | - | - |
| Total = 70 | 149 | 195 |
| Total Amount of cations and anions in mg/lit | 300 $mg.L^{-1}$ | 289 $mg.L^{-1}$ |

**Water samples from our institute region*

## 3.12 RESULTS AND DISCUSSION-PART-II

### *Structural studies for ZrT*

Physical and ion exchange characteristics of ZrT are presented in **(Table 3.11)**. ZrT was obtained as hard glassy transparent granules. A gel is formed when an aqueous solution of TETA is added to an aqueous solution of $ZrOCl_2$ (pH=1). The solution first turns neutral (pH=7) and then basic (pH=9). The gel formed is entirely different as compared to addition of an inorganic base to $ZrOCl_2$. The gel formation probably takes place in two steps: (a) Formation of hydrous $ZrO_2$ gel **[24,25]** followed by (b) Surface interaction and polymerization of amine molecules involving weak and strong bonding, resulting in the formation of a macro-particle **[24,25]** which can be formulated as $[(ZrO)_n(TETA)_n](OH)_n$ **(Figure 3.21)** .

Elemental analysis for ZrT shows % Zr = 50.49, % C = 16.52, % N = 15.21 which matches well with formula $[(ZrO)_8(C_{24}H_{60}N_{16})](OH)_4$. Further, the presence of Zr and N is confirmed by EDX (**Figure 3.22**).

In FTIR spectrum of ZrT, sharp bands are expected in the region ~3300cm$^{-1}$ (–NH stretching frequency) and at ~3400cm$^{-1}$ (-OH stretching frequency), indicating presence of free -$NH_2$ groups and -OH in ZrT. However, the FTIR (**Figure 3.23**), spectrum of ZrT shows a broad band in the region ~3400-3220 cm$^{-1}$ which is probably due to merging of -OH and -NH stretching frequency. Band at~1580 cm$^{-1}$ is attributed to C-C stretching vibration, while, band at ~1360 cm$^{-1}$ is attributed to C-N bending.

Since the unit Zr-TETA in ZrT is positively charged, it therefore behaves as an anion exchanger where –OH part of ZrT behaves as the anion exchange unit. The pH titration curve **(Figure 3.24)** of ZrT exhibits mono functional behavior **[16, 17, 24]**. When ZrT was kept in contact with a solution of sodium nitrate, no release of $H^+$ was observed. However, the presence of NaOH was tested by phenolphthalein indicator (which turns the solution pink) confirming -OH as anion exchange sites.

It is quite clear that the component [Zr(TETA)] contains free amino groups, offering chelating sites to metal ions and behaves as the cation exchange unit. Due to lone pair of electrons present on the nitrogen atom of amine groups (**Figure 3.21**), ZrT can act as chelating exchanger. The chelating property of ZrT was studied by a batch process. When ZrT was treated with $Cu^{2+}$ salt solution it turns to a deep blue color confirming the chelation of $Cu^{2+}$ with ZrT. Accordingly, $Cu^{2+}$ chelated ZrD could be depicted as proposed **(Figure 3.25).**

The presence of $Cu^{2+}$ on exchanger was confirmed by scanning an FTIR spectra of $Cu^{2+}$ exchanged ZrT, in which the ~1360 $cm^{-1}$ band shifts to ~1460 $cm^{-1}$ due to coordination of $Cu^{2+}$ with nitrogen atom of amine group(**Figure 3.23**). From UV-DRS spectrum for ZrT (**Figure 3.26**), it is evident that $Cu^{2+}$ chelated ZrT exhibits peak around 500 nm which could be attributed to d–d transition band of a $Cu^{2+}$ ion centered in pseudo-octahedral environment **[26]**. EDX **(Figure3.27)** is also supportive to $Cu^{2+}$ exchanged ZrD. NMR spectra of ZrT (**Figure 3.28)** exhibits a peak at $\delta$ 4.57 which corresponds to a singlet for proton of secondary amine group ($-Zr-N\underline{H}-CH_2-$), while peak at $\delta$2.62 and $\delta$2.47 corresponds to triplet of methylene protons ($-Zr-NH-CH_2-C\underline{H}_2-NH-$) and ($-Zr-NH-C\underline{H_2}-$ $CH_2-NH-$), which shift to $\delta$7.02, $\delta$3.10 and $\delta$3.43 respectively (**Figure 3.29**) attributed to $Cu^{2+}$ chelated ZrT.

Anion exchange capacity was determined for $Cl^-$, $Br^-$, $Cr_2O_7^{2-}$, $F^-$ and $As_2O_4^{3-}$. The AEC values in meq.$g^{-1}$ are presented in **(Table 3.11)**.

TGA **(Figure 3.30)** of ZrT exhibits two regions of weight loss. The first weight loss in the temperature range 30-150°C could be attributed to loss of moisture/hydrated water. A second weight loss in the temperature range 150-500 ºC, is attributed to dehydoxylation, and decomposition of the organic moiety. The thermal behavior of the materials is further supported by the effect of calcination on AEC. As observed from **(Table 3.11)**, AEC values decrease as calcination temperature increases. Decrease in AEC with increasing temperature could be attributed to dehydroxylation and decomposition of organic moiety.

The absence of sharp peaks in the XRD **(Figure 3.31)** of ZrT indicates amorphous nature of the materials. SEM image of ZrT **(Figure 3.32)** shows irregular morphology of the material. When using ion exchangers, it is to be subjected to various environments and chemical media. A study on the chemical stability of ZrT shows that it is stable in acids, bases and organic solvent media. No transmetalation or zirconium metal washout is also observed, confirming the ZrT moiety to be the rigid framework.

### *Cation exchange properties of ZrT*

A plot of the fractional attainment of equilibrium $U(^{2:})$ versus time (*t*) **(Figure 3.33)** in case of $Cu^{2+}$ shows that the exchange equilibrium for ZrT appears to have attained within 6 h. For all studies therefore a maximum equilibrium time of 6h was allowed.

The effect of pH on the sorption behaviour of metal ions (under study) have been presented in (**Table 3.12).** It is observed that at pH values less than ~3, very less sorption has been observed for all metal ions. The lack of sorption at low pH could be attributed to high concentration of hydrogen ions competing with the metal ions for sorption/exchange sites. The observed order for % uptake of metal ion at optimum pH, is $Cu^{2+}$ > $Ni^{2+}$ > $Zn^{2+}$ > $Co^{2+}$ (amongst transition metal ions) and $Hg^{2+}$ > $Pb^{2+}$ > $Cd^{2+}$ (amongst heavy metal ions)**.**

It is observed that with increase in metal ion concentration, $K_d$ values increase. Above a particular concentration $K_d$ values are constant attributed to the fact that at lower concentrations, almost all the ions are exchanged due to availability of exchangeable sites, which are not available at higher concentrations. Results are presented in (**Table 3.13).**

The distribution coefficient ($K_d$) values evaluated at optimum conditions using ZrT have been presented in **(Table 3.14)**. $K_d$ values in aqueous medium follows the order: $Cu^{2+}$ > $Ni^{2+}$> $Zn^{2+}$ > $Co^{2+}$ amongst the transition metal ions and $Hg^{2+}$> $Pb^{2+}$ > $Cd^{2+}$ amongst the heavy metal ions.

