# Chapter -1

## INTRODUCTION

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1.1. **Statement of current problem**

Atharav Veda says, “Water is the elixir of life”. Water has most appropriately been compared to 'ambrosia' because it purifies the body from all kinds of toxins and gives new life. It also frees the body from different 'doshas' (ailments) and is hence known as Bheshagya- which purifies the body from all kinds of impurities. For any civilization to sustain, access to clean water is one of the basic necessities. Clean and plentiful water provides the foundation for prosperous communities. We rely on clean water to survive, yet right now we are heading towards a serious scarcity of clean water. The United Nations reports that though access to improved drinking water has expanded, nearly one billion people do not have safe drinking water [1].

As the world population increases, water consumption also increases. Some observers have estimated that by 2025, more than half of the world population will be facing water-based vulnerability or a water crisis [2,3]. Advancements in science and technology have improved the quality of life but at the same time it has led to an adverse impact on environment, especially on water resources. A wide variety of toxic inorganic and organic chemicals are discharged into the environment as industrial wastes, causing serious water, air, and soil pollution. The extensive growth of industrial activities during this century has generated serious water pollution problems especially in developing countries like India for both the surface water and groundwater resources.

Water pollution caused by toxic heavy metal ions has become a serious environmental problem. Heavy metals (such as Pt, Pd, Ag, Cu, Cd, Pb, Hg, Ni, Co, Zn, etc.) are natural constituents of the earth crust and present in the environment as a result of weathering
and erosion of parent rocks [4]. In addition to natural sources, they are introduced in ecosystems through wastewaters originating from anthropogenic sources such as chemical manufacturing, metal finishing, welding, alloys manufacturing, painting, mining, extractive metallurgy, plating, tannery and battery industry and using metal-containing fertilizers and pesticides [5]. The presence of low concentration of a these toxic ions cause a major difficulty in the use and reuse of water streams. Water containing significant concentrations of these pollutants is harmful to human beings, animals and aquatic organisms. Some of these toxic ions get easily accumulated in the human body through the food chain, causing a variety of diseases and disorders [6]. It is estimated that, worldwide, approximately 250 million new cases of waterborne diseases occur each year with over 10 million resulting in death.

There are now regulations governing the disposal of industrial waste water in terms of toxic chemicals content. People around the globe are also being urged to use water responsibly for present and future generations, and there is a lot of technological advancement dealing with the recycling of industrial water and its treatment before it is discharged into the environment. In this regard, it has become necessary to remove various toxic ions from industrial effluents for their subsequent safe disposal. The other alternative is to rely on nontraditional sources of water to supplement the ever increasing demands of growing population. In the last few decades, ground water has become one of the important sources of water for meeting the requirements of various sectors in developing countries. Though groundwater contributes only 0.6% of the total water resources on earth, it is the major and the preferred source of drinking water in rural as
well as urban areas because treatment of the same, including disinfection is often not required. The groundwater present caters to 80% of the total drinking water requirement and 50% of the agricultural requirement in countries like parts of rural India. But the increasing industrial advancement and urbanization leads to the pollution of available groundwater resources [7,8]. During to its complex flow history, groundwater passes through various geological formations leading to consequent contamination in shallow aquifers. In India itself, as many as 19 states, including Delhi are affected by groundwater contamination problem. Geogenic contaminants, including salinity, iron, fluoride, and arsenic have affected groundwater in over 200 districts spread across 19 states [7]. Elevated levels of different ions found in water resources have restricted their use for human activities. It has been estimated that fluorosis, a disease associated with consumption of fluoride contaminated water is prevalent in 17 states of India as many ground water sources have fluoride concentration as high as 30 mg L$^{-1}$. Hence, removal of such toxic ions from contaminated natural waters and wastewaters has been a subject of extensive industrial research. Although the list of such toxic ions prevailing in water bodies is exhaustive the present thesis work has been focused on developing polymer sorbents for extracting fluoride, boron and mercuric ions from contaminated aqueous streams.

Fluoride (F$^-$), Boron (B) and mercury (Hg) are some of the most toxic inorganic contaminants found in the environment [9]. Apart from their natural sources, they are released into the aquatic systems from a number of industries such as metal plating,
smelting, mining, paint industries, leather tanning, pigments, textiles and alloy industries as well as from sewage [10-11].

Exposure of fluoride has been associated with dental fluorosis which slowly progresses to skeletal fluorosis at later stages. Water contamination by boron is another widespread environmental problem due to the wide application of boron compounds in industries such as food preservation, agriculture, electronics, glass and ceramics, health care products, and nuclear power production. The signs of acute toxicity in humans include nausea, vomiting, diarrhoea, dermatitis and lethargy, irritation of the eye, the upper respiratory tract and the nasopharynx. Hence removal of boron from natural waters is gaining lot of attention these days. Due to several industrial applications of mercury, it has become a widespread pollutant in ground waters. Mercury is of high concern because of its potential long-term accumulation in the ecosystem. It has a tendency to accumulate in the biological system via bioaccumulation. Bioaccumulation is defined as the process where at each level in a food chain, from bacteria to plankton to small fish, larger fish, and fish-eaters, organisms take in more element than they excrete thereby accumulating the excess in their organs. For instance, when a fish feeds on a marine or aquatic organism that had consumed methyl mercury contaminated plankton, the methyl mercury is not excreted but instead, it is retained in its tissues. When this fish is preyed upon by another fish or another marine predator, the accumulated methyl mercury in the fish is passed on to the predator and in a similar fashion the methyl mercury is passed on up the food chain until eventually the concentration of the methyl mercury becomes far higher than its initial concentration. For this reason therefore, any organism at the top of the food
chain i.e. humans, polar bears, etc. faces a serious risk of mercury poisoning upon eating such a fish. The infamous Minamata is caused by mercury poisoning as a result of eating mercury contaminated fish. Mercury has very high tendency to bind to protein and it mainly affects the renal and nervous system. Looking at the disastrous consequences of these toxic ions, there is an ever growing need to remove or reduce them from contaminated water streams by different methods and methodologies.

A number of methods are available for the removal of these inorganic pollutants from water streams. Their removal from (drinking) water can be achieved through precipitation, flocculation, solvent extraction, ion exchange, reverse osmosis, etc. [12]. However, most of these methods are unacceptable, owing to the disposal of sludge, their high cost, low efficiency and inapplicability to a wide range of pollutants.

Among various methods, the process of adsorption has now become one of the preferred methods for the removal of toxic contaminants from water as it has been found to be effective, versatile and relatively simple [13]. Adsorption has the additional advantages of its applicability at very low concentrations, suitability for using batch and continuous processes, ease of operation, little sludge generation, possibility of regeneration and reuse of adsorbents and low capital cost. The adsorption process has now acquired global importance for reducing the problem of contamination of water as well as air. The process has also become a significant addition to Green Chemistry endeavors.

