CHAPTER 7
CONCLUSION AND SCOPE

Innovative techniques involving ion exchangers extended its presence in diverse fields stretching from conventional water softener to applications in emerging branches of technologies such as hydrometallurgy, food and beverages, petrochemical industries, potable water management and as host of other industries. The escalating applications of ion exchangers offer a big stimulus for advance study and researches in this field. Separation technologies like ion exchange and sorption intend the capability of fast and effective removal of targeted contaminants and toxic heavy metal ions from various industrial solutions. Due to high selectivity and thermal and radiation stability, inorganic cation exchangers got vast awareness in analytical chemistry and therfore in the field of separation science and technology, their development, characterizations and applications are abiding.

The survey of literature based on inorganic cation exchangers has showed that ion exchange materials with mixed metallic acid salts possess improved properties than their single salt counterparts. Reports show that mixed materials containing two anions and a cation have been widely investigated. However, not much effort has been done on mixed materials containing two cations and an anion. The quest for achieving materials with enhanced ion exchange properties, higher selectivity for toxic metal ions and improved catalytic activities led to the development of novel ion exchangers of this class. Several bimetallic inorganic cation exchangers were synthesized and they were found to be fairly stable and obsessed good ion exchange properties. Our work is very talented in the field of ion exchangers as cation substitution has fashioned materials with typical ion exchange properties and metal ion selectivities.

A simple general method was adopted for the synthesis of all the bimetallic cation exchangers, followed by conversion into the H⁺ form. Structural, morphological and optical characterizations of the synthesized materials were done by using various instrumental techniques. Elemental composition was determined by chemical analysis/EDS method. The ion exchange characteristics of the materials were assessed through the determination of ion exchange capacity, distribution/sorption studies of various metal ions in different electrolyte media, pH titration curves, effect of hydrated ionic
radii and temperature on ion exchange capacities and stability in various solvents. Various instrumental techniques provided exciting informations regarding the physicochemical properties of the exchangers.

Our study outlined in this thesis was mainly concentrated on the synthesis of ion exchangers of polyvalent bimetallic acid salts containing titanium/zirconium as one of the component. Titanium based bimetallic ion exchangers synthesized were titanium tin molybdate (TiSnMo), titanium tin tungstate (TiSnW), titanium tin selenate (TiSnSe) titanium cerium molybdate (TiCeMo), titanium cerium tungstate (TiCeW) and titanium cerium selenate (TiCeSe). The synthesized polyvalent bimetallic exchangers based on zirconium were zirconium bismuth iodate (ZrBiI), zirconium bismuth molybdate (ZrBiMo), zirconium bismuth tungstate (ZrBiW), zirconium cerium tungstate (ZrCeW), zirconium cerium molybdate (ZrCeMo) and zirconium tin molybdate (ZrSnMo). Ion exchange properties of all these materials were studied well and were subjected to various instrumental techniques for physicochemical characterization. Optical studies disclose that all the synthesized exchangers have narrow band gap energy, emphasizing the semiconducting nature of the materials. pH titration studies revealed monofunctional behaviour of the synthesized exchangers. Most of the exchangers showed high selectivity towards toxic heavy metal ion Pb²⁺. Besides this, most of the titanium based exchangers show high affinity for Bi³⁺ also. In addition to Pb²⁺ ions, TiSnSe showed high selectivity for Hg²⁺, ZrBiW and ZrCeMo showed affinity to Th⁴⁺, ZrBiMo showed high affinity towards Cu²⁺, Co²⁺ and Ni²⁺, ZrBiI showed selectivity for Co³⁺ etc. In addition to the ion exchange properties some of the synthesized exchangers proved their ability to remove toxic organic pollutants by adsorption on their surface. Hence the adsorptive removal of toxic organic dyes like methylene blue by TiSnMo, methyl red by ZrBiW, indigo carmine by TiSnMo and toxic organic pollutant phenol by TiSnW were carried out with the help of UV-Vis DRS. All these highlight the practical utility of the exchangers for the separation and removal of toxic heavy metal ions and organic pollutants from industrial effluents.

In order to acquire allied inorganic and organic materials as ion exchangers, our attempts have been made to build up a new class of composite ion exchangers by the assimilation of electrically conducting organic polymers like polyaniline and poly-o-toluidine into the matrices of inorganic precipitates of multivalent metal acid salts. These materials are attractive for the purpose of building high performance materials.
that are anticipated to provide many possibilities with better chemical, mechanical and thermal stabilities, reproducibility and having good selectivity for heavy metals signifying their useful environmental applications. In this regard, a number of inorganic-organic composite cation exchanger samples were prepared, well characterized and their applications in environmental remediation were carried out successfully. They were poly-o-toluidine zirconium bismuth tungstate (POT-ZrBiW), poly-o-toluidine zirconium cerium molybdate (POT-ZrCeMo), polyaniline titanium cerium molybdate (PANI-TiCeMo) and polyaniline titanium cerium tungstate (PANI-TiCeW). The study showed that the composite exchangers have talented features regarding the synthesis, characterization as well as cation exchange and other properties for which the exchanger is evaluated and it is also observed that the composite exchangers show better ion exchange properties than their corresponding inorganic counterparts.

Based on the differential selectivity of various metal ions by the exchangers in different electrolyte media, some analytically important binary separations were carried out on the column of synthesized exchangers and elution curves were drawn for some separations. The differential selectivity of metal ions on the exchangers also showed their practical utility in removing toxic heavy metal ions from various solutions. ZrBiMo exchanger has high selectivity towards Pb\(^{2+}\), Cu\(^{2+}\), Co\(^{2+}\) and Ni\(^{2+}\) ions in comparable to other metal ions studied. These are the most toxic pollutants drawn from most of the industries and persist in the environment as nondegradable. Hence the selectivity of the exchanger towards these metal ions showed its environmental applicability in the adsorptive removal of these metal ions from various industrial effluents.