### *Elution and Separation Studies using ZrT*

The elution behaviour of transition metal ions and heavy metal ions (under study) have been carried out using different electrolytes such as $HNO_3$, citric acid and $HClO_4$, of 0.02 and 0.2M concentration and results presented in **(Table 3.15)**. The % metal eluted in all cases is in the range 70 to 99 %. Good elution is observed due to presence of single metal ion and non interference of elements. Higher concentration of eluant and acids in general, are better eluants. Further, all elution curves {**(Figure 3.34(a-g)}** are symmetrical bell shaped indicating elution efficiency. Using 0.2M $HNO_3$, order of % metal eluted amongst transition metal ions is $Co^{2+}$ (99%) > $Zn^{2+}$ (88 %) > $Ni^{2+}$ (87 %) > $Cu^{2+}$ (79 %) and amongst heavy metal ions is $Cd^{2+}$ (88%) >$Pb^{2+}$ (87%) > $Hg^{2+}$ (84%). This observation is in keeping with the fact that metal ions with high $K_d$ values are less eluted and vice-versa.

Binary separations for following metal ion pairs (under study) $Co^{2+}$- $Cu^{2+}$ , $Co^{2+}$- $Zn^{2+}$, $Ni^{2+}$-$Cu^{2+}$, $Zn^{2+}$-$Cu^{2+}$, $Cd^{2+}$-$Hg^{2+}$, $Cd^{2+}$- $Pb^{2+}$ have been performed using concept of high separation factor in a particular medium. In binary separations

{**Figure 3.35(a-f)}**, separation efficiency is in the range 65–86 % amongst transition metal ions and 66-81% amongst heavy metal ions **(Table 3.16)**. In all cases of binary separation, irrespective of metal ion pair, maximum % metal eluted is, $Co^{2+}$ (86%), $Zn^{2+}$ (82%), $Ni^{2+}$ (74%), $Cu^{2+}$(68%) (amongst transition metal ions) and $Cd^{2+}$ (81%), $Pb^{2+}$ (70%), $Hg^{2+}$ (66%), (amongst heavy metal ions). This observation is in keeping with separation factor ($\alpha$) and $K_d$ values of metal ions. % metal eluted decreases with decreasing separation factor and increases with increasing separation factor and as explained earlier, metal ions with high $K_d$ values are less eluted and vice-versa.

## *Amphoteric Behaviour of ZrT*

On treating a ZrT packed column with $CuCl_2/HgCl_2$ simultaneous exchange of cations and anions occurred. Respective cations and anions present before and after exchange are presented in **(Table 3.17)**. Further, the presence of exchanged $Cu^{2+}$, $Hg^{2+}$ and $Cl^-$ on ZrT is confirmed by EDX. **(Figure 3.36 and 3.37)**.

## *Case study*

Practical utility of ZrT has been demonstrated in a case study. Simultaneous exchange of cations and anions occurred on treating a ZrT packed column using tap water sample from our institute region. Analysis of water sample by EDX **(Figure 3.38)** in wt. % is $Mg^{2+}$=1.93, $Ca^{2+}$ = 21.76, $Cu^{2+}$ = 1.09 and $Cl^-$ = 19.85. Since, concentration of $Cu^{2+}$ and $Mg^{2+}$ is very less we have focused towards $Ca^{2+}$ and $Cl^-$ in the present study. The initial concentration of $Ca^{2+}$ and $Cl^-$ in tap water sample was found to be 300 $mg.L^{-1}$ and 289 $mg.L^{-1}$ respectively, whereas eluent (after passing through column containing ZrT) contains 123 $mg.lit^{-1}$ and 82 $mg.lit^{-1}$ of $Ca^{2+}$ and $Cl^-$ respectively.The water samples were analyzed for $Ca^{2+}$ and $Cl^-$ by EDTA titration and argentometric titration respectively before and after passing through the column containing ZrT. The presence of $Ca^{2+}$, $Mg^{2+}$, $Cu^{2+}$ and $Cl^-$ on ZrT column (after passing water samples) is confirmed by EDX **(Figure 3.39)**. The amount of cations and anions removed from water sample is presented in (**Table 3.18).**

## *Regeneration and reusability of Ion exchanger ZrT*

A study on regeneration and reuse of exchanger ZrT was performed as described in experimental section 3.10. It is observed that the exchanger, once used, can be converted back to its original form by desorption of the metal ions with concentrated nitric acid. A plot of % retention in $K_d$ values *vs* Number of cycles is presented in **(Figure 3.40)** which shows that % retention in $K_d$ values is almost the same upto 6 cycles, indicating that ZrT could be regenerated and reused without much decline in performance.

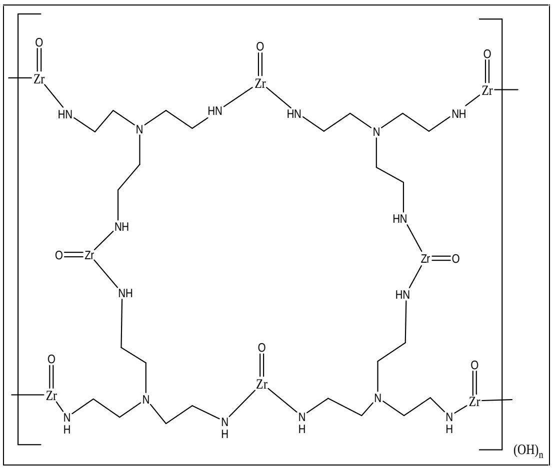
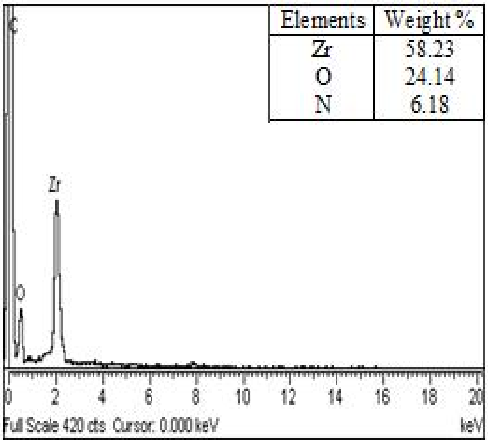


