1.1 INTRODUCTION

Amongst the various separation methods outlined ion exchange method of separation is making a huge impact. Ion exchange is now a well established technique and is applied in many industrial processes and chemical laboratories.

Ion exchange resins have been broadly classified as - **cation exchange resins-** those of the resins which are capable of exchanging cations and **anion exchange reins-** those which are capable of exchanging anions. Both cation and anion exchange resins are organic in nature. These resins have been further classified and categorized by the nature of functional groups attached to a matrix – (I) Strong acid and weak acid cation exchangers, (II) strong base, and weak base anion exchangers.

Other classes of ion exchangers are Chelating ion exchangers, Liquid ion exchangers, Organic ion exchangers and Inorganic ion exchangers which includes, Clay minerals, Zeolites, Hetropoly acid salts, Oxides/ hydrous oxides, Insoluble hexacyanoferrates and Tetravalent metal acid salts (TMA).

"Tetravalent Metal Acid (TMA) Salts" have been researched since the last 50 years, and have emerged as promising advanced materials owing to their good thermal stability, chemical resistivity, resistance towards ionizing radiations, and found important applications in the area of ion exchange, catalysis and solid state proton conduction. An extensive literature on TMA salts, exists today, which have been reviewed and detailed in four books **[1-4]**.

Salient features of tetravalent metal acid (TMA) salts

- TMA salts are cation exchangers, possessing the general formula M(IV) $(HXO_4)_2.nH_2O$, where M(IV) = Zr, Ti, Sn, Ce, Th etc. and X = P, Mo, As, Sb, W etc.
- The materials possess structural hydroxyl groups, the H^+ of the –OH being the exchangeable sites, due to which the material possesses cation exchange properties.
- TMA salts can be prepared both in amorphous and crystalline forms that exhibit selectivity for certain metal ions.
- The materials possess granular nature and can be obtained in a range of mesh sizes, very suitable for column operations.

- The materials are generally hard and range in physical appearance from totally opaque to transparent.
- TMA salts have shown a great promise in preparative reproducibility and ion exchange behavior.
- TMA salts exhibit both thermal and chemical stability.

When a tetravalent metal is treated with phosphoric acid/Na salts of phosphoric acid, M – O – P bonds are formed. In this process, a number of hydroxyl groups do not participate in the condensations which are referred to as pendant hydroxyl groups or defective P – OH, H^+ of the P – OH contributing to cation exchange. TMA salts are prepared by sol gel routes of different compositions and crystallinities varying parameters such as mole ratio of reactants M : X (M = tetravalent metal, X = polyvalent anion), temperature of mixing, mode of mixing (metal salt solution to anion salt solution or vice versa), pH and rate of mixing. Variation in any of these parameters yields materials with different characteristics. The cation exchange capacity (CEC) thus depends on preparation procedure/parameters varied and hence performance as an ion exchanger. From our laboratory, TMA salts have been widely explored as cation exchangers.

1.2 HYBRID ION EXCHANGERS

Different types of metal pollutants from chemical process industries necessitates finding new ion exchangers, that have good ion exchange capacity, stability towards temperature, ionizing radiation, and oxidizing solutions and that are capable of removing toxic substances from effluents. Heavy metals when present in water in concentrations exceeding the permitted limits are injurious to health. Hence, it is very important to treat such waters to remove the metal ions present before it is supplied for any useful purpose. Out of the several investigations on developing more effective processes to treat such waste streams, ion-exchange has been widely adopted for treating heavy metal containing wastewater. Most of the ion-exchangers currently being used are commercially mass-produced organic resins.