All the adsorption based separation procedures commonly used involve the application of different sorbents that can bind selectively with the element of interest to be removed from water sources. However, the major problem in this field is to select novel types of
adsorbents. The major disadvantages of the existing adsorbents such as activated carbon, zeolites, clays and agricultural residues are their low adsorption capacities and their relatively weak interactions with the targeted ions. Sometimes the targeted element is present in ultra-trace quantities in natural waters which make its separation even more challenging. Therefore, the use of highly selective sorbents for the removal or preconcentration of toxic ions remains in demand, especially in developing countries where ground water is commonly used for consumption. However, specific requirements of modifying the existing sorbents depending upon prevailing chemical conditions have to be optimized in view of the above considerations.

More recently, promising organic-inorganic hybrid polymers have been used for the removal of toxic ions from wastewater [14-22]. In these compounds, the functional variation of organic materials is combined with advantages of a thermally stable and robust inorganic substrate, resulting in strong binding affinities towards targeted ions and relatively high adsorption capacities. Functionalized hybrid polymeric materials as adsorbent are regarded as one of the most effective techniques because metal ions can be chemically bonded to them by the organic-inorganic polymer hybrids. These kinds of materials often present the best properties of each of its components in a synergic way and have high performances of physical, chemical and mechanical properties [23].

Currently organic-inorganic hybrid polymeric materials are intensively studied for their efficient applications. The intrinsic multifunctional character of these materials makes them potentially useful in multiple fields such as in electroanalytical applications [24], their extensive use in the field of membranes such as ultra-and nanofiltration [25,26],
superhydrophobic surfaces [27,28], highly transparent films [29,30], pH sensitive composites [31], solar cells [32,33], electrolyte [34], molecular shuttles [35], semiconductors [36], gas separation [37,38], catalysts [39], biosensors [40], drug delivery systems [41], coatings for corrosion protection [42], adsorbents of toxic compounds [14-22] etc. Looking at the widespread use of these polymers, in this work, as a first step, efforts were focused to develop newer inorganic-organic polymeric sorbents with improved sorption capacities which could be used as cheaper adsorbents. Particular attention is focused on application of these sorbents for the sorption of selected ions from environmental samples as well as in understanding the mechanism behind that.

However, prior to developing methods of separation and preconcentration, the chemistry of the targeted element and its composition needs to be understood. Therefore the occurrence, uses, chemistry and the need of these elements for sustaining human life is described in the introduction part of their respective chapters.

In this chapter an overview on the fundamentals of separation, different available methods of separation, the chemistry involved behind their separation and the need to develop various simple, cost effective and environmental friendly separation and preconcentration methods for fluoride, boron and mercuric ions has been emphasized. Based on the existing literature on the chosen subject, the chapter ends with a brief description of the objectives and the scope of the thesis. An overview of different available methods used for the separation of targeted elements from aqueous streams has been discussed briefly in what follows.

1.2. Different Methods of Separation and preconcentration
The growing demand for safe potable water, the increasing amount of industrial wastes containing varying concentrations of toxic ions and the need for highly efficient and clean technologies for water decontamination, has led to an emphasis on selective removal and preconcentration of ions from variety of matrices. The aim of the research study undertaken was to meet the above demands by developing different functionalized polymer sorbents for the selective extraction of fluoride, boron and mercuric ions from various aqueous streams. In other words developed sorbents should be able to achieve separation of targeted ion in its native form from contaminated water sources in the presence of different interfering ions.

The literature survey showed that adsorption, ion-exchange, precipitation-coagulation, and solid-phase extraction methods are the most frequently used methods for the uptake of these ions from aqueous medium (Fig 1.1) [43]. Membrane based methods like reverse osmosis, nanofiltration, and electrodialysis [44-46] find limited application for the removal of these ions. Basic theory and principle involved in each of the above separation method is described individually in the following sections.

![Fig. 1.1 Classification of various separation methods](image-url)
1.2.1. Precipitation and Co-precipitation

The process of precipitation transforms dissolved contaminants into insoluble solids, assisting in the contaminant's subsequent removal from the liquid phase through sedimentation or filtration. A precipitate is formed when the ionic product exceeds the solubility product of a particular compound. Precipitation can be carried out in two ways, i.e. (i) matrix precipitation (ii) precipitation of trace components. Matrix precipitation is associated with large consumption of reagents, prolonged duration of the process and co-precipitation. The precipitation method has limited applications because the precipitate formation process depends on various factors, such as composition of the aqueous phase, pH, temperature, nature of the counter ions forming the precipitate and sequence in which solutions are mixed. A slight alternation in any of these factors leads to poor precipitation yield.

Co-precipitation, which was earlier regarded as an unpleasant companion of a desired precipitate, is now considered as an effective method of preconcentration. Co-precipitation is the transfer of a substance into a precipitate of some compound if the substance does not form its own solid phase under the given conditions. Depending on the physical and chemical properties of the components and the experimental conditions, co-precipitation is due to the adsorption of the trace component on the surface of the collector. It also occurs because of the formation of isomorphic mixed crystals, mixed chemical compounds, occlusion and mechanical inclusion of small amounts of other phases. Sometimes, all these factors act simultaneously to some extent. Some of the
applications of precipitation and co-precipitation methods for the removal of fluoride, boron and mercuric ions from aqueous streams are discussed in the following section.