**Figure 3.21** ***Proposed Structure of ZrT Gel***



| Elements | Weight % |
|---|---|
| Zr | 58.23 |
| O | 24.14 |
| N | 6.18 |

**Figure 3.22** ***EDX of ZrT***

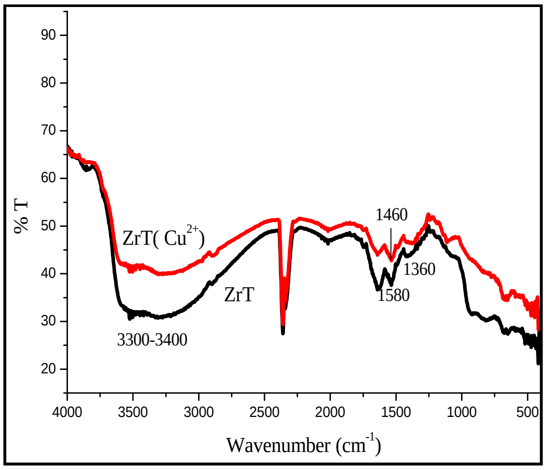


**Figure 3.23** ***FTIR spectrum of ZrT and $Cu^{2+}$ chelated ZrT***

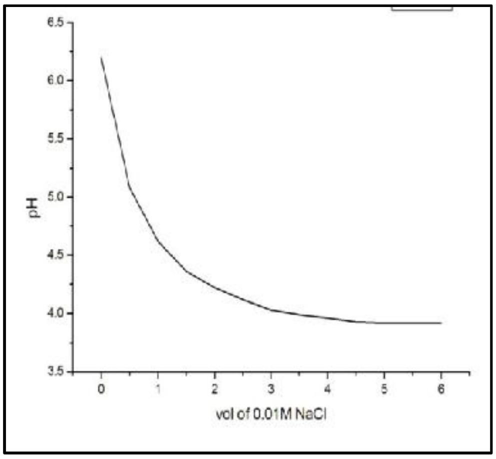


**Figure 3.24** ***pH titration curve for ZrT***

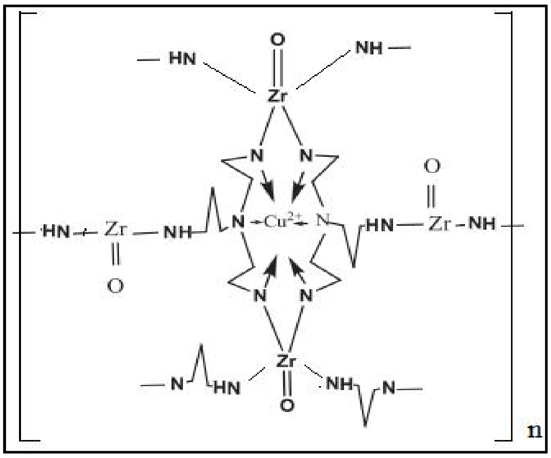


**Figure 3.25** ***Proposed Structure of $Cu^{2+}$ chelated ZrT***

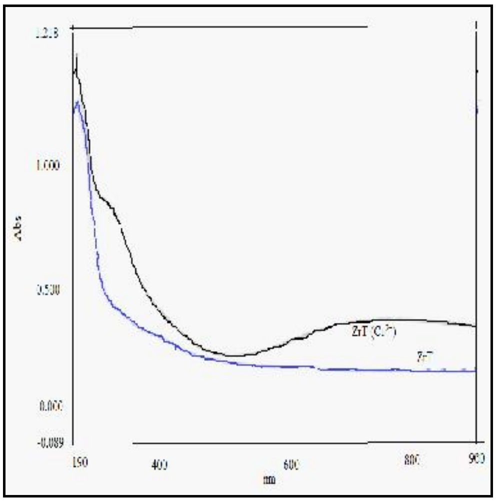
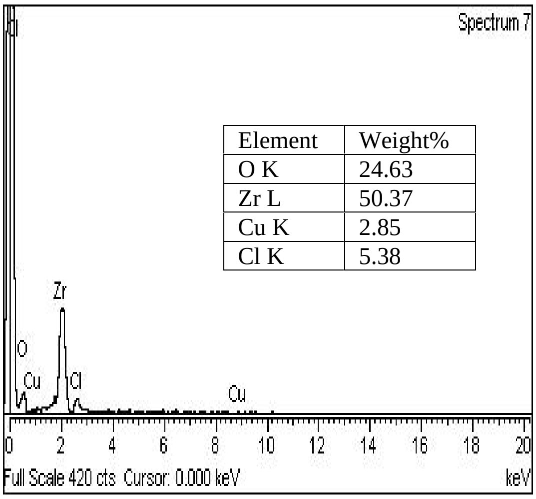


**Figure 3.26** ***UV-DRS Spectrum of ZrT and Cu$^{2+}$ chelated ZrT***



| Element | Weight% |
|---|---|
| O K | 24.63 |
| Zr L | 50.37 |
| Cu K | 2.85 |
| Cl K | 5.38 |

