CHAPTER - 5

Conclusion and Future Outlook
Summary and Conclusion

Growing environmental concerns with regard to possible air, groundwater and drinking water contamination by toxic chemicals gave rise to necessity of portable instruments that can be employed as long term monitoring aids, used primarily as alarms. Membrane technologies offer the possibility of simple and continuous monitoring of trace level of contaminants in the environment with minimum human involvement (automation). The aim of the thesis is to develop ion-selective membranes like membrane optodes and pore-filled grafted functionalized membranes which are having numerous advantages over conventional ion-exchange membranes mainly due to their selectivity towards target ions. Thus, it is possible to integrate them in a simple analytical device for the preconcentration and determination of toxic metal ions in aqueous samples.

A brief description of membrane based processes and ion-selective membranes such as membrane optodes based on polymer inclusion membranes (PIMs) and grafted membranes have been described. General outline about different instrumental techniques like UV-visible absorption spectroscopy, Energy Dispersive X-ray Fluorosence (EDXRF), Neutron Activation Analysis (NAA), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Cold Vapour Atomic Absorption Spectrophotometry (CV-AAS) used in the present work are also given. The working principles of two types of detectors, namely NaI(Tl) and liquid scintillation counters were used for measuring different types of radioactivity.

The possibility of developing chemical sensor (optode) based on polymer inclusion membrane has been explored. Membrane optode for Hg(II) was prepared by physical immobilization of a dye 4-(2-pyridylazo)resorcinol (PAR) and a liquid ion-exchanger trioctylmethylammonium chloride (Aliquat-336) in the tri-(2-ethylhexyl) phosphate plasticized cellulose triacetate matrix (CTA). The proportions of CTA, TEHP and Aliquat-336 in the optode were optimized in terms of better uptake, kinetics and uniformity. The optode was self-supporting, having good mechanical strength for its application in the stirred aqueous solution. Hg(II) and CH$_3$Hg$^+$ from aqueous samples could be quantitatively preconcentrated in this transparent optode producing a distinct colour change ($\lambda_{max} = 520$ nm) within 5 min.
equilibration time in bicarbonate aqueous medium or 30 min in natural water. The uptake of Hg(II) was found to be pH dependant with a maximum (>90%) at a pH=7.5. The absorbance at $\lambda_{\text{max}} = 520$ nm increased proportionally with increase in the amount of Hg(II) sorbed in the optode. Aliquat-336 in the optode was found to facilitate the transfer of Hg(II) from aqueous medium to optode matrix, and its preconcentration as PAR-Hg(II) complex in the optode. The uptake of ions like Cu(II), Fe(II), Zn(II) and Pb(II) was negligible in the optode where as the uptake of Cd(II) and Zn(II) ions was 10-15% at pH=7.5. The optode developed in the present work was studied for its analytical application for Hg(II) in the aqueous samples by spectrophotometry, radiotracer ($^{203}$Hg), Energy Dispersive X-ray Fluorescence (EDXRF) analyses and Instrumental Neutron Activation Analysis (INAA). The advantages of using membrane optode samples for INA and EDXRF analyses of Hg(II) is that it contains mainly low Z elements like H, C, and O that do not produce significant amount of background. Since INAA and EDXRF is element specific, the Hg(II) sorbed in the optode matrix can be unambiguously quantified. The minimum amount of Hg(II) required to produce detectable response by spectrophotometry, INAA and EDXRF were found to be 5.5, 1 and 12 µg, respectively. This optode showed a linear increase in the absorbance at $\lambda_{\text{max}} = 520$ nm over a concentration range of 0.22 to 1.32 µg/mL of Hg (II) ions in aqueous solution for 5 min. The preconcentration of Hg(II) from large volume of aqueous solution was used to extend the lower limit of concentration range that can be quantified by the spectrophotometry of optode. It was observed that preconcentration of 11 µg Hg(II) in 100 mL (0.11 µg/mL) in aqueous samples gives a distinct color change and absorbance above 3 $\sigma$ of the blank absorbance. Hg(II) could be desorbed quantitatively from the optode within 2-5 min equilibration in 0.02 mol L$^{-1}$ aqueous solution of disodium salt of EDTA. The optode developed was found to be reusable and successfully applied for the determination of Hg(II) in tap water and surface waters.