Although organic ion-exchangers have a wide applicability, a few limitations of the organic resins have been reported. One of the severest limitations of organic resins is its poor thermal stability; for instance, the mechanical strength and removal capacity of ordinary organic ion-exchange resins tend to decrease under high temperature conditions which are frequently encountered in processing liquid radioactive waste stream **[5]**. Since organic ion-exchangers were found to be unstable at high temperatures inorganic ion-exchangers were taken as alternatives for such cases. However, the inorganic adsorbents have their own limitations. For instance, these materials, in general are reported to be not very much reproducible in behavior and fabrication of the inorganic adsorbents into rigid beads suitable for column operation is quite difficult. Further, they have generally worse mechanical and chemical strength than the organic counterparts because of their inorganic nature.

In order to overcome the above limitations of organic resins and inorganic adsorbents, many investigators have introduced inorgano–organic hybrid ion-exchangers consisting of inorganic ion-exchangers and organic binding matrices **[6]**.

Anchoring of organic units on the backbone of TMA salts is of particular interest. From our laboratory inorgano-organic ion exchangers have been prepared by anchoring organic moieties onto various TMA salts.

Inorgano-organic ion exchangers have been synthesized by anchoring chromotropic acid (4,5-dihydroxynapthalene-3,7-disulphonic acid, disodium salt), tiron (1,2-dihydroxybenzene-3,5-disulfonic acid, disodium salt), o-chlorphenol and p-chlorophenol onto TMA salts. The materials were subjected to ion exchange and instrumental methods of characterization. Distribution behaviour of several metal ions were studied and binary separations were performed. From the above studies it was concluded that the anchored ion exchangers reported presented characteristics of promising ion exchangers.

1.3 NEW DEVELOPMENTS IN ION EXCHANGE MATERIALS

There is currently high interest in engineering mixed materials (organic / inorganic) where features of the organic and inorganic components complement/amalgamate/cooperate leading to the formation of new solid-state/lattice structures and materials with new composite properties, that have the potential to provide improved and tunable properties. In all cases, there is promise of developing new materials that offer a wide range of interesting properties not seen in purely organic or purely inorganic solids. Such materials are termed as hybrid inorgano-organic compounds. This new field of materials science is expanding rapidly. Several international meetings are now devoted to this promising area of research and many review papers have been published.

M(IV) phosphates have been widely used as cation exchangers and have shown a number of advantages as an ideal host lattice **[7]**. In the tetrahedral moiety of phosphoric acid, $PO(OH)_3$, if H or OH is replaced by R (where R = alkyl or aryl possessing ionogenic groups), phosphonic acids are obtained, which when treated with tetravalent metals such as Zr, Ti, Sn, Th, Ce, etc. give rise to metal phosphonates **[8]**. They are very insoluble compounds and their structure and reactivity, can be modified and tailored for specific purposes **[9]**. Depending on the complexity of the phosphonic acid used, the resulting M(IV) phosphonate material gives rise to two or three dimensional hybrid polymeric structures. They can be described as molecularly engineered solids and represent a relatively new class of compounds **[5]**. Their preparation is an example of soft chemistry route to new materials and are obtained at low temperatures, often from aqueous.

Though several metal(IV) phosphonates have been synthesized and characterized, the focus has been on structure elucidation. These materials are interesting because of their potential utility as sorbents and supports, in the area of catalysis, as ion exchangers, proton conduction, intercalation chemistry, photochemistry and materials chemistry.

Synthetic inorganic ion exchangers of class of (TMA) salts has been an area of considerable study owing to its high selectivity for certain metal ions and excellent ion exchange behaviour. Organic derivatives of inorganic ion exchanges of the class of TMA salts is of particular interest. A major advantage of inorgano- organic hybrid materials is the rigid inorganic backbone and flexibility of the organic groupings. This flexibility creates opportunity to design compounds with specific properties such as, when the organic functionalities possess iongenic groups (-OH, -COOH, $-SO_3H$, etc.) the surface area, ion exchange capacity (IEC), surface acidity etc. can modified.

The importance of inorgano-organic hybrid materials in general and hybrid ion exchangers in particular prompted us to synthesize M(IV) phosphonates of the class of TMA salts.