**Figure 3.27** ***EDX of Cu$^{2+}$ chelated ZrT***

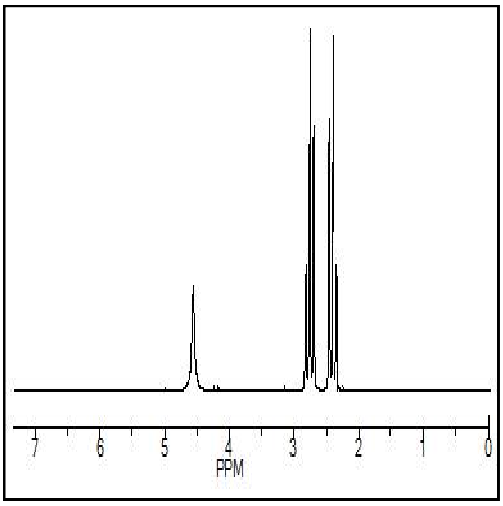


**Figure 3.28** ***NMR Spectra of ZrT***

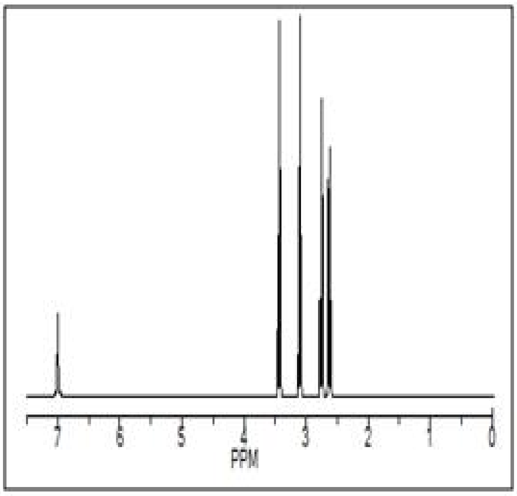


**Figure 3.29** ***NMR Spectra of Cu$^{2+}$ chelated ZrT***

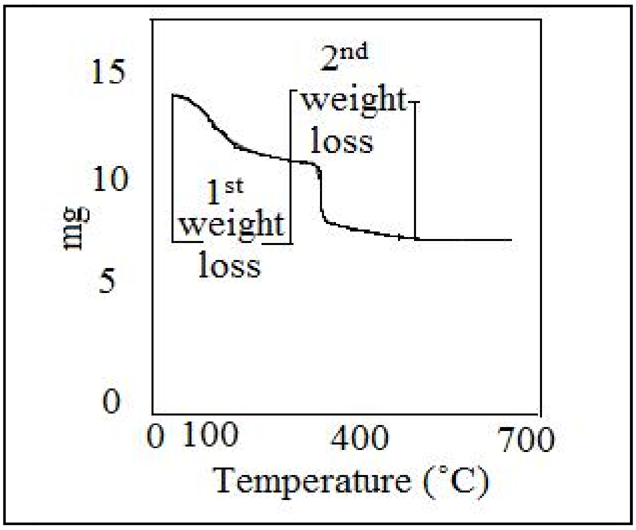


**Figure 3.30** ***TGA of ZrT***

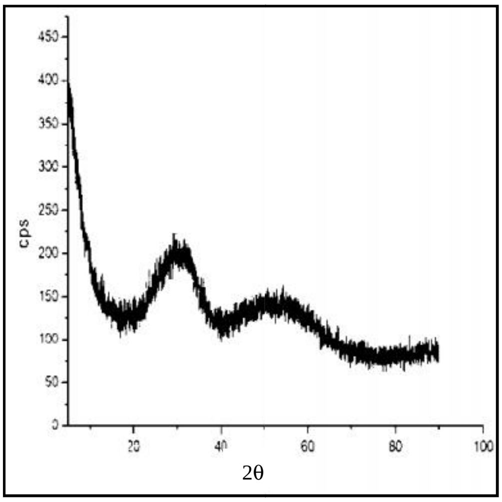


**Figure 3.31** *XRD of ZrT*

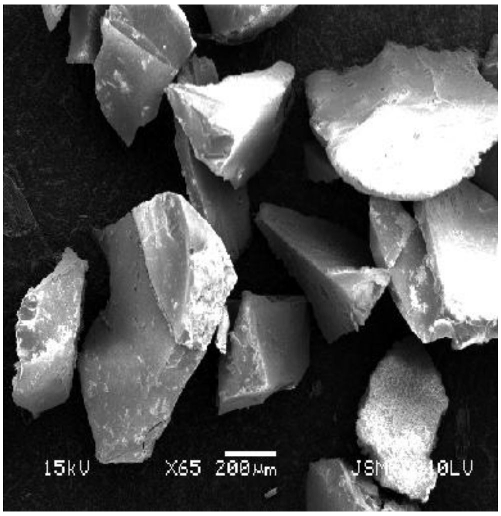


**Figure 3.32** *SEM of ZrT*

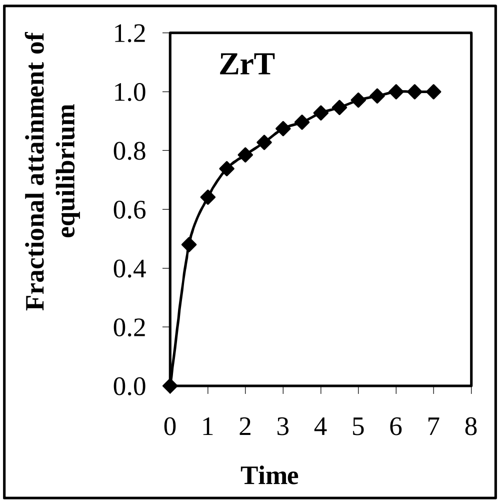
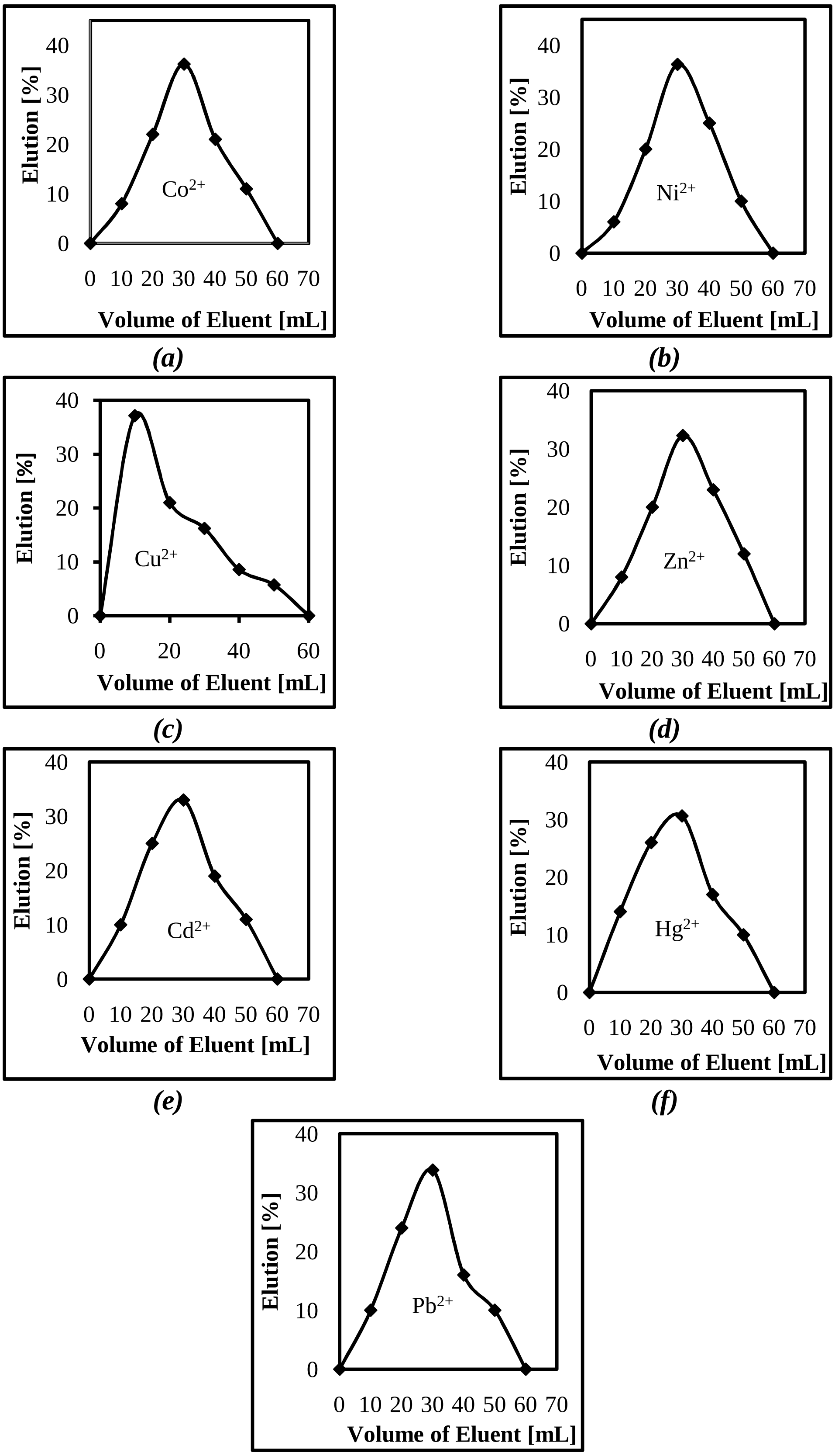