1.2.1.1 Applications of precipitation and co-precipitation methods for removal of fluoride, boron and mercury

Precipitation method for defluoridation involves addition of chemicals and formation of fluoride precipitates. Lime and alum are the commonly used precipitating agents. Fluoride precipitates as insoluble calcium fluoride on addition of lime and thus can be removed from water. But the addition of lime raises the pH value of water to 11-12. Complete removal of fluoride is impossible by addition of lime and a residue of 8.0 mg L$^{-1}$ is left so this method is always used in conjunction with alum treatment to ensure the proper fluoride removal [47]. The Nalgonda technique of defluoridation is based on combined use of alum and lime in a two-step process and it has been used as the most effective technique for fluoride removal [48,49]. But this commonly followed method has several limitations. The major limitations include daily addition of chemicals, large amount of sludge production and it is least effective with water having high total dissolved solids and hardness. Moreover, it converts a large portion of ionic fluoride into soluble aluminum complex and practically removes only a small portion of it (18-33%) [50]. Residual aluminum from 2.01 to 6.86 mg L$^{-1}$ was also reported which is dangerous to human health as aluminum is a neurotoxin, concentration as low as 0.08 mg L$^{-1}$ in drinking water has been reported to cause Alzheimer’s disease. Due to use of aluminium sulfate as coagulant, the sulfate ion concentration increases tremendously and in few cases, it crosses the maximum permissible limit of 400 mg/L, which causes cathartic
effect in human beings. Use of alkaline oxides like MgO and CaO followed by the adjustment of pH with NaHSO₄ has also been used to remove fluoride [51]. Several other precipitating agents such as calcium hydroxide [Ca(OH)₂], calcium chloride [CaCl₂] and calcium sulphate [CaSO₄] have also been applied for the fluoride removal purposes [52, 53]. Cement paste and combined use of calcium salts as precipitant and polymeric aluminium hydroxide as coagulant have also been studied for the fluoride removal by precipitation method [54]. But the method of precipitation yields results only at higher initial concentration of fluoride as it is easy to attain super saturation level. However, at lower concentration of fluoride precipitation methods become insufficient to remove fluoride [55]. So, to decrease the fluoride from 10-20 mg/L to drinking water level (1.5 mg/L) by precipitation method is itself a challenge.

The literature on the precipitation methods used for boron removal is very less because there is no known compound that can quantitatively precipitate boron [56]. Usually the secondary acid effluents are generally neutralized and then evaporated to dryness to obtain a solid product. This operation is tedious and expensive since it involves the necessity of totally evaporating the water. Powdered Ca(OH)₂ and MgCl₂ has been used for precipitating boron from aqueous solution in form of calcium and magnesium borate [57, 58]. The flocks thus formed are separated by the means of physical sedimentation. However, reported boron precipitation methods using magnesium, aluminum and various other metal hydroxides typically require large volumes of adsorbent and produce large quantities of sludge, making them uneconomical for many industries [59-60]. Boron co-precipitation with calcium carbonate was researched by Kitano et al. in which calcium
carbonate was added to solutions containing various ratios of sodium chloride, magnesium chloride, and boric acid [61].

The precipitation methods used for mercury treatment are based on precipitation of mercury compounds using hydroxides and sulfides [62]. Hydroxide precipitation is ineffective, with soluble levels exceeding 75 mg L\(^{-1}\) mercury over a pH range of 3.5 to 11.5. Sulfide precipitation is the most common method of removing mercury and yields more complete removal of mercury than hydroxide precipitation but it leaves the residue of toxic sulfides in solution. The method works on less than 85% acid concentrations, at higher acidity sulfur is oxidized to sulfur dioxide and the product contains the undesirable sodium sulfate. This method is much more expensive than hydroxide precipitation since the excess sulfides are usually regulated and the resulting sludge may be difficult to landfill. Therefore, it is not as widely used as hydroxide precipitation. Toho process of mercury removal involves the addition of KI which precipitates mercury as mercury iodide and precipitated mercury is removed by filtration [63].

1.2.2. Liquid/Liquid extraction (Solvent Extraction)

Solvent Extraction as a method of separation and preconcentration has been reviewed by Zolotov and Kuzmin [64]. The knowledge gained in this direction in subsequent years is summarized in several books, reviews and general papers [65,66]. Separation and preconcentration procedures using liquid/liquid extraction generally result in a high enrichment factor due to the difference between the volumes of aqueous and organic phases. Solvent extraction is distribution of a dissolved substance between two
immiscible liquid phases- one of them is usually an aqueous phase and the other phase is an organic solvent. Extraction, being a heterogeneous process, is governed by the phase rule

\[ P + F = C + 2 \]  \hspace{1cm} (1.1)

where \( P \) is the number of phases, \( F \) is the number of degrees of freedom and \( C \) is the number of components. If the number of phases is equal to two and one substance (\( C=1 \)) is distributed then at constant temperature and pressure the system is univariant. In such cases, at equilibrium, the ratio of concentrations of the substance distributed in both the phases is a constant value and this is independent of total concentration of the substance.

This value, designated as distribution constant or partition constant is described as

\[ D \ (\text{Distribution or Partition constant}) = \frac{C_o}{C_{aq}} \]  \hspace{1cm} (1.2)

where \( C_o \) and \( C_{aq} \) are the equilibrium concentrations of the substance in organic phase and aqueous phase respectively. This is known as Nernst distribution law.

Solvent extraction separations are mainly dependent for their successful operation upon the distribution ratio of the species between the organic and aqueous phase and the pH and salt concentration of the aqueous phase. Much of the selectivity which is achieved in liquid-liquid extraction is dependent upon adequate control of the pH of the solution. The addition of masking agents such as EDTA and cyanide can greatly improve selectivity, but they too are dependent upon the pH of the solution to exert their full effect. In many cases complete extractions and separations are obtained only in the presence of salting-
out agent. There are some of the major disadvantages of liquid-liquid solvent extraction such as the process is cumbersome for a large number of samples or for large samples and often requires toxic or flammable solvents. It can be time consuming, especially if attainment of equilibrium is slow and can require costly amounts of organic solvents and generate large volumes of organic waste. Solvent extraction is affected by small impurities in the solvent(s) and multiple extractions might be required, thereby increasing time, consumption of materials, and generation of waste. Sometimes, the formation of emulsions can interfere with the phase-separation process and in addition to that, alteration of chemical form of the species to be extracted can change on going from one phase to the other, thereby altering the distribution coefficient and effectiveness of the extraction.

1.2.2.1 Applications of solvent extraction methods used for removal of fluoride, boron and mercury

The applications of solvent extraction method for fluoride removal are limited in literature however a few of the reports involves extraction of fluoride using trimethylchlorosilane (TMCS) in toluene to produce trimethylfluorosilane (TMFS) [67,68]. Solvent extraction method has been used for boron removal from concentrated boron liquors. Diols, triols and other polyols having long aliphatic chains with low solubility in water have been applied for extracting boron from waste effluents [69-74]. Based on the literature survey on solvent extraction of boron, the mechanism can be divided into three groups: simple extraction, extraction forming borate complex and extraction by forming non-ionic borate ester complex. Although a large number of
extractants have been used, the extraction process suffers from the loss of extractants as these diol based extractants have appreciable solubility in water.