Since M(IV) phosphates (where M(IV) = Zr, Ti, Sn, Ce, Th etc.) of the class of TMA salts have been widely explored as cation exchangers, it was thought of interest to explore the ion exchange properties of M(IV) phosphonates which have not been wieldy explored. Though the potential use of M(IV) phosphonates as ion exchangers has been suggested, a literature survey reveals that no systematic studies have been performed nor explored on the ion exchange characteristics of these materials.

Claw molecules of the type amino phosphonic acids have received considerable attention **[10, 11]** due to diverse binding ability/chelating ability/ effectiveness of donor group in the binding of tetravalent metal ions and contain multi-dentate building blocks. Further, the organic species incorporated in an inorganic phase, permits control of porosity, hydrophobicity/hydrophilicity, ion exchange characteristics (organic moiety containing ionogenic groups), using a sol-gel chimie douce approach.

Chapter II of the thesis is entitled as “***M(IV) phosphonates- as cation exchangers”***. Amorphous novel hybrid metal amino phosphonates, ZrATMP and TiATMP (ATMP = amino tris methylene phosphonic acid) have been synthesized by sol-gel method. ZrATMP and TiATMP have been subjected to physical, ion exchange and instrumental methods of characterization, from which it can be concluded that both ZrATMP and TiATMP exhibit promising ion exchange characteristics - good CEC values, granular nature suitable for column operation, good chemical (insoluble in aqueous, acid and organic solvent media) and thermal stability.

To explore feasibility of ZrATMP and TiATMP as cation exchangers thermodynamics, kinetics and adsorption studies were performed. The equilibrium exchange of transition metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and heavy metal ions (Cd^{2+}, Hg^{2+}, Pb^{2+}) with H^+ ions contained in Zr-ATMP and Ti-ATMP has been studied at different temperatures (303 K, 313 K, 323 K and 333 K) at constant ionic strength. On the basis of equilibrium isotherms, thermodynamic parameters such as equilibrium constant (K), standard Gibbs free energy (aG^o), standard enthalpy (aH^o) and standard entropy (aS^o) have been evaluated.

In the present study, equilibrium constant (K) values increase with increase in temperature for all metal ions under study, indicating that the metal ions have higher affinity for the exchanger and that the mechanism is ion exchange. $\Delta G°$ values for all the exchange reactions are negative and become more negative with increasing temperature indicating increase in feasibility and spontaneity of the exchange process. $\Delta H°$ is positive in all cases indicating complete dehydration of ions for exchange to take place. $\Delta S°$ values are also found to be positive in all cases and follows same trend as $\Delta H°$.

Kinetics of Ion Exchange

Ion exchange kinetics of transition metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and heavy metal ions (Cd^{2+}, Hg^{2+}, Pb^{2+}) ions with H^+ ions contained in ZrATMP and TiATMP has been studied varying temperature, applying the Nernst-Planck equation. Kinetic parameters such as self-diffusion coefficient (D_o), energy of activation (E_a) and entropy of activation (ΔS^*) have been evaluated under the conditions favouring a particle diffusion-controlled mechanism. It is expected that larger values of D_0 and ΔS^*, and smaller values of E_a indicate a faster rate of exchange. In the present study the observed order for D_0, E_a and ΔS^* for ZrATMP and TiATMP are as follow,

ZrATMP follows order: $Cu^{2+}>Ni^{2+}>Co^{2+}>Zn^{2+}$ (for transition metal ions)
$Pb^{2+}>Cd^{2+}>Hg^{2+}$ (for heavy metal ions)
TiATMP follows order: $Cu^{2+}>Zn^{2+}>Co^{2+}>Ni^{2+}$ (for transition metal ions)
$Pb^{2+}>Cd^{2+}>Hg^{2+}$ (for heavy metal ions)

Adsorption of metal ions (under study) has been performed by varying metal ion concentration, pH, contact time and temperature and Langmuir constants (b and V_m), Freundlich constants (K and $1/n$) (using Langmuir and Freundlich isotherms respectively), and R^2 values (goodness of fit criterion) have been computed by linear regression for both types of isotherms. For both ZrATMP and TiATMP, R^2 values are found to be close to unity (for both Langmuir and Freundlich isotherms) providing a good fit to the experimental data for sorption of all the metal ions studied.