**Figure 3.33** *Plot of fractional attainment of equilibrium for $Cu^{2+}$-$H^+$ exchange vs. time using ZrT*



*(a)* *(b)* *(c)* *(d)* *(e)* *(f)* *(g)*

**Figure 3.34(a-g)** ***Elution behaviour of transition and heavy metal ions using 0.2 M $HNO_3$ as eluent (a) $Co^{2+}$; (b) $Ni^{2+}$; (c) $Cu^{2+}$; (d)$Zn^{2+}$; (e) $Cd^{2+}$; (f) $Hg^{2+}$ ; (g) $Pb^{2+}$ using ZrT***

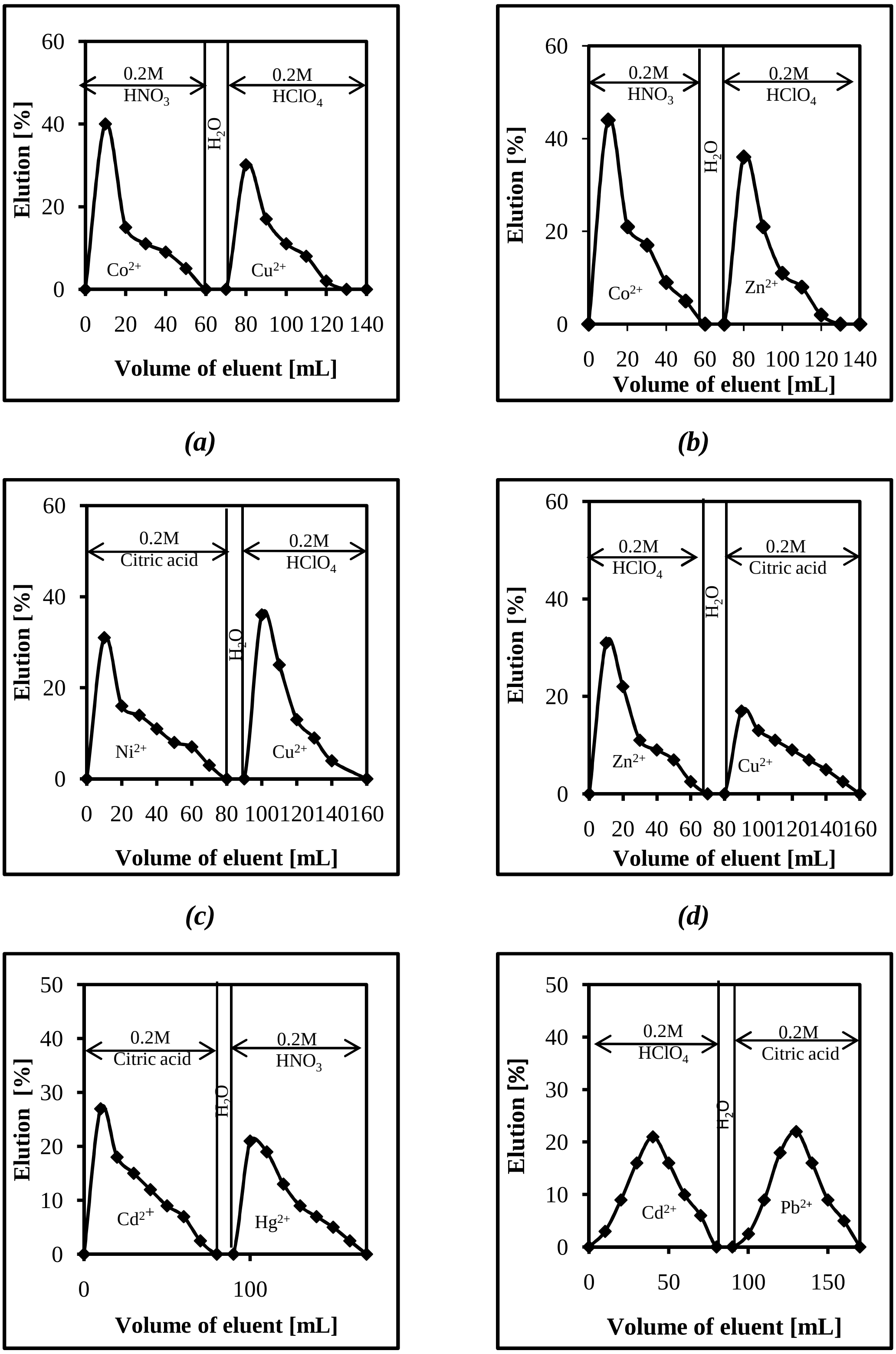
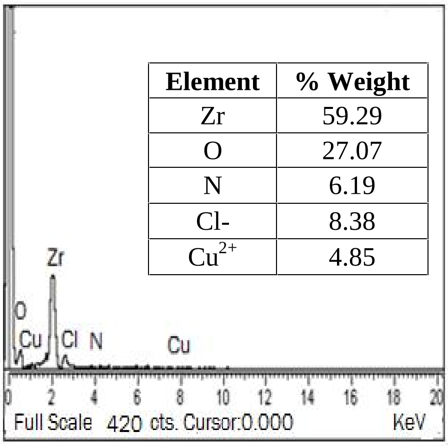
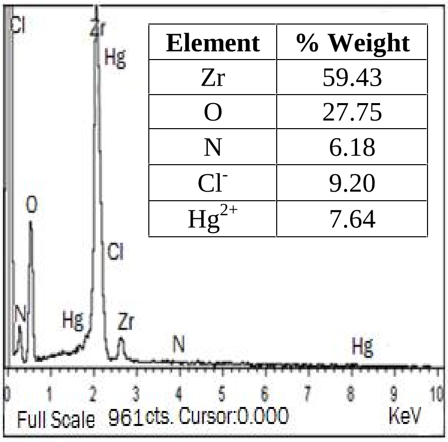