In the case of mercury, different amines and organophosphorus based extractants have been used for the removal of mercury(II) ions from aqueous streams. However, these extractants containing nitrogen or oxygen as donor atom show poor selectivity for mercury(II) over other metals. On the other hand the extraction reagents containing sulphur as donor (soft base) atom bind selectively with mercury because of the soft acid-soft base (SASB) principle [75]. In recent years, various sulphur containing reagents such as thiophosphorus, triisobutylphosphine sulphide (TfiiPS), marketed under the trade name of CYANEX 471X by Cytec Canada Inc. have been used for the extraction of mercury(II) from from aqueous solutions [76-78]. Recovery of mercury from paper industry effluent using TfiiPS as an extractant has been carried out by Singh and Tandon [77]. Extraction behaviour of mercury(II) from thiocyanate solutions using TfiiPS in benzene as an extractant has been investigated [79]. Reddy et al. [80] have studied the extraction behaviour of mercury(II) from iodide solutions using bis-2-ethylhexyl sulphoxide (B$_2$EHSO) in benzene as an extractant and reported the extracted complexes as HgI$_2$, HgI$_2$.B$_2$EHSO and Hg$_2$.B$_2$EHSO. Inoue et al. synthesised 2-ethyl-2-(isobutylthiomethyl)butane thiol (EIBTMT), 3,3-diethylthietane (DETE) and3,3-dibutylthietane (DBTE) [81] and utilized for the extraction of mercury(II) from acidic chloride solutions. Crown thioethers have been studied for the selective extraction of mercury from acidic solutions because of their high affinity towards Hg(II) as well as their resistance towards degradation under acidic conditions [82-84]. Tri-n-butyl
phosphate(TBP) and tri-n-octylphosphine oxide (TOPO) have been reported as efficient extractants for mercury(II) [85,86]. Brewer et al. investigated the extraction of mercury from acidic aqueous solutions using the TRUEX process solvent, a mixture of n-octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO) and TBP in n-dodecane [87]. The most recent studies on the liquid-liquid extraction of mercury (II) are based on the use of calixarenes derivatives with different number of atoms and several structural modifications. p-tert-butylcalix[4]arene derivatives having S-containing functionalities in the upper and lower rim have also been studied for the extraction of mercury from aqueous phase [88-92]. The existing problems associated with solvent extraction as listed above makes its use limited.

1.2.3. Solid phase extraction

Solid phase extraction (SPE) is highly useful separation/preconcentration method which eliminates many problems associated with liquid liquid extraction (LLE). SPE is more efficient than liquid-liquid extraction and yields quantitative extractions that are rapid, easy to perform and can easily be automated for analytical applications or integrated to water treatment plants. Consequently, in recent years SPE has been successfully used for the separation and sensitive determination of toxic ions in water samples.

The principle of solid phase extraction (SPE) is similar to that of Liquid-Liquid extraction, involving partitioning of solutes between two phases. However, instead of two immiscible liquid phases, as in LLE, SPE involves distribution between a liquid (sample matrix) and a solid phase. Partitioning of a solute usually involves its sorption on a particular solid support known as sorbent. There are different ways in which a particular
solute can interact with a sorbent surface. The different sorption mechanisms are briefly discussed below.

1.2.3.1 Sorption

Surface adsorption retains a major place in water treatment because of its greater accessibility and lower cost. Sorption is a process that occurs when a solute (the sorbate) accumulates on the surface of a solid sorbent, forming a molecular or atomic film. Both short range (repulsive) and longer range (attractive) forces between the solute and the sorbent become balanced, when adsorption occurs. Depending on the type of bonding involved, sorption can be classified as follows:

(a) **Physisorption** or physical adsorption is a type of sorption in which the sorbate adheres to the surface only through weak intermolecular van der Waals interactions. Physisorption is characterized by interaction energy comparable to heat of vaporization (condensation), and multiple layers may be formed, with approximately the same heat of sorption. The heat of physisorption is, at the most, a few kcal/mole, and, therefore, this type of sorption is stable only at temperatures below 150 °C, depending on the sorbate-sorbent pair.

(b) **Chemisorption** is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the van der Waals forces which cause physisorption. Chemisorption is characterized by interaction energy between the surface and the sorbate to be comparable to the strength of a chemical bond (tens of kcal/mol), and, consequently, is much stronger, and more stable at high temperatures, than physisorption.
(c) Ion exchange

Ion exchange process involves exchange of counter ions at fixed sites by electrostatic interactions in the matrix. The negative or positive groups attached to the matrix are called fixed sites and available opposite sign ions are called counter ions. The selectivity of an ion-exchanger towards different ions is dependent upon the strength of their electrostatic binding.

An ion exchanger is characterized by its capacity, resulting from the effective number of functional groups per unit mass of material. Ion exchange resins are classified as cation exchangers, which have positively charged mobile ions available for exchange, and anion exchangers, whose exchangeable ions are negatively charged.

Both anion and cation resins are functionalized organic polymers. They differ in the ionizable group attached to the hydrocarbon network. It is this functional group that determines the chemical behavior of the resin. Resins can be broadly classified as strong or weak acid cation exchangers and strong or weak base anion exchangers.

*Strong acid cation resins:* Strong acid resins are so named because their chemical behavior is similar to that of a strong acid. The resins are highly ionized in both the acid (R-SO\(_3\)H) and salt (R-SO\(_3\)Na) form of the sulfonic acid group. The hydrogen and sodium forms of strong acid resins are highly dissociated and the exchangeable Na\(^+\) and H\(^+\) are readily available for exchange over the entire pH
range. Consequently, the exchange capacity of strong acid resins is independent of solution pH.

*Weak acid cation resin:* In this the ionizable group is a carboxylic acid (COOH). These resins behave similar to weak organic acids that are weakly dissociated. The degree of dissociation of a weak acid resin is strongly influenced by the solution pH. Consequently, resin capacity depends on the solution pH.

Similarly there can be strong anion exchangers and weak anion exchangers dependent on the type of groups attached to it. Ion exchange process is usually reversible. This means that ion exchange is a physical separation process in which the ions exchanged are not chemically altered. Some commonly used ion exchangers used in water treatment are listed in the Table 1.1

**Table 1.1 Commonly use ion–exchangers with their exchange capacities**

<table>
<thead>
<tr>
<th>Type</th>
<th>Ionogenic group</th>
<th>Trade name</th>
<th>Exchange capacity (m equiv./g)</th>
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<tr>
<td>Cation exchanger</td>
<td>-SO_3^H</td>
<td>KU-2</td>
<td>4.9–5.1</td>
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<tr>
<td></td>
<td>-SO_3^H, -OH</td>
<td>Dowex 50</td>
<td>5</td>
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<td></td>
<td>-COOH</td>
<td>Amberlite IR-120</td>
<td>5</td>
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<td></td>
<td>-N(CH_3)_3Cl</td>
<td>KU-1</td>
<td>4.5–5.1</td>
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<tr>
<td>Anion Exchanger</td>
<td></td>
<td>KB-4</td>
<td>10</td>
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<tr>
<td></td>
<td>=NH, ≡ N</td>
<td>AV-17</td>
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<td>- NH_2, = NH</td>
<td>Dowex 1</td>
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<td>Amberlite IRA-400</td>
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The ion exchangers are extensively used in wastewater treatment for the removal of hazardous ionic materials from the wastewater and some of their applications for the removal of chosen ions are given below.