Distribution coefficient (K_d) has been determined (batch process) at optimized conditions (optimum pH, optimum metal ion concentration and optimum equilibrium time) in aqueous as well as various electrolyte media/concentration (HNO_3, NH_4NO_3, $HClO_4$ and CH_3COOH of 0.2 M and 0.02 M).

Breakthrough curves have been plotted, breakthrough capacity (BTC) determined (column method) and compared with K_d values to confirm the selectivity order of metal ions.

ZrATMP follows the order: $Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+}$ (transition metal ions)
$Pb^{2+} > Cd^{2+} > Hg^{2+}$ (heavy metal ions)
} aqueous medium

TiATMP follows the order: $Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$ (transition metal ions)
$Pb^{2+} > Cd^{2+} > Hg^{2+}$ (heavy metal ions)
} aqueous medium

In the present study, K_d and BTC are observed to follow the same selectivity order, for both ZrATMP and TiATMP.

Elution behaviour of metal ions has been studied using acids and electrolytes (HNO_3, NH_4NO_3, $HClO_4$ and CH_3COOH of 0.2 M and 0.02 M). Elution of various metal ions performed towards ZrATMP and TiATMP exhibits, 79 to 99 % and 70 to 99 % elution efficiency (% E) respectively. In conclusion, acids in general, are better eluents, and metal ion exchange and elution are easy and possible with both ZrATMP/TiATMP using various electrolytes.

Based on the separation factor α a few binary and ternary metal ion separations have been performed (**Table 1**).

Table 1 *Metal ion separations performed using* ZrATMP and TiATMP

	Metal ion pairs	**Separation Factor (α)**	**Separation/Elution Efficiency range (% E)**	**Ternary Separations performed**	**Separation/Elution Efficiency range (% E)**
ZrATMP	Ni^{2+}- Cu^{2+}	3.30	75–93 %	Co^{2+}- Ni^{2+}-Cu^{2+}	59-73%
	Co^{2+}- Cu^{2+}	7.88			
	Zn^{2+}-Ni^{2+}	1.64			
	Co^{2+}- Ni^{2+}	2.38	74-91%	Hg^{2+}-Cd^{2+}- Pb^{2+}	62-75%
	Hg^{2+}-Pb^{2+}	28.89			
	Hg^{2+}- Cd^{2+}	12.88			
	Cd^{2+}- Pb^{2+}	2.24			
TiATMP	Ni^{2+}- Cu^{2+}	8.29	69–93 %	Co^{2+}-$Ni^{2+}$$Cu^{2+}$	55-70%
	Co^{2+}- Cu^{2+}	7.53			
	Zn^{2+}-Cu^{2+}	6.04			
	Ni^{2+}- Zn^{2+}	1.37	64-95%	Hg^{2+}-Cd^{2+}- Pb^{2+}	61-72%
	Hg^{2}- Pb^{2+}	3.83			
	Cd^{2+}- Pb^{2+}	1.53			
	Hg^{2+}- Cd^{2+}	5.88			

For ZrATMP and TiATMP, efficient binary separations in terms of (elution efficiency % E) is observed in all cases, attributed to high α values and symmetrical bell shaped curves. In ternary metal ion separations, for both ZrATMP and TiATMP, in all cases, three distinct peaks are observed, however, with tailing effects for every metal ion eluted. % metal eluted is also lower as compared to single and binary metal ion separations.

The most promising property of the materials ZrATMP and TiATMP is their high selectivity for copper (Cu^{2+}) and lead (Pb^{2+}) which suggests the possibility of their separation from other pollutants.