**Figure 3.35 (a-f)** ***Binary separations of transition and heavy metal ions using ZrT (a) $Co^{2+}$-$Cu^{2+}$ (b) $Co^{2+}$-$Zn^{2+}$ (c) $Ni^{2+}$-$Cu^{2+}$ (d)$Zn^{2+}$-$Cu^{2+}$ (e) $Cd^{2+}$-$Hg^{2+}$ (f) $Cd^{2+}$-$Pb^{2+}$***



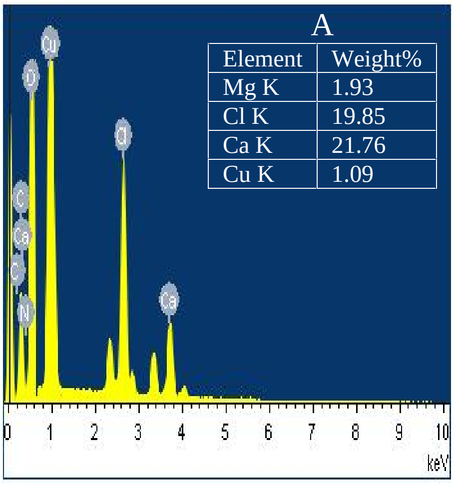
| Element | % Weight |
|---|---|
| Zr | 59.29 |
| O | 27.07 |
| N | 6.19 |
| Cl- | 8.38 |
| $Cu^{2+}$ | 4.85 |

**Figure 3.36** ***EDX of ZrT treated with $CuCl_2$***



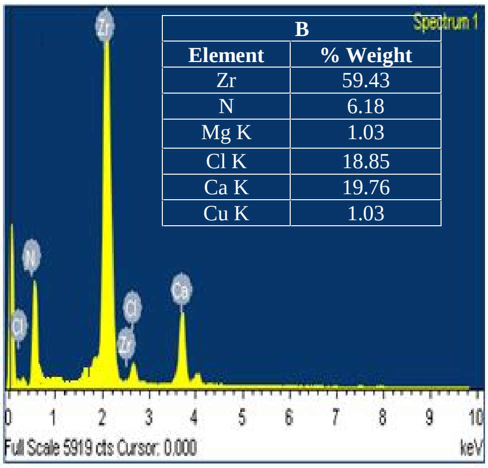
| Element | % Weight |
|---|---|
| Zr | 59.43 |
| O | 27.75 |
| N | 6.18 |
| $Cl^-$ | 9.20 |
| $Hg^{2+}$ | 7.64 |

**Figure 3.37** ***EDX of ZrT treated with $HgCl_2$***



| Element | Weight% |
|---|---|
| Mg K | 1.93 |
| Cl K | 19.85 |
| Ca K | 21.76 |
| Cu K | 1.09 |

**Figure 3.38** ***EDX of tap water sample***



| B | |
|---|---|
| **Element** | **% Weight** |
| Zr | 59.43 |
| N | 6.18 |
| Mg K | 1.03 |
| Cl K | 18.85 |
| Ca K | 19.76 |
| Cu K | 1.03 |

**Figure 3.39** ***EDX of ZrT treated with tap water sample***

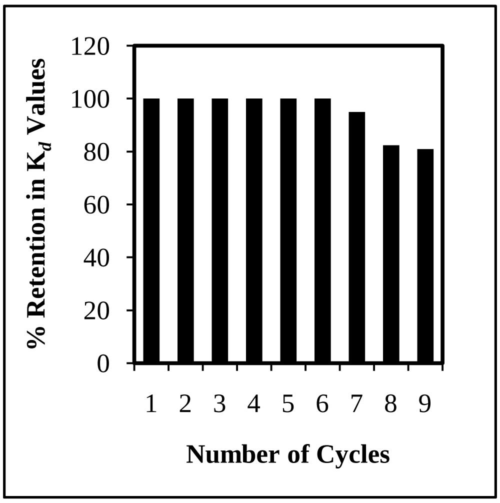


**Figure 3.40** ***Plot of % retention in $K_d$ values versus number of cycles using ZrT***

**Table 3.11** ***Physical and ion exchange characteristics of ZrT***

| **Characteristics** | **Observation** |
|---|---|
| Appearance | Glassy transparent granules |
| Particle size(range) | 250-590 µm |
| % Moisture content | 13.38 % |
| True density | 2.12g.mL$^{-1}$ |
| Apparent density | 0.71 g.mL$^{-1}$ |
| Void volume fraction | 0.79 |
| Concentration of fixed ionogenic groups | 2.64 mmol.g$^{-1}$ |
| Volume capacity of resin | 2.43mL.g$^{-1}$ |
| Nature of Exchanger | Mono functional |
| **Anion Exchange Capacity (AEC) (meq.g$^{-1}$)** | |
| Cl- | 2.76 |
| Br- | 2.20 |
| $Cr_2O_7^{2-}$ | 1.78 |
| $F^-$ | 0.96 |
| $AsO_4^{3-}$ | 1.89 |
| **Effect of calcination on AEC for $Cl^-$(meq.g$^{-1}$)** | |
| AEC (RT) | 2.70 |
| 100°C | 1.71 |
| 200°C | 1.21 |
| 300°C | 0.75 |
| 400°C | 0.41 |
| 500°C | 0.10 |
| Chemical stability | Maximum tolerable limits |
| i) Acids | 18 N $H_2SO_4$, 16 N $HNO_3$, 11.3 N HCl |
| ii) Bases | 2 N NaOH, 5 N KOH |
| iii) Organic solvents | Ethanol, Benzene, Acetone, Acetic acid |

**Table 3.12** ***Effect of pH on adsorption of metal ions using ZrT***

| **pH** | **Percentage Uptake of metal ions** | | | | | | |
|---|---|---|---|---|---|---|---|
| | **$Co^{2+}$** | **$Ni^{2+}$** | **$Cu^{2+}$** | **$Zn^{2+}$** | **$Hg^{2+}$** | **$Cd^{2+}$** | **$Pb^{2+}$** |
| 1 | 7.78 | 11.76 | 26.67 | 9.17 | 16.67 | 18.00 | 13.41 |
| 2 | 5.77 | 25.45 | 45.62 | 16.73 | 34.29 | 28.26 | 22.00 |
| 3 | 15.45 | 37.74 | 67.35 | 44.35 | 49.49 | 47.87 | 84.55 |
| 4 | **23.90** | **53.58** | 86.23 | 50.82 | **94.69** | **64.40** | 63.7 |
| 5 | 22.11 | 39.00 | **95.76** | **63.12** | 69.80 | 63.32 | **91.44** |