1.2.3.3 Applications of solid phase extraction methods for removal of fluoride, boron and mercury

Applications of solid phase extraction methods usually employs the use of adsorption and ion-exchange processes involving the passage of water through a contact bed where desired analyte is removed by ion exchange or surface chemical reaction with the solid bed matrix. For defluoridation the use of powdered activated carbon was demonstrated by Mckee and Johnston as early as 1934 and the results were appreciable but the process needs adjustment of pH thus making it tedious [93]. Bauxite, magnetite, kaolinite, serpentine, various types of clays and red mud are some of the naturally occurring materials studied for defluoridation [94]. The general mechanism of fluoride uptake by these materials is the exchange of metal lattice hydroxyl or other anionic groups with fluoride. Fluoride uptake capacity can be increased by certain pre-treatments like acid washing, calcinations, etc. however none of the mentioned materials generally exhibits high fluoride uptake capacities.

Some of the other sorbents reported in literature for fluoride removal are activated alumina, activated carbon, activated alumina coated silica gel, calcite, activated saw dust, activated coconut shell carbon and activated fly ash, groundnut shell, coffee husk, rice husk, magnesia, tricalcium phosphate, bone charcoal, activated soil sorbent, are [95-107].
Among these activated alumina and activated carbon are the most commonly used adsorbents. Activated alumina has been the sorbent of choice for defluoridation of drinking water in developed countries. Generally it is implemented on a large scale source community plants. Small defluoridation units employing activated alumina have been developed which can be directly attached to the tap. During recent years this technology is gaining wide attention even in developing countries. Domestic defluoridation units have been developed in India using indigenously manufactured activated alumina, which is commercially available in bulk quantities. Choosing the proper grade of activated alumina is important for its effective reuse in multiple defluoridation cycles. Around 500-1500 litres of safe water could be produced with 3 kg of activated alumina when the raw water fluoride is 11 and 4 mg/l respectively at natural water pH of 7.8-8.2. The frequency of regeneration is once in 1.5-3 months [108]. But there are certain limitations using these adsorbents. Hardness and surface loading (the ratio of total fluoride concentration to activated alumina dosage) affects the fluoride removing tendency of sorbents. In addition to this the pH of the solution should be between 5.0 and 6.0 because at pH > 7, silicate and hydroxide become stronger competitor of the fluoride ions for exchange sites on activated alumina and at pH less than 5, activated alumina gets dissolved in acidic environment leading to loss of adsorbing media. The adsorption process has a low adsorption capacity, it requires acidification and pretreatment and its effectiveness for fluoride removal reduces after each cycle of regeneration [109].
Anion-exchange resins containing quaternary ammonium functional groups can be used for the removal of fluoride from aqueous solution using simple ion exchange mechanism. The removal takes place according to the following reaction:

\[
\text{Matrix- NR}_3^+\text{Cl}^- + F^- \rightarrow \text{Matrix- NR}_3^+\text{F}^- + \text{Cl}^-
\]  

(1.3)

The fluoride ions replace the chloride ions of the resin. This process continues until all the sites on the resin are occupied. The resin is then backwashed with water that is supersaturated with dissolved sodium chloride salt. New chloride ions then replace the fluoride ions leading to recharge of the resin and starting the process again. The driving force for the replacement of chloride ions from the resin is the stronger electronegativity of the fluoride ions. Alum treated ion exchange resins, polystyrene resins, sulphonated saw dust resin have been used in the defluoridating process [110-112]. Synthetic inorganic ion exchangers, eg. complex metal chloride silicates, formed from barium or ferric chloride with silicic acid, also showed selectivity for fluoride. Novel materials such as Indion FR 10 (IND), and Ceralite IRA 400 (CER) [111] have also been used for removing fluoride from aqueous medium. Though percentage removal is quantitative but the efficiency is reduced in presence of other ions. Regeneration of sorbed ion-exchanger leads to fluoride rich waste which again needs to be treated. Further, the pH of the treated water changes making it unfit for drinking purpose.

**Magnetic materials as sorbents**

Magnetic solid phase extraction (MSPE) using magnetic particles (MPs) as the adsorbents have aroused great interest in water treatment in recent years [113]. MSPE involves the use MPs or magnetic nanoparticles which are added into the aqueous solution where the
target analyte is sorbed on the surface of the magnetic sorbent which are further separated from the aqueous solution by applying an external magnetic force. The target analyte is then either desorbed by using an eluent or directly quantified on the sorbent using a suitable analytical technique. Magnetic materials especially the class of magnetic nanomaterials represents an important class of compounds that are known for their unusual properties as well as multidiscipline applications [114-119]. Advances in nanoscale and engineering suggest that many of the issues involving water quality can be addressed by use of appropriate nanoparticles. The nano-sorbents have immense potential in water purification. The high surface area to volume ratio and particle size is some of the properties of nanoparticles that provide better kinetics for the sorption of contaminants from aqueous solution. However, success of nano-size particles in the application of water purification depends on their retrieval from water bodies. Incorporation of magnetic properties to nano-sorbents provides their easy retrieval from aqueous medium using external magnetic field. Hence, the magnetic nano-sorbents based aqueous treatment processes have become one of the promising methods for the removal of toxic metal ions from aqueous streams. This approach has become more useful when polluted water contains solid residues that lead to the risk of fouling of the columns used for purification. Water treatment is greatly simplified by the employment of MSPE considering that there is no need for packing of the column with the sorbent in the case of batch mode operation, since the phase separation can be quickly and easily accomplished by applying an external magnetic field. Fig 1.2 shows a general schematic diagram of
MSPE where the sorption and elution steps are shown using a magnetic sorbent along with its retrieval of treated solution using an external magnet.