To explore the performance ability, ZrATMP and TiATMP have been regenerated and reused. It is observed that % retention in K_d values is almost ~100 % upto 4 cycles for ZrATMP and 5 cycles for TiATMP, indicating that materials could be regenerated and reused without much decline in performance.

The innumerable separation procedures published so far are almost exclusively based on the use of monofunctional ion exchangers, mostly strongly basic anion exchangers with quaternary ammonium groups and strongly acidic cation exchangers with sulfonic acid groups **[12]**. Amphoteric ion exchangers in contrast to conventional monofunctional exchangers contain anionic and cationic exchange sites, and under appropriate conditions, can retain/exchange simultaneously anions and cations from external solutions. Although it was surmised long ago **[12]**, 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 **[12]**. 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. Since these complex forming groups contain basic nitrogen atoms that can be protonated, the resins may also act as weakly basic anion exchangers.

Chapter III of the thesis entitled as "***Hybrid materials- M(IV)Polyamines as Amphoteric Exchangers*"**, deals with synthesis of new and novel, amorphous amphoteric chelating ion exchangers, by sol gel routes using inexpensive and easily available chemicals, $ZrOCl_2$ and polyamines (D = diethylene triamine and T= triethylene tetraamine) to yield zirconium diethylene triamine (ZrD) and Zirconium triethylene tetraamine (ZrT). ZrD and ZrT have been subjected to physical, ion exchange and instrumental methods of characterization. Using ZrD and ZrT anion exchange capacity (AEC) for Cl^-, Br^-, $Cr_2O_7^{2-}$, F^- and AsO_4^{3-} has been determined, and distribution coefficient K_d for Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (transition metal ions) and Hg^{2+},Cd^{2+}, Pb^{2+} (heavy metal ions) has been evaluated by batch equilibration techniques in aqueous and various electrolyte media/concentrations. Based on α the separation factor, a few binary separations have been achieved on a chromatographic column packed with ZrD/ZrT. The amphoteric behavior of ZrD and ZrT has been demonstrated by simultaneous exchange of cations Cu^{2+}, Hg^{2+} and anion Cl^- in $CuCl_2$ and $HgCl_2$. The practical applicability of ZrD and ZrT as amphoteric exchangers has been highlighted by performing a case study.

The structural formula for ZrD and ZrT is proposed as $[(ZrO)_n(DETA)_n](OH)_n$ and $[(ZrO)_n(TETA)_n](OH)_n$ respectively. Based on elemental analysis ZrD and ZrT are formulated as $[(ZrO)_6(C_8H_{18}N_6)](OH)_4$ and $[(ZrO)_8(C_{24}H_{60}N_{16})](OH)_4$ respectively.

Since the unit Zr-DETA and Zr-TETA in ZrD and ZrT are positively charged, it therefore behaves as an anion exchanger where –OH part of ZrD and ZrT behaves as the anion exchange unit. The pH titration curve of ZrD and ZrT exhibits mono functional behavior. When ZrD and ZrT were 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)] and [Zr(TETA)] contain 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, ZrD and ZrT can act as chelating exchangers. The chelating property of ZrD and ZrT were studied by a batch process. When ZrD and ZrT were treated with Cu^{2+} salt solution it turns to a deep blue color confirming the chelation of Cu^{2+} with ZrD and ZrT. Accordingly, Cu^{2+} chelated ZrD and ZrT could be depicted as proposed **(Figure 1 and 2)** respectively.

The presence of Cu^{2+} on exchanger (ZrD and ZrT) was confirmed by FTIR, UV-DRS spectra, EDX and NMR spectra.