*After 6 pH = precipitation take place.*

**Table 3.13** ***Distribution coefficient ($K_d$) values ($mL \cdot g^{-1}$) evaluated varying metal ion concentration in aqueous medium using ZrT***

| **Concentration (M)** | **Distribution Coefficient ($K_d$)** | | | | | | |
|---|---|---|---|---|---|---|---|
| | **$Co^{2+}$** | **$Ni^{2+}$** | **$Cu^{2+}$** | **$Zn^{2+}$** | **$Cd^{2+}$** | **$Hg^{2+}$** | **$Pb^{2+}$** |
| 0.002 | N.S | NS | 220 | NS | NS | 280 | 190 |
| 0.004 | N.S | 50 | 390 | NS | NS | 469 | 245 |
| 0.006 | 29 | 110 | 560 | 71 | 85 | 651 | 363 |
| 0.008 | 40 | 290 | 720 | 109 | 180 | 756 | 660 |
| 0.01 | 69 | 380 | 860 | 260 | 240 | 806 | 870 |
| 0.012 | **78** | 490 | 910 | **282** | 308 | 920 | **923** |
| **0.014** | **-** | **567** | **1040** | **-** | **314** | **1045** | 920 |
| 0.016 | - | 563 | 1038 | - | - | - | - |

*NS = No Sorption, Maximum deviation in $K_d$ values = ± 3*

**Table 3.14** ***Distribution coefficient ($K_d$) ($mL \cdot g^{-1}$) evaluated at optimum conditions in aqueous and various electrolyte media/concentration using ZrT***

| **Metal Ions** | **OC** | **DIW** | **0.02M $HNO_3$** | **0.2 M $HNO_3$** | **0.02M Citric acid** | **0.2M Citric acid** | **0.02 M $HClO_4$** | **0.2 M $HClO_4$** |
|---|---|---|---|---|---|---|---|---|
| $Co^{2+}$ | 0.012 | 78 | 23 | N.S | 109 | 77 | 221 | 185 |
| $Ni^{2+}$ | 0.014 | 567 | 123 | 89 | 23 | N.S | 234 | 125 |
| $Cu^{2+}$ | 0.014 | 1039 | 345 | 164 | 307 | 98 | 348 | 97 |
| $Zn^{2+}$ | 0.012 | 283 | 130 | 99 | 39 | 55 | 16 | 25 |
| $Cd^{2+}$ | 0.014 | 314 | 189 | 169 | 249 | 120 | 98 | 29 |
| $Hg^{2+}$ | 0.014 | 1045 | 200 | 49 | 756 | 398 | 269 | 193 |
| $Pb^{2+}$ | 0.012 | 923 | 389 | 209 | 95 | 29 | 159 | 109 |

*$K_d$*Values obtained at optimum condition [Optimum metal ion concentration (OC), Optimum pH of solution and maximum equilibrium time]; DIW = Deionized water, Maximum deviation in $K_d$ values = ± 3.*

**Table 3.15** ***Percentage elution (% E) of metal ions in different electrolyte media using ZrT***

| **Metal Ions** | **0.02M $HNO_3$** | **0.2 M $HNO_3$** | **0.02M Citric acid** | **0.2M Citric acid** | **0.02 M $HClO_4$** | **0.2 M $HClO_4$** |
|---|---|---|---|---|---|---|
| $Co^{2+}$ | 97 | 99 | 91 | 96 | 91 | 94 |
| $Ni^{2+}$ | 86 | 87 | 83 | 84 | 85 | 87 |
| $Cu^{2+}$ | 75 | 79 | 73 | 75 | 70 | 71 |
| $Zn^{2+}$ | 85 | 86 | 83 | 88 | 81 | 84 |
| $Cd^{2+}$ | 85 | 88 | 76 | 79 | 81 | 84 |
| $Hg^{2+}$ | 75 | 79 | 82 | 84 | 80 | 83 |
| $Pb^{2+}$ | 85 | 87 | 84 | 86 | 87 | 88 |

*Eluent volume = 60 mL and 50 mL for 0.02 M and 0.2 M electrolytes respectively*
*Maximum deviation in % elution of metal ions = ±2*

**Table 3.16** *Binary separations of transition and heavy metal ions using ZrT*

| Metal ion pairs | Separation factor(~) | Eluent | Metal ion loaded [mg] | Metal ion Eluted [mg] | Elution [%] |
|---|---|---|---|---|---|
| $Co^{2+}$-$Cu^{2+}$ | 13.32 | a) 0.2 M $HNO_3$ ($Co^{2+}$)<br>b) 0.2 M $HClO_4$ ($Cu^{2+}$) | 8.25<br>8.89 | 6.99<br>6.12 | 84<br>68 |
| $Co^{2+}$-$Zn^{2+}$ | 3.62 | a) 0.2 M $HNO_3$ ($Co^{2+}$)<br>b) 0.2 M $HClO_4$ ($Zn^{2+}$) | 8.25<br>9.15 | 7.12<br>7.23 | 86<br>79 |
| $Ni^{2+}$-$Cu^{2+}$ | 1.82 | a) 0.2 M Citric acid ($Ni^{2+}$)<br>b) 0.2 M M $HClO_4$ ($Cu^{2+}$) | 8.21<br>8.89 | 6.1<br>6.01 | 74<br>67 |
| $Zn^{2+}$-$Cu^{2+}$ | 3.67 | a) 0.2 M $HClO_4$ ($Zn^{2+}$)<br>b) 0.2 M Citric acid ($Cu^{2+}$) | 9.15<br>8.89 | 7.56<br>5.8 | 82<br>65 |
| $Cd^{2+}$-$Hg^{2+}$ | 3.32 | a) 0.2 M Citric acid ($Cd^{2+}$)<br>b) 0.2 M $HNO_3$ ($Hg^{2+}$) | 17.36<br>28.00 | 14.23<br>18.56 | 81<br>66 |
| $Cd^{2+}$-$Pb^{2+}$ | 2.93 | a) 0.2 M $HClO_4$ ($Cd^{2+}$)<br>b) 0.2 M Citric acid ($Pb^{2+}$) | 17.36<br>29.00 | 13.78<br>20.45 | 79<br>70 |

*Maximum deviation in % Elution = ± 2 %.*

**Table 3.17** *Simultaneous uptake of $Cu^{2+}$, $Hg^{2+}$ and $Cl^-$ using ZrT*

| Cations and Anions | $Cu^{2+}$ | $Cl^-$ | $Hg^{2+}$ | $Cl^-$ |
|---|---|---|---|---|
| Amount of cation/anion in solution | 1.27 | 1.41 | 1.28 | 1.41 |
| Amount of cation/anion after exchange in solution | 0.52 | 0.04 | 0.14 | 0.06 |
| Amount of cation/anion on exchange | 0.74 | 1.39 | 1.14 | 1.35 |
| Percentage uptake of cation/anion | 58 | 98 | 89 | 95 |

*Maximum deviation in Percentage uptake of cation and anion = $\underline{+}$1 %*