![Fig. 1.2 Schematic diagram of a magnetic solid phase extraction process](image)

Generally, MPs consist of magnetic elements such as iron, nickel, cobalt or their oxides and alloys having ferromagnetic or superparamagnetic properties. Ferromagnetic materials once magnetized behave like small permanent magnets and have a permanent magnetism whereas superparamagnetic particles are magnetized in a magnetic field but retain no residual magnetism after the field is removed. There are many magnetic nanoparticles which are used in MSPE. The size of these magnetic particles varies from micro meter to nanometer. The nanometer-sized MPs (1–100 nm) have attracted a specific interest currently due to their superparamagnetic nature as well as their unique physical and chemical properties such as high dispersibility, relative large surface area and the high ratio of surface-to-volume resulting in a higher adsorption capacity [120,121].
In the recent years, Fe₃O₄ magnetic nanoparticles have attracted attention in the field of MSPE. However these magnetic iron oxide particles have some limitations such as difficulty of recycling the sorbent as Fe₃O₄ is highly susceptible to oxidation when exposed to the atmosphere and its hydrophobic surface properties which limit its dispersion into aqueous solutions and matrices [122,123]. Their lack of selectivity towards the targeted analyte in the complex matrices makes them unsuitable for real water samples.

In order to overcome such limitations, modification of existing magnetic particles with specific active groups has become a promising technique (Fig. 1.3). Modification is usually achieved by the attachment of inorganic components (e.g., silica or alumina) or organic molecules (e.g., modified with polymer or surfactant, etc.) on the surface of magnetic nanoparticles thereby improving their chemical stability by preventing their oxidation and selectivity for ion uptake. Further modification of polymer coated magnetic nanoparticles with various hydrophilic functional groups prevents the agglomeration of particles as well as provides an environment for transferring the hydrophobic iron oxide nano-particles into a hydrophilic system.

Fig 1.3 Functionalization of magnetic nano-particles
Most of the adsorbents used in the defluoridation of aqueous streams are in the form of powders or resins and have a tendency to block the sewer and as such are difficult to separate from the aqueous solution. Therefore, an ideal adsorbent with high surface area, good physical and chemical stability and ease of its removal should be developed for fluoride removal. The literature survey of few magnetic sorbents which have been synthesized for the removal of fluoride is discussed in the introduction chapter of the corresponding chapter.

The solid phase extraction methods for boron uptake are based on using boron selective ion exchange resins or adsorbents such as activated carbon impregnated with salicylic acid [124,125]. Several waste products of natural materials have been used as ion exchange material for removing boron. Cellulose and chitosan derivatives modified with NMDG were synthesized for boron uptake from aqueous streams [126,127]. Sawdust of several species of trees like pine, birch and oak has been used as adsorbents [128]. Tannin gel synthesized from tannin molecules, amine-modified tannin gel, calcined magnesite tailing are some of the lesser known adsorbents for boron removal [129-131].

Apart from using the natural available sorbents, there are some polymeric adsorbents which have been used for deboronation of aqueous feed. Glycidyl methacrylate (GMA)-methyl methacrylate (MMA)-DVB (divinyl benzene) terpolymer beads have been reported as an efficient method for boron removal from drinking water [132]. Several polymeric resins have been applied for the treatement of water. Diaion CRB02 and Dowex XUS 43594.00 boron selective resins have also been tested for boron removal from simulated seawater samples. A few commercial boron selective resins (BSRs) are
macroporous crosslinked polystyrenic resins, functionalized with Nmethyl- D-glucamine (1-amino-1-deoxy-D-glucitol; NMG) group. The performance of these resins from model seawater was appreciable and it also eliminated boron from natural seawater reverse osmosis permeate [133,134]. There are some polymer bound sugar derivates like sorbitol and mannitol that have been widely employed for the removals of boron at trace levels but the major disadvantage is their high cost of regeneration [135-140]. For instance Amberlite IRA- 743 containing sorbitol functional groups reduces boron concentration below 1 mg L⁻¹. Despite high boron removal efficiency of 90%, this process is unsatisfactory because of expensive resin regeneration and the capacity loss during each step of regeneration [141].

The SPE method has also been applied for extracting mercury using different sorbents as extractants. Activated carbon is one of the most well-known adsorbents which have been mostly used for decontamination of mercury contaminated water [142-145]. While raw activated carbon can be effective in removing mercury at high sorbent to mercury ratios impregnation of functional groups, especially sulfur, can significantly improve the adsorption capacity. Although it was the widely used method but the high costs of the process has limited its use in real water situations. Alternative bio-materials, such as fern, fruit derived biomass and leaves of casto tree have also been investigated for mercury sorption with encouraging results [146-148]. Bark is available as a by-product of the timber industry and is effective because of its high tannin content. The polyhydroxy polyphenol groups of tannin are the active species in the adsorption process. Ion exchange
takes place as mercury cations displace adjacent phenolic hydroxyl groups, forming a chelate [149-153].

Adsorbents containing sulfur-bearing groups have a high affinity for heavy metals like mercury. Some sulfur-bearing compounds include sulfides, thiols, dithiocarbamates and dithiophosphates which have been used for mercury sorption [154]. Zeolites, clay and fly ash were used for the uptake of mercury from aqueous solution [155,156]. Roberts and Rowland et al.[157] studied the removal of Hg using modified cotton. Masri et al. [158] presented mercury adsorption capacities for several natural materials but no information is given on the sorption mechanisms of these materials or their chemical constituents. Many researchers also have used natural or synthetic polymers to selectively remove Hg(II) from aqueous solution using batch process [159]. Although various conventional methods of extraction as described earlier are being used at present to solve the problem of groundwater pollution, none of them is user friendly due to some or the other limitations and has either no or very long payback period. In the recent years, membrane process has emerged as an alternative to provide safe drinking water as discussed below.

1.2.4. Membrane based methods

The use of membranes for the removal of contaminants from aqueous feed is increasing day by day because of the following advantages:

- Membranes provide an effective barrier to suspended solids, all inorganic pollutants, organic micropollutants, pesticides and microorganisms, etc.
- The process permits the treatment and disinfection of water in one step and ensures constant water quality.
 No chemicals are required and very little maintenance is needed.
 Life of membrane is sufficiently long, so problem of regeneration or replacement is encountered less frequently.
 It works under wide pH range and shows no interference from other ions.

Hence, membranes based methods are now supplementing the above listed methods that are widely used on industrial scale for the separation of targeted analytes from aqueous feed. Nowadays membrane based methods which were earlier limited to chemical laboratories as analytical tools have become an important part of industrial applications. They are used for water treatment, in packaging materials, sensors, ion-selective electrodes, fuel cells, battery separators, beverage industries and last but not the least in organic/inorganic separations. The pressure driven membrane processes have dominated the field of membrane separation till date.

**Membrane** is a thin sheet of natural or synthetic material that is permeable to certain substances and prevents the passage of others in solution. The first milestone of “Synthetic Membrane” was its application in the water softening during the Second World War [160]. The principal development in the 1980 was the emergence of industrial membrane gas separation processes e.g. Monsano prism membrane for hydrogen separation [161]. Today, membrane separation processes find wide ranging applications as discussed above.

