Chapter -6

SUMMARY AND FUTURE SCOPE
6.1. Outcome of present work

Monitoring the quality of water and decontamination of water containing toxic elements, above permissible limits has been a subject of topical interest. Various analytical methods and methodologies for the monitoring and removal of ultra-trace concentration of toxic metal ions have been developed. The major limitation associated with highly sensitive analytical methods is because of the fact that they are lab based methods which are not amenable for on-site quantification. Similarly the sorbents developed so far have problem of desirable selectivity and applicability for environmental conditions. It is not desirable to alter the chemical conditions of natural waters. Most of the work till date is limited to synthesizing sorbents in form of polymeric beads and resins which can be easily applied for column applications in laboratory.

In the present thesis, the scope was limited to developing functionalized polymer sorbents for removal of fluoride, mercuric and boron from various aqueous streams. Different routes of functionalization of the sorbents were studied for tailoring the properties of existing polymers. For analytical applications, special emphasis was given for synthesizing the sorbents in form of polymer sheets having fixed binding sites and reproducible geometry. The microporous sheets used for anchoring the desired polymers via different polymerization routes were commercially available poly(propylene) membranes and in-house synthesized polymer inclusion membranes.

In-situ UV irradiation is one of the methods which has been used for in situ polymerizing the desired monomers in the pores of the selected host poly(propylene) substrate. This
method of polymerization is amenable to synthesize matrix supported tailored polymer sheets for solid phase extraction of fluoride and mercuric ions from various aqueous streams. A new inorganic-organic hybrid polymer sorbents consisting of poly (bis[2-(methacryloyloxy)-ethyl]phosphate) crosslinked in the pores of two different types of substrates viz. fibrous and microporous (sheet) with varying morphology were prepared. These substrates were further conditioned for selective fluoride sorption by forming thorium complex with phosphate groups on bis[2-methacryloyloxy]-ethyl] phosphate (MEP). In order to test stability of the Th-complex in the sorbent, thorium leaching from the sorbents was studied in ground water and aqueous solutions with varying pH. ICP-MS analyses confirmed that there was no leaching of thorium from the sorbent in the treated aqueous samples. After confirming the non leachability of thorium in the sample solutions, these tailored sorbents were further studied for their selectivity towards fluoride in aqueous media having different chemical conditions. The fibrous sorbent was found to take up fluoride with a faster rate (15 min for ≈76% sorption) than the sheet sorbent. This clearly shows that the fluoride sorption characteristics varied with the physical architecture of poly(propylene) host substrates used for anchoring Th-poly(MEP). Comparison of the fluoride loading capacity with the reported sorbents showed that the loading capacity of sheet sorbent (4320 mg kg⁻¹) developed in this work was higher than many other sorbents reported in the literature.

The integrated process which couples magnetic separation together with surface complexation, adsorption, ion-exchange and solvent extraction is called as “Magnetically
Assisted Chemical Separation” (MACS). MACS has high potential for treating large volume of samples with faster rates. Therefore a fluoride ion selective magnetic sorbent has been synthesized by the encapsulation of Fe$_3$O$_4$ nanoparticles in a network of Zr(IV) complexed poly(acrylamide) (Zr–PAM).

This magnetic sorbent has been found to be efficient for the selective preconcentration of fluoride ions from natural waters. The Zr-PAM/Fe$_3$O$_4$ composite developed in the present work retains the super paramagnetic properties of Fe$_3$O$_4$ nanoparticles, and the results reveal that the sorption is rapid. The composite has a considerably higher fluoride sorption capacity (124.5 mg g$^{-1}$) compared to other super-paramagnetic fluoride sorbents reported in the literature. ICP-MS analysis showed that there was no leaching of Zr(IV) ions from the sorbent in the treated aqueous samples indicating a strong chemical binding between the Zr(IV) ions and the functional groups of PAM. Since PAM is a neutral polymer, the positive charge on ZrO$^{2+}$ ions provide binding sites for anions, particularly fluoride ions, which have a strong affinity towards Zr(IV). The water content of the synthesized composite was found to be 98 wt% suggesting that the composite has reasonably good hydrophilicity and free volume which are the properties required for sorption as the SEM images showed that the composite does not have a microporous structure. The saturation magnetization of 4.5 emu g$^{-1}$ of the magnetic composite with 10 wt% Fe$_3$O$_4$, was high enough for magnetic separation to be carried out using external magnet.
Both the polymer sorbents developed in the present work for fluoride extraction were found to be reusable after desorption of fluoride using NaOH solution. The applicability of the sorbents was tested for selective removal of fluoride from water samples collected from Channu region of Punjab, India. The fluoride concentration left in the treated samples was found to be well below the permissible limit of WHO.

Using in-situ crosslinking of a preformed polymer, a sorbent selective for boron under seawater conditions was developed. The pores of a commercially available poly(propylene) membrane were functionalized by room temperature in situ crosslinking of poly(vinylbenzyl chloride) with a cyclic diamine piperazine. The precursor membranes were chemically modified with N-methyl D-glucamine (NMDG) which is selective for boron. The specific affinity between the vicinal diols of NMDG and the boric acid leads to formation of highly stable tetradeutate complex. In addition to that the presence of an amine functional group helps in efficient chelating of boric acid by neutralizing the protons released in the formation of tetradeutate complex during complexation thus leading to increase in boron uptake. The maximum boron sorption capacity in form of boric acid determined experimentally was 28 mg g$^{-1}$ outperforming most of the sorbents reported in literature in terms of the sorption capacity. The studies also showed that trace concentrations of boron were quantitatively removed from water at neutral pH. Therefore, it can be applied easily to seawater samples having pH 6-7 without varying its chemical parameters. Due to matrix elimination in the sorption process, the sorbent based preconcentration method was extended for its applicability in the determination of boron.
by widely used curcumin method of boron determination. The selective preconcentration of boron in the NMDG-sorbent followed by its desorption makes quantification feasible in the presence of nitrate. The results obtained using the developed method was also validated using ICPMS, and the results were found to be in a reasonably good agreement.