The colour changeable membrane optode for U(VI) ions were developed. Preconcentration and quantification of uranium(VI) ions based on a synergistic combination of 4-(2-thiazolyazo)- resorcinol with 8-hydroxyquinaldine was developed by using another membrane optode. This membrane optode utilized the
8-hydroxyquinaldine (HQ) facilitated preconcentration of UO$_2^{2+}$ ions and subsequent colored complex formation of UO$_2^{2+}$ with the 4-(2-thiazolylazo)-resorcinol (TAR) in optode matrix. On sorption of UO$_2^{2+}$ ions in the optode matrix, TAR changes color of the optode from yellow to magenta having a maximum absorbance ($\lambda_{\text{max}}$) at 546 nm. The uptake of UO$_2^{2+}$ ions in the optode was found to be pH dependent and was maximum (>90%) at pH above 3. The acetate buffer (0.1 mol L$^{-1}$ sodium acetate + 0.1 mol L$^{-1}$ acetic acid) was found to be necessary for the stable response. The optimum equilibration time for the optode (2x1 cm$^2$) was found to be 30 min in 10 mL aqueous sample containing acetate buffer (pH=4.75). The equilibration time was found to increase with increase in aqueous sample volume. The optode response was found to be linear in the UO$_2^{2+}$ ions concentration range of 0.01 µmol L$^{-1}$ - 0.11 µmol L$^{-1}$ in tap water as well as aqueous solutions containing 0.1 mol L$^{-1}$ NaCl or NaN$O_3$. It was observed that the optode in the presence of buffer can tolerate large amounts of interfering cations (Ce$^{4+}$, V$^{4+}$, Eu$^{3+}$, Al$^{3+}$, Fe$^{3+}$, Ni$^{2+}$, Cd$^{2+}$, Co$^{2+}$, Pb$^{2+}$, Hg$^{2+}$, Cu$^{2+}$ and Th$^{4+}$) ions without hindering the sorption of UO$_2^{2+}$ ions in the optode matrix. This work indicated that 50 ppb UO$_2^{2+}$ ions in 100 mL sample can easily be quantified using this optode. The optode was found to be fully reversible, can readily be regenerated by equilibration it with 0.1 mol L$^{-1}$ HNO$_3$ and reusable upto 3 cycles. The applicability of the developed optode in real samples was studied by determining uranium in the ground water samples spiked with a known quantity of UO$_2^{2+}$ ions.

In the developed membrane optodes for Hg(II) and U(VI), tri-(2-ethylhexyl) phosphate (TEHP) was found to form a uniform optode with better kinetics as compared to other plasticizers like Igepal, 2-nitrophenyl octyl ether (NPOE) and dioctyl phthalate (DOP). As dye and extractant are physically immobilized in the optode matrix, the hydrophobic interactions make them stable in the plasticized polymer matrix. The presence of extractant in the optode provides an increase in selectivity and sensitivity of the optodes as compared to the corresponding solution method using a chromophore.