**Table 3.18** *Simultaneous removal of cations and anions in tap water samples using ZrT*

| Amount of Water samples* loaded on ZrT column in (mL) | Cations | Anions |
|---|---|---|
| | $Ca^{2+}$ | $Cl^-$ |
| 10 | 57 | 80 |
| 10 | 41 | 43 |
| 10 | 35 | 32 |
| 10 | 25 | 27 |
| 10 | 14 | 13 |
| 10 | 5 | 11 |
| 10 | - | - |
| Total = 70 | 177 | 207 |
| Total Amount of cations and anions in mg/lit | 300 mg.$L^{-1}$ | 289 mg.$L^{-1}$ |

**Water samples from our institute region*

## 3.13 CONCLUSIONS

Oxides and hydrous oxides of Zr, Ti, Fe, Al, Nb, Cr, Th, etc. exhibit amphoteric behaviour, however the major drawback as amphoteric exchangers is their high solubility in acids or bases, and poor performance in column operations**[3,4]**. Succinylated mercerized cellulose modified with triethylenetetramine and polyethyleneimine bonded to silica gel involves tedious synthesis strategies **[18].**

In the present endeavour a new and novel, amphoteric ion exchanger ZrD and ZrT have been synthesized by a simple sol-gel route using inexpensive and easily available chemicals. ZrD and ZrT exhibit good affinity for anions ($Cl^-$, $Br^-$, $F^-$ and $AsO_4^{3-}$) as well as cations ($Cu^{2+}$, $Hg^{2+}$, $Pb^{2+}$).The practical applicability of the materials as amphoteric exchangers has been well established through case studies including regeneration and reuse. ZrD and ZrT can be used upto 4 and 6 cycles respectively without much decline in performance. The study reveals the promising use of ZrD and ZrT as amphoteric exchangers.

# REFERENCES

[1] Samczynski Z, Dybczynski R, *Some examples of the use of amphoteric ion exchange resins for inorganic separations*, **J Chromatogr A**, 789(1997)157–167.

[2] Tongwen Xu, Ion exchange membranes: *State of their development and perspective*, **J Mem Sci,** 263(2005)1–29.

[3] Kraus K A, Philips H O, *Anion Exchange Studies. XIX. Anion Exchange Properties of Hydrous Zirconium Oxide*, **J Am Chem Soc,** 78 (1956) 249-249.

[4] Nancollas G H, Reid D S, *Calorimetric studies of ion exchange on hydrous zirconia*, **J Inorg Nucl Chem,** 31(1969)213-218.

[5] Woittiez J J R, la Cruz M, Tangonan D, *Determination of Cd, Mo, Cr, and Co in Biological Materials by RNAA*, **J Radioanal Nucl Chem,** 158(1992)313-321.

[6] Moeller P, Dulskp I, Luck P, *Determination of rare earth elements in seawater by inductively coupled plasma-mass spectrometry,* **Spectro Chem Acta,** 47B(1992)1379-1387.

[7] Maihara V A, Gallorini M, Vasconcellos M B A, *Radiochemical Separation for the Certification of Some Trace Elements in Biological Reference Material by Neutron Activation Analysis,* **J Radioanal Nucl Chem**, 198(1995)343-348.

[8] Jimbo T, Higa M, Minoura N, Tanioka A, *Surface characterization of poly(acrylonitrile) membrane graft-polymerized with ionic monomers as revealed by zeta potential measurement,* **Macromolecules,** 31(1998)1277-1284.

[9] Matsumoto H, Koyama Y, Tanioka A, *Preparation and characterization of novel weak amphoteric charged membrane containing cysteine residues,* **J Collo Inter Sci,** 239(2001)467-476.

[10] Nonaka T, Matsumura S, Ogata T, Kurihara S, *Synthesis of amphoteric polymer membranes form epithiopropylmethacrylate-butylmethacrylate-butylmethacrylate-N,N dimethylaminopropyl acrylamide-methacylic acid copolymer and the permeation behavior of various solutes through the membranes,* **J Mem Sci,** 212(2003)39-53.

[11] Alexandratos S D, *Ion-Exchange Resins: A Retrospective from Industrial and Engineering Chemistry Research,* **Ind Eng Chem Res,** 489(2009)388–398.

[12] Beauvais S, Alexandratos S D, *Polymer- Supported reagent for the selective complexation of metal ions: an overview,* **Recat Funct Polym,** 36(1998)113-123.

[13] Kaliyappan T, Kahana P, *Co-ordination polymers*, **Prog Polym Sci**, 25(3)(2000)343-370.

[14] Warshawsky A, Kahana N, Kampel V, Rogachev I, Meinhardt E, Kautzmann R, Cortina J L, Sampailo C, *Ion exchange resins for gold cyanide extraction containing a piperazine functionality, 1. Synthesis and physico-chemical properties,* **Macromol Mater Eng,** 283(2000)103-114.

[15] Bozena B N, Trochimaczuk A W, Jermakowicz-Bartkowiak D, Jezierska J, *Synthesis and some sorption properties of anion exchangers bearing ligand of different length with guanidyl and biguanidyl groups,* **Polymer**, 43(2002)1061-1068.

[16] Rawat J P, Masqod A, *Thorium Triethanolamine as a New Chelating Material and an Anion- exchanger,* **J Indian Chem Soc,** Vol.-LXV(1988)285-287.

[17] Rawat J P, Masqod A, Hasan M, Aziz A, Singh B, *Zirconium–Bis (triethylamine): A New Class of Chelate Ion and Anion Exchanger,* **J Indian Chem Soc**, Vol-LXI(1985)2619-2626.

[18] Gurgel L Vi A, Gil F, *Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by succinylated mercerized cellulose modified with triethyleneteramine,* **Carbohydrate Polymers,** 77(2009)142-149.

[19] Helfferich F., *Ion exchange.* Mcgraw-hill, new york (1962).

[20] Kunin R, *Ion Exchange Resin*. Wiley, london (1958).

[21] Thakkar R, Chudasama U, *Synthesis and characterization of zirconium titanium phosphate and its application in separation of metal ions,* **J Hazard Mater**,172(2009)129–137.

[22] Jeffery G H, Bassett J, Mendham J, Denney R C, In: *Vogel's Text Book of Quantitative Inorganic Analysis*, 5th ed.; Longman Group Green: London (1978).

[23] Gopalan R, Amirtha A, Wilfred Sugumar R, *A Laboratory Manual for Environmental Chemistry*, I. K. Intentional Publishing House, New Delhi, India (2009).

[24] Qureshi S Z, Ahmad I, Asif G, Rahman N, *Synthesis and Characterization of a New Inorganic Ion Exchange Material: Zirconium(IV) Phenylethylamine,* **Ann Chim Fr**, 21(1996) 593-608.

[25] Clearfield A, *Role of Ion Exchange in Solid State Chemistry*, **Chem Rev,** 88(1988)125-148.

[26] Marion M C, Garbowski E, Primet M, *Physicochemical properties of copper oxide loaded alumina in methane combustion,* **J Chem Soc,** 86(1990)3027-3032.