Two type of sheet sorbents has been synthesised for the preconcentration and determination of mercuric ions in aqueous solution. These are silver nanoparticles (AgNPs) embedded poly(acrylamide) grafted poly(propylene) sheet (Ag-PAM-PP) and 1,8-octanedithiol functionalized gold coated poly(propylene) sheet (HS-octyl-S-Au-PP). The functional groups acrylamide and thiol provided the binding sites for mercury ions; whereas the in-situ formed silver nanoparticles further enhanced the mercury sorption by reducing the mercuric ions to Hg$^0$ through the galvanic reaction. The reduced mercury was held on the sheet sorbent by amalgam formation. Various factors that influence the preconcentration of mercuric ions from aqueous solution have been investigated. Based on the comparison of the experimental results, it has been observed that, Ag-PAM-PP has showed 96% uptake compared to 64% by HS-Octyl-S-Au-PP sorbent. Therefore Ag-PAM-PP substrate was used as a template to preconcentrate and measure mercury in aqueous solution. Ag-PAM-PP had shown superior performance for Hg$^{2+}$ uptake from the natural water samples in terms of other parameters such as sorption capacity, sorption kinetics and working pH range. The preconcentration of mercury ions from a large volume of aqueous solution was used to extend the lower limit of concentration range that can be quantified by the EDXRF and CVAAS. The sorbed Hg(II) from aqueous samples
was quantitatively detected within 1 min using EDXRF. The LOD (3\(\sigma\)) for CV-AAS (RSD = 2\%) and EDXRF (RSD = 5\%) are 6 and 30 \(\mu g \, L^{-1}\).

Preconcentration methods not only help in enhancing the detection limits of the method but also eliminate the spectral interference caused by undesirable components in the matrix. In this method the preconcentration of \(\text{Hg}^{2+}\) on polymeric sheets lowered the existing detection limits of EDXRF 100 fold as the poly(propylene) matrix of the base substrate being of low Z elements does not interfere with the determination of mercury which is a high Z element. The extremely low detection limits achieved by the developed methodology were further used for the determination of \(\text{Hg}^{2+}\) in the ground water and seawater samples in the presence of a high concentration of interfering ions. The results demonstrate the validity of these sorbents for the preconcentration of \(\text{Hg}^{2+}\) from the real sample solutions. It was observed that the preconcentration factor of 12 can be achieved in the 1x1 cm\(^2\) Ag-PAM-PP sample which can further be enhanced by increasing the initial sample volume. The mechanism of mercury sorption is clearly explained by taking into account its complexation with the amide groups of poly(acrylamide) grafted on poly(propylene) substrate and the galvanic reaction of Ag Nps (formed in situ by sodium borohydride reduction) with the sorbed \(\text{Hg}^{2+}\).

A highly selective and sensitive color changeable optode for \(\text{Hg(II)}\) detection in aqueous solution has been developed by immobilizing a phenylthiosemicarbazide rhodamine 6G derivative in a cellulose triacetate plasticized support using room temperature solution casting method. The developed transparent film changes its color on interaction with
mercuric ions which inturn facilitates the quantitative detection of mercury from aqueous matrices spectrophotometrically with a detection limit of 1.3 ng mL\(^{-1}\). The high selectivity of the developed optode towards mercuric ions in presence of high concentration of commonly occurring cations in ground water samples can be further explored for its use as a colorimetric strip sensor for the on-site detection and determination of mercury.

6.2. Future scope

The tailored polymer sorbents developed for fluoride, boron and mercuric ions have high potential for the remediation as well as analytical applications. However, the remediation of the targeted ions from large volume samples has not been explored. This requires development of appropriate process scheme using suitable physical form of sorbent developed in the present work. It should be noted that the chemical architecture of the sorbent is responsible for the selective sorption of targeted ion. Therefore the functionalized sorbents developed in the present work with higher sorption capacities would lead to lower inventory of the sorbents. The better mechanical integrity and the ease of handling of the sheet sorbents can make the decontamination process more user-friendly and cost-effective technique and it does not suffer from the problems associated with other conventional methods. Using bulk polymerization, the same sorbents can also be made in the bead forms for using them in the ion-exchange columns. The functionalized sheet sorbents developed can be utilized for modifying the transport properties of the membranes and as a base material for developing the membrane based chemical sensors. The understanding of mechanism of incorporation of nanoparticles in a
sheet would be useful for controlling the shape, size and spatial distribution of several metal nanoparticles in the polymer matrix. This study would also be useful for designing nanocomposite membranes for a desired application. The optode developed in the present work can be used for the on-site mercury detection by just a visual colour change. Similarly other sheet sorbents can be synthesised and further be explored as a base material for developing the membrane based analytical methods for other toxic ions.