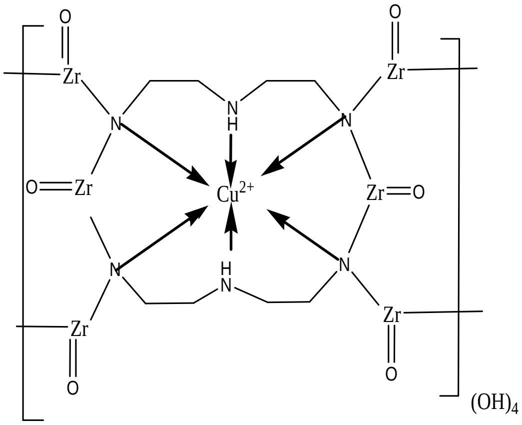	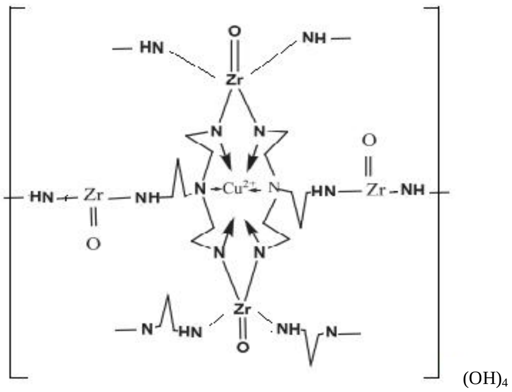
Figure 1 ***Proposed Structure of Cu^{2+} chelated ZrD***	**Figure 2** ***Proposed Structure of Cu^{2+} chelated ZrT***

For both the exchangers anion exchange capacity was determined for Cl^-, Br^-, $Cr_2O_7^{2-}$, F^- and $As_2O_4^{3-}$.

TGA of ZrD and 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 150-500ºC, could be attributed to loss of moisture/hydrated water. The thermal behavior of the materials is further supported by the effect of calcination on AEC. It is observed that 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 of ZrD and ZrT indicates amorphous nature of the materials. SEM image of ZrD and ZrT shows irregular morphology of the materials. When using ion exchangers, it has to be subjected to various environments and chemical media. A study on the chemical stability of ZrD and ZrT shows that both exchangers are stable in acids, bases and organic solvent media. No transmetalation or zirconium metal washout is observed, confirming the ZrD and ZrT moiety to be the rigid framework.

The distribution coefficient (K_d) values were evaluated at optimum conditions (optimum metal ion concentration, optimum pH of solution and maximum equilibrium time) for ZrD and ZrT. 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 for ZrD and $Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+}$ amongst the transition metal ions, and $Hg^{2+} > Pb^{2+} > Cd^{2+}$ amongst the heavy metal ions for 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. The % metal eluted in all cases is in the range 78 to 99 % for ZrD and 70 to 99 % for ZrT. All elution curves are symmetrical bell shaped in both cases indicating elution efficiency. Using 0.2M HNO_3, order of % metal eluted are as follows.

ZrD follows the order: Zn^{2+}(99%)>Ni^{2+}(96%)>Co^{2+}(93%)>Cu^{2+}(88%)(transition metals)
Cd^{2+} (96%) >Pb^{2+} (89%) > Hg^{2+} (88%) (heavy metals)

ZrT follows the order: Co^{2+}(99%)>Zn^{2+}(88%)>Ni^{2+}(87%)>Cu^{2+}(79%)(transition metals)
Cd^{2+} (88%) >Pb^{2+} (87%) > Hg^{2+} (84%) (heavy metals)

Based on the separation factor α a few binary metal ion separations have been performed using ZrD and ZrT. Efficient binary separations in terms of (elution efficiency % E) is presented in (**Table 2**).