In order to improve sorption kinetics and physical stability of the membrane, the pore-filled membrane was developed by in situ graft polymerization of the
monomers in the pores of host polyethersulfone membrane. The chemical linking of carrier with polymer chains is expected to provide physical stability of the carrier/extractant in the membrane. Unlike polymer inclusion membrane, these membrane are hydrophilic and carriers are confined to transport channels in the membranes. Thus, this class of membranes is expected to have better performance than polymer inclusion membrane. Pore-filled functionalized membrane was developed for preconcentration and quantification of heavy metal ions by grafting cross-linked micro-gel in the pores of host polyethersulfone membrane. The micro-gel in the membrane was formed by in situ photo-polymerization of itaconic acid (ICA) along with co-monomer acrylamide (AM) and crosslinker pentaerythritol tetraacrylate (PETA). α,α'-dimethoxy-α'-phenyl acetophenone (DMPA) was used to initiate photo-polymerization. Gravimetric and Fourier Transform Infrared Spectroscopy confirmed extent of anchoring of micro-gel (225 wt.%) in the membrane. The comparison of scanning electron microscopic images of blank and grafted membranes indicated that pores of membrane were completely blocked after grafting micro-gel in the membrane. It was observed that only U(VI) and Hg(II) sorbed with high efficiency (>80%) in the grafted membrane in presence of other competing cations like Th(IV), V(IV), Eu(III), Fe(III), Cu(II), Pb(II) and Cd(II). It was also observed that desorption of Hg(II) and U(VI) from the membrane sample is possible by 0.01 mol L⁻¹ EDTA disodium salt and 0.5 mol L⁻¹ Na₂CO₃, respectively. The preconcentration of uranium from leach solution of mining soil samples in the grafted membrane was studied using ICP-OES. The concentrations of Hg²⁺ ions in the mining soil samples were determined first by preconcentrating mercury ions in the grafted membrane samples and then subjecting these membrane samples to CV-AAS. The uptake studies of U(VI) and Hg(II) from seawater and polluted soil samples indicated the possibility of using the itaconic functionalized membrane for the real samples. Using this method, the mercury ions present in complex aqueous sample at ppb range could be easily determined. Hg(II) preconcentrated in the membrane samples could be quantified by CV-AAS. This
membrane based method would not only preconcentrate $\text{Hg}^{2+}$ ions for enhancing analytical detection limit but also safe handling of $\text{Hg}^{2+}$ ions.

Optical chemical sensors (Optodes) offer many advantages over other conventional sensors, including miniature size, resistance to harsh environmental conditions, immunity to electromagnetic and electrical interference, rugged design and capability of remote analysis. Development of pore-filled grafted functionalized membrane by anchoring hydrogels within pores of a robust microporous host membrane are better for preconcentration from the complex matrices and subsequent direct determination of preconcentrated metal ions, as host membrane provides a containment and mechanical strength to the hydrogel and mitigates the impact of osmotic forces. This is important to get reproducible geometry in analytical technique and ease of handling of toxic metal ions like mercury. Overall, the developed membranes (membrane optodes/pore-filled grafted functionalized membranes) serves as a selective preconcentration layer for the analyte and therefore, offers a possibility of simultaneous preconcentration and detection of the target analyte. The membranes developed in the present work would find applications for the monitoring of toxic metal ions in various environmental samples.

Future Outlook

Ion-selective membranes play an important role in various fields of science and technology. These membranes can play an important role in various industries, especially in continuous monitoring, process and quality control at different stages and also can be used to have a check on the amount of elements being disposed in waste streams. Current investigation helps to fabricate optical chemical sensors for sensing other metallic and gaseous species and enzyme based sensors for monitoring (heavy metals, pesticides) toxicity of aqueous samples.

Optical chemical sensors can advantageously be utilized in environmental analysis to probe small volumes and for difficult samples due to their small size and also selectivity/sensitivity in analysis. For continuous on-line industrial applications, a much more robust and reliable sensor with rapid response may be constructed by
using stable substrates, whereby the reagents are chemically attached to a support polymer. By appropriate choice and design of the sensing functionalized hydrogel layer, sensors can be constructed that respond to a wide variety of different analytes, including proteolytic enzymes, alcohol, trace water in organic solvents and metal ions. However, optical chemical sensors do require further development in terms of superior selectivity and stability over time. A detailed understanding of the sensor analyte interaction through (a) quantitative study of the structure activity relationships; (b) investigation of the effect of physical variables such as humidity, temperature, and pressure on sensor performance; and (c.) experimental identification of the influence of diffusion, mass transport surface stress, and binding affinity on selectivity and sensitivity will possibly lead to better performing chemical sensors for a wide variety of applications. Chemical sensor systems will continue to provide a less expensive and portable alternative to bulky analytical systems for a wide variety of applications.

One of most promising future prospects appears to be nanoparticles embedded membranes. The nanoparticles of Ag, Au and Cu have very intense surface plasmon absorption bands. Therefore, the response mechanism based on these metal nanoparticles will be very sensitive to target analyte due to very high molar extinction coefficient than any other existing dyes. Also, the nanoparticles may improve the physical and chemical architectures of the membrane leading to better functional properties. The functional groups can be easily attached to Au nanoparticles by sulphide bonds. Thiols with required functional groups can be utilized for developing new generation of membranes.