Membranes can be divided into different types: homogeneous or heterogeneous, symmetric or asymmetric in nature, neutral membranes, ion-exchange membranes, functionalized membranes etc. Among all these the neutral membranes involve only
physical interaction between diffusing species and membrane matrix. This class of membranes is generally used for water desalination as discussed in the underlying sections.

Apart from physical interactions, diffusing species can have electrostatic interactions (in ion-exchange membranes) or covalent interactions (functionalized membranes) with the membrane matrix. These interactions provide a basis for utilizing the membranes as sorbents. The use of membrane technology can provide an alternative to existing chemical processes such as distillation, extraction, fractionation and adsorption.

Membranes can in principle be used to carry out most of the separation processes and can be broadly used in two ways:

i. Membranes for filtration

   ii. Membranes as sorbents

### 1.2.4.1. Membrane filtration

Membranes in filtration mode provide physical barriers that permit the passage of materials only up to a certain size and shape. Different membrane separation processes include micro-filtration, ultra filtration, nanofiltration and reverse osmosis.

Among these, micro filtration and ultra filtration are pressure-dependent processes, which remove dissolved solids and other substances from water to a lesser extent than nanofiltration and reverse osmosis. All these membrane based methods are used for physical separation. The extent to which dissolved solids, turbidity and microorganisms are removed by the membranes is determined by the size of the pores in these membranes. Substances that are larger than the pores are fully removed. Substances that
are smaller than the pores of the membranes are partially removed, depending on the construction of a refuse layer on the membrane. All the four types of above listed membrane filtration processes are briefly described below.

**Micro-filtration:** Membranes with a pore size of 0.1 – 10 µm perform micro filtration. These membranes remove all the bacterial components from the solution. Micro filtration is usually implemented in different water treatment processes where particles with a diameter greater than 0.1 mm need to be removed from a liquid.

**Ultra filtration:** Ultrafiltration (UF) is a pressure-driven process that removes emulsified oils, metal hydroxides, colloids, emulsions, dispersed material, suspended solids, and other large molecular weight materials from water. UF membranes are characterized by their molecular weight cut-off. In ultra filtration, particles of 0.001 – 0.1 µm dimensions can be removed from the fluids.

**Nano filtration (NF):** Nanofiltration membranes have pore sizes from 0.0001-0.001 µm which are smaller than those used in microfiltration and ultrafiltration, but just larger than that in reverse osmosis. Nanofiltration (NF) is generally targeted to remove only divalent and larger ions. Monovalent ions such as sodium and chloride will pass through an NF membrane, thus many of the uses of NF involve de-salting of the process stream.

**Reverse Osmosis (RO):** The membrane with the smallest pore size comes under reverse osmosis (RO) category. These RO membranes involve reversal of the osmotic process of a solution in order to drive water away from the dissolved molecules. RO depends on ionic diffusion to effect the separation. A common application of RO is seawater and
brackish water desalination. Below is the diagram outlining the process of RO (Fig 1.4). When pressure is applied to the concentrated solution, the water molecules are forced through the semi-permeable membrane whereas the contaminants are not allowed through.

![Reverse Osmosis Diagram](image)

**Fig. 1.4 Typical diagram of Reverse Osmosis process**

In the recent years, RO membrane process has emerged as a preferred alternative to provide safe drinking water without posing the problems associated with other conventional methods. For proper water treatment in desalination plants a series of membranes has to be applied for water decontamination. Dialysis is another membrane treatment process which involves transport of solute from feed compartment to the receiver compartment using a membrane rather than retaining it in on membrane itself. The pores of the membrane used in dialysis are much less restrictive compared to NF and RO membranes. The solute is driven through the membrane either by Donnan effect or by an applied electric field. Electro-dialysis is another membrane based process which
involves the removal of ionic components from aqueous solutions through ion exchange membranes under the driving force of an electric field.

1.2.4.2 Applications of membrane filtration methods for removal of fluoride, boron and mercury

Reverse osmosis and electrodialysis are two membrane filtration processes which are used for the removal of the above listed contaminants from aqueous feed. Defluoridation from effluents using RO technique was carried out by Ndiaye et al and it was observed that the rejection of fluoride ion was typically higher than 98% [162]. Work has been carried out by many researchers using NF and RO membranes to optimize both theoretical and experimental conditions for the retention of fluoride in the membrane system [163-172]. The removal of fluoride from diluted solution with Neosepta AHA anion-exchange membrane has been studied by Donnan dialysis and the transport efficiencies of different membranes have been compared [173]. It was observed that the transport of fluoride was maximum at pH 6 of feed phase and at pH 1 of receiver phase. Electrodialysis phenomenon has also been used for the defluoridation of aqueous streams by many research groups [174-176].

Combination of reverse osmosis with selective ion exchangers for selective removal of boron in the desalination of seawater and brackish water has been carried out [177-179]. These hybrid methods consisting of two step pathways are followed where borate is complexed using ion exchange resins and it is further separated using ultra filtration membranes [180-182]. This method is known as polymer enhanced ultra filtration method
(PEUF). The polymers used in PEUF method were: poly(vinyl alcohol) [183], glucoheptanamide derivatives of poly(amidoamine) and poly(ethyleneimine) [184], poly(glycidyl methacrylate) and poly(N,N’-diallylmorpholinumbromide) modified with hydroxyethylaminoglycerol [185], hydroxyethylaminoglycerol functionalized to poly(glycidylmethacrylate) and poly(4-vinyl-1,3-dioxalan-2-one-co-vinyl acetate) [181], alkyl monol, diol, or triol containing polyethyleneimines [186]. But usually the membrane fouling, high cost of regeneration of adsorbents and preparation of water soluble polymers for complexing boron are some of the major limitations of these hybrid methods.

Membrane filtration method has also been applied for mercury removal. Reverse Osmosis (RO) system for mercury removal consists of granular activated carbon pre-filters followed by a RO membrane. Thin Film Composite (TFC) and Cellulose Triacetate (CTA) are commonly used RO membranes for mercury removal. TFC membranes are relatively more efficient compared to CTA membrane. Both have a very high rejection rate for different forms of mercury.

However, there are certain limitations of using membranes in filtration mode such as it removes all the ions present in water, though some minerals are essential for proper growth. The water after treatment becomes acidic and needs pH correction therefore remineralization of the treated water is an added step. Lot of water gets wasted as brine and disposal of brine is a problem itself. In addition to this, the scaling up of membrane process is expensive in comparison to other methods such as adsorption based methods.