Table 2 *Metal ion separations performed using* ZrD and ZrT

	Metal ion pairs	**Separation Factor (α)**	**Separation/Elution Efficiency range (% E)**
ZrD	Zn^{2+}-Co^{2+}	5.47	68–97 %
	Zn^{2+}-Cu^{2+}	9.55	
	Ni^{2+}-Cu^{2+}	7.15	
	Co^{2+}-Cu^{2+}	1.76	64-90 %
	Cd^{2+}-Hg^{2+}	5.29	
	Cd^{2+}-Pb^{2+}	2.72	
ZrT	Co^{2+}-Cu^{2+}	13.32	65–86 %
	Co^{2+}-Zn^{2+}	3.62	
	Ni^{2+}-Cu^{2+}	1.82	
	Zn^{2+}-Cu^{2+}	3.67	66-81 %
	Cd^{2+}-Hg^{2+}	3.32	
	Cd^{2+}-Pb^{2+}	2.93	

% 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.

On treating a ZrD and ZrT packed column with $CuCl_2$/$HgCl_2$ simultaneous exchange of cations and anions occurred. Simultaneous exchange of cations and anions also occurred on treating a ZrD and ZrT packed column using tap water sample from our institute region. The initial concentration of Ca^{2+} and Cl^- in tap water sample was found to be 300 $mg.lit^{-1}$ and 289 $mg.lit^{-1}$ respectively, whereas eluent (after passing through column containing ZrD) contains 151 $mg.lit^{-1}$ and 94 $mg.lit^{-1}$ of Ca^{2+} and Cl^- respectively, and eluent (after passing through column containing ZrT) contains 123 $mg.lit^{-1}$ and 82 $mg.lit^{-1}$ of Ca^{2+} and Cl^- respectively.

A study on regeneration and reuse of exchanger ZrD and ZrT was performed in the case of Copper ion by batch method. 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. It is observed that % retention in K_d values is almost ~100 % upto 4 cycles for ZrD and 6 cycles for ZrT, indicating that materials could be regenerated and reused without much decline in performance.

Chapter IV of the thesis entitled as "***Fabrication and utility of Chelating membranes",*** deals with the applicability of zirconium tri-ethylene tetra-amine (ZrT) gel for fabrication of hybrid chelating membrane. In the present study hybrid chelating membranes, based on cross-linked ZrT gel and poly vinyl alcohol (PVA) has been reported. The chelating membranes have been designated as ZrTETA-45, ZrTETA-50 and ZrTETA-55, based on different weight percentage of ZrT gel used to prepare the membranes. The chelating membranes have been synthesized by an acid catalyzed sol-gel process followed by chemical crosslinking via formal reaction. The membranes have been subjected to (a) physicochemical methods of characterization which include water uptake, swelling, ion exchange capacity (IEC), fixed-ion concentration, oxidative stability and hydrolytic stability. (b) electrochemical methods of characterization which include, transport number, membrane conductivity, electro-osmotic permeability and metal ion transport studies and (c) instrumental methods of characterization which include spectral analysis (ATR-FTIR), thermal analysis (TGA/DSC), DMA, XRD, SEM and EDX. Metal ion transport studies have been performed for different bivalent ions namely Mn^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}. The experiments have also been carried out using mixed metal electrolyte (equi-molar) for achieving separations.

Amongst the chelating membranes prepared of varying gel composition, crosslinked ZrTETA-55 hybrid chelating membrane exhibits strong interaction towards all metal ions, specially Cu^{2+}. Thus, thermodynamic, kinetic and adsorption studies were performed using ZrTETA-55 chelating membrane which involves effect of time, temperature, pH, adsorbent dose, and adsorbate concentration, towards adsorption of Cu^{2+}. Pseudo-first and pseudo second order kinetic models, thermodynamic parameters {(Standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°)} have been evaluated and adsorption isotherms (Langmuir and Freundlich) studied.