To study the adsorption process in detail, determination of kinetic and thermodynamic parameters is important. The adsorption experiments were carried out in batch mode at ambient temperatures and evaluated some kinetic and thermodynamic parameters. Isotherm analysis showed that Pb\(^{2+}\) and Ni\(^{2+}\) follows Freundilich model, while Cu\(^{2+}\) and Co\(^{2+}\) follows Langmuir model. Kinetic studies showed that pseudo-second-order rate equation model yields better kinetic model than the first-order model. Thermodynamic studies revealed the adsorption process is spontaneous and endothermic in nature. The adsorption behavior of the exchanger was utilized in environmental remediation process by achieving the separation and removal of Pb\(^{2+}\) and
Cu$^{2+}$ from textile industry effluents, determination of Co$^{2+}$ in pharmaceutical samples and removal of Ni$^{2+}$ from storage battery effluents.

Structural hydroxyl protons present in the ion exchangers improve their catalytic activity for several organic reactions. The newly synthesized bimetallic cation exchangers TiCeMo and its poly-o-toluidine composite are found to have the ability to catalyze the degradation of hazardous organic dyes such as methyl red (MR) and crystal violet (CV) from aqueous solutions. The degradation studies were carried out with the help of UV-Vis DRS. The results of the study showed that the polyaniline composite has great degradation potential in comparison to its inorganic precipitate, due to its high surface area. The catalytic activity of the synthesized exchangers was also estimated by studying the esterification reaction between iso-amyl alcohol and acetic acid in presence of TiCeW and ZrCeW as catalysts. ZrCeW give better yield and maximum efficiency than TiCeW due to its high surface area. The study reveals the promising use of the materials as a solid acid catalysts in the synthesis of esters, the advantageous being operational simplicity, mild reaction conditions and eco-friendly nature.

The development of new ion exchange materials with the ability to inhibit the growth of microbial organisms is of great importance. Hence, our study has been focused on analysing the antimicrobial activities of newly synthesized poly-o-toluidine based composite cation exchangers POT-ZrBiW and POT-ZrCeMo against human pathogens, gram negative strains of *Escherichia coli* and gram positive strains of *staphylococcus aureus* and antifungal activity towards the organism *candida albicans*. Results indicated that the exchangers show significant antimicrobial activity towards these pathogens. The exchangers TiCeW and its polyaniline composite PANI-TiCeW are effectively used for the quantitative separation of highly toxic metal ions Cd$^{2+}$ and Zn$^{2+}$ from textile industry effluents and Th$^{4+}$ from phosphate fertilizer plant. Due to the high selectivity of TiCeSe exchanger for Pb$^{2+}$ ions, it was selected for the extractive determination of lead in ayurvedic (herbal) samples like Garbhapal Ras, Nag Bhasma, Tribang Bhasma and in various paint samples. The bimetallic cation exchanger ZrCeMo have good separation factor for Mg$^{2+}$ and Ca$^{2+}$ and hence it was used for the separation of Mg$^{2+}$ and Ca$^{2+}$ ions from dolomite samples. Satisfactory results were obtained for all analysis and hence the exchangers can be effectively used for the environmental remediation process.
The enhanced ion exchange properties and differential selectivity of the synthesized bimetallic inorganic cation exchangers over their single salt counterparts motivates us to continue studies on the synthesis, properties and analytical applications of novel materials of this class. The studies on applications of the synthesized inorganic-organic composite exchangers proved their potency in various fields and they will contribute much to find solutions of various environmental problems.

The band gap energy of the synthesized bimetallic exchangers obtained from UV-Vis DRS studies were found to be in the range of semiconducting materials and this showed their widespread applications in solar cells and other electronic devices. Bimetallic ion exchangers with cerium as one of the component were found to absorb light in the UV region and are chemically and thermally stable. These facts can be applied for the photostability of pigments by launching these exchangers and for the preparation of UV protective coatings. Cerium containing exchangers are also able to show ionic and electronic conduction. These exchangers are applicable in various fields by merging their enhanced ion exchange properties, electron exchange properties, catalytic activity, optical and electrical properties, semiconducting nature etc.

Development of ion exchange membranes also finds amazing applications in various fields. Electrodes modified by an ion exchange membrane are important in applications to electrocatalysis, electrosynthesis, electroluminescence, sensors and energy conversion. Chemical modification of electrode surface (potentiometric, voltammetric or conductometric electrodes) using ion exchangers can enhance analytical selectivity of an electrode towards one ion in comparison with the interfering ions and the benefit is the improvement of sensitivity and other characteristics of the electrochemical device. Polyaniline based composite exchangers can be employed for constructing proton conducting membrane and hence they can find applications in various electrochemical devices.

A comprehensive study of ion exchangers is however beyond the scope of this report. Nevertheless we succinctly shed light on the efficacy of the synthesized exchangers in various fields. The study can be extended to the preparation of ion selective electrodes, which provide fast, accurate and low cost analysis. The development and use of ion exchange papers in chromatographic techniques for the separation and determination of various types of species like cations, anions,
radionuclides, aminoacids, pharmaceuticals etc will contribute another important area of the study in separation science. Inorganic cation exchangers were found to have the ability of adsorbing toxic organic pollutants and pesticides, which is also an important aspect of the study and will contribute to several environmental remediation processes.

It is hoped that the studies presented in this thesis will add to the present knowledge of ion exchange and separation chemistry and in that respect this is a modest contribution to the rapidly mounting fields of analytical chemistry and separation science.