Prepared ZrTETA-X chelating membranes exhibited high thermal, mechanical and chemical stabilities along with good IUC and conductivity. Counter-ion transport number in the membrane phase and *i–v* characteristics of ZrTETA-X membranes suggested their specific selectivity for Cu^{2+} in comparison with other bi-valent metal cations. Adsorption studies confirmed very high uptake for Cu^{2+} in comparison to other bi-valent metal ions (Ni^{2+}, Zn^{2+}, and Mn^{2+}). Electro-dialytic separation studies of bi-valent metal cations also confirmed very high flux for Cu^{2+} in comparison to other cations. Moreover, high separation factor (3.0–4.0) for separating Cu^{2+}/Ni^{2+}, Cu^{2+}/Mn^{2+} and Cu^{2+}/Mn^{2+}, suggested practical applications of developed membrane for selective separation/recovery of Cu^{2+} from industrial waste water.

ΔH° and ΔS° values increased with temperature, while ΔG° values decreased. Thus, the Cu^{2+} adsorption on crosslinked ZrTETA-55 hybrid membrane is endothermic in nature. It was further observed that the Cu^{2+} adsorption is spontaneous and spontaneity increased with the temperature. Positive value of ΔS° suggests randomness at the solid-solution interface during adsorption.

Adsorption process of Cu^{2+} on ZrTETA-55 membrane followed second order kinetics under studied concentration range (25-100 mg. l^{-1}). Further, the values of correlation coefficients (R^2) for pseudo-first-order kinetic model are slightly lower than the pseudo-second-order kinetic model, indicating that pseudo second order kinetic model is better obeyed in comparison with the pseudo-first-order kinetic model. Based on a linearized correlation coefficient, the Langmuir isotherm model gives better fit than the Freundlich isotherm model.

REFERENCES

[1] Varshney K G and Khan A M, 1991, *Inorganic Ion Exchangers in Chemical Analysis*, (Eds.) Qureshi M and Varshney K G, CRC Press, Boca Raton, Florida.

[2] Clearfield A, 1982, *Inorganic Ion Exchange Materials*, CRC Press, Boca Raton, Florida.

[3] Clearfield A, Nancollas G H and Blessing R H, 1973, *Ion Exchange and Solvent Extraction*, (Eds.) Marinsky J H and Marcus Y, Marcel Dekker, Vol 5, New York.

[4] Amphlett C B, 1964, *Inorganic Ion Exchangers*, Elsevier, Amsterdam.

[5] Carely-Macauly K W, 1981, *Radio-active waste, advanced management methods for medium active liquid waste*, Harwood Academic.

[6] Khan A A, Alam M M, *New and novel organic–inorganic type crystalline 'polypyrrolel/polyantimonic acid' composite system: preparation, characterization and analytical applications as a cation-exchange material and Hg(II) ion-selective membrane electrode*, **Anal Chim Acta,** 504(2004)253-259.

[7] Varshney K G, Pandith H A, *Thermodynamics of the Na(I)-H(I), K(I)-H(I) and Ca(II)-H(I) exchanges on zirconium(IV)aluminophosphate cation exchanger*, **Coll Surf A**, 201(2002)1-7.

[8] Mar M, Alcantara G, Cabeza A, Maria Martinez-Lara, Miguel A G Aranda, *Synthesis and characterization of a new bisphosphonic acid and several metal hybrids derivatives,* **Inorg Chem,** 43(2004)5283-5293.

[9] Menna B, Shanon I, *Synthesis and characterization of new layered mixed metal phosphonate materials magnesium–zinc phosphonates* $Mg_{(1-x)}Zn_x(O_3PR).H_2O$ *and nickel–zinc phosphonates* $Ni_{(1-x)}Zn_x(O_3PR).H_2O$ *using mixed divalent magnesium–zinc and nickel–zinc hydroxides,* **J Mater Chem,** 12(2002)350-355.

[10] Clearfield A, *Coordination chemistry of phosphonic acids with special relevance to rare earths*, **J Alloys Compds**, 418(2006)128-138.

[11] Vivani R, Alberti G, Costantino F, Nocchetti M, *New advances in zirconium phosphate and phosphonate chemistry: Structural archetypes*, **Micro Meso Mater**, 107(2008)58–70.

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