1.2.4.3 Membranes as sorbents
Membrane-based processes, with their inherent advantages, emerge as a highly competitive candidate for reclamation and reuse of water, owing to its efficiency, ease of implementation, cost, and low environmental impact. Furthermore, day by day the capital, operational, and maintenance costs for membrane systems continue to decline, making them increasingly attractive for water purification applications [187-189]. Separation using polymer membranes has become an effective technology for the removal and recovery of various metal ions. Selectivity in the membrane separation has become possible only by tailoring the existing membranes with various functional groups required for binding the ion of interest. Selectivity of a membrane towards a specific analyte is governed by many factors. Some of these are: (i) size exclusion, (ii) diffusivity, (iii) Donnan exclusion and electrostatic interactions of ions with fixed charges in the membrane, (iv) solubility/partition coefficients, (v) conditions at aqueous membrane interface and (vi) covalent interactions of desirable component (mostly metal ions) with the functional groups present in the membrane.

The physical structure of the selected membranes also plays an important role in the membrane process. Some of the parameters responsible for providing different physical structures in polymer membranes are: (a) primary structure of matrix polymers, (b) crosslinking and grafting, (c) crystallites (d) pore structure (e) connectivity of pores and (f) free volume. Pore size, pore size distribution, pore density etc. are usually controlled more precisely to improve membrane performance whenever they are to be used for any application.
Currently the membrane based separation methods are gaining attention in analytical applications because of the preconcentration step which is achieved simultaneously with separation, enhancement in the selectivity gained by using various selective functional groups, mechanical strength of the base membrane as a support, use of low concentrations of reagents and possibility of onsite application. However, use of membranes as a solid phase extractants for removal and detection of toxic ions is scarcely reported in literature. This is because the type of the matrix of the sample governs the choice of a proper type of membrane. Depending on the type of the matrix, different types of membranes are needed whose brief overview is as follows.

1.3. Types of polymeric membranes

1.3.1 Plasticized membrane

Plasticized membranes are also referred to as polymer inclusion membranes (PIM). Polymer inclusion membranes (PIMs) were first introduced by Sugiura et al [190]. PIMs are prepared by the physical immobilization of a selective extractant into a plasticized polymer matrix (Fig. 1.5). Two of the commonly used polymer matrices are poly (vinyl chloride) (PVC) and cellulose triacetate (CTA) [191-192]. They are inert and highly hydrophobic polymers. The base polymer forms the skeleton of the PIM to provide mechanical strength. The chemical structure of the base polymer also plays an important role in transport of ions across the PIMs. These matrix forming polymers can be plasticized upto 70 – 80% by weight with a variety of plasticizers like 2-nitrophenyl octyl ether (NPOE), dioctyl phthalate (DOP), bis(2-ethylhexyl) terephthalate (DOTP), dioctyl
sebacate (DOS) and tri-(2-ethylhexyl) phosphate (T2EHP). The network of overlapping chains of the polymer provides mechanical support to the PIMs.

The properties of these membranes can be tuned by appropriate selection of matrix forming polymer, plasticizer and extractant. Therefore, these membranes can be tailor made for a specific application without involving exotic synthetic chemistry. These membranes exhibit many advantages, viz. ease of operation, minimum use of hazardous chemicals and flexibility in membrane composition to achieve desired selectivity and separation efficiency [193,194].

**Fig 1.5** Schematic diagram showing steps involved in the preparation of plasticized membrane

**Thin homogenous transparent film**
The stability of these polymer inclusion membranes (PIMs) is amongst the major reasons for the recent rejuvenation of interest in carrier-mediated transport for selective separation and recovery of metal ions as well as numerous organic solutes. This is reflected by an increasing number of PIM investigations reported in the literature over the last two decades [195,196]. In addition to the use of the PIMs in the separation experiments a few reports in literature are also available on PIM based optical sensors for metal ion detection [197-202]. PIMs are usually preferred for making optodes for optical detection because of the high selectivity, flexibility, and chemical and mechanical stability offered by its matrix. In addition to this, the major advantage of using PIMs as optodes is based on their ease of synthesis. For the membrane type optical sensing layer, these PIMs not only act as the support for the immobilized reagent, but also enable permeation of the targeted chemical species. Therefore, researchers are focusing on the development of PIM based optodes which can be used for on-field detection of metal ions in natural waters.

1.3.2 Grafted membrane

Grafted polymer membranes are a class of membranes containing segmented copolymers with a linear backbone of one composite and randomly distributed branches of another composite (Fig 1.6). Grafting is an attractive method to impart desired functionality to any base polymer matrix. Grafting can be carried out in two ways either end-functionalized polymer chains can be grafted to the solid substrate (grafting to) or the grafting reaction can proceed by polymerization from the surface (grafting from). In both the cases a thin polymer brush layer on the solid surface is formed that determines the surface properties. The grafting mechanism is usually irreversible. Selectivity of the
grafted membranes is achieved by incorporating various inorganic or organic groups that can bind to the desired analyte.

**Fig 1.6 Pictorial representation of grafted polymer**

Grafting of polymers as described above have a variety of potential applications resulting from the wide range of properties when different polymer chains are connected to form hybrid branched macromolecules. Graft polymers have been synthesized for many decades and are especially used as impact resistant materials, thermoplastic elastomers, compatibilizers, or emulsifiers for the preparation of stable blends or alloys. One of the more well known examples of a graft polymer is high impact polystyrene, which consists of a polystyrene backbone with poly butadiene grafted chains.

Crosslinking of the polymer network in the base matrix is another probability along with grafting. Formation of network structures using multidirectional chain extension is defined as crosslinking (Fig 1.7). Crosslinking may occur intramolecularly or intermolecularly.
Crosslinking of polymers enhances its stability, improves the mechanical characteristics and results in improved resistance to stress cracking and better fluid resistance. The grafted membranes can be synthesized using different methods of polymerization. Among various existing methods, radiation induced polymerization method has been used in the present work and hence it has been discussed in detail in the following section.

1.4 Methods of modification of polymer membranes

Depending upon the type of polymer, different techniques may be used to carry out its modification. Radiation induced method of grafting/crosslinking includes irradiation of polymeric materials with either high energy radiation (gamma rays, X rays, accelerated electrons, ion beams) or low energy U.V radiation. In all methods, the chemical structure of the polymer is altered either through the crosslinking or the grafting process as discussed above. Modification using high energy radiation such as gamma irradiation is usually most economical at lower doses (~80 kGy and below) and for large, high density parts whereas electron beam is commonly used for small parts, particularly low density parts. For easily degradable polymers, low energy UV irradiation method is used. In all
these methods, the degree of crosslinking or grafting depends upon the type of base polymer and applied radiation dose. One of the benefits of using irradiation is that the degree of polymerisation can be easily controlled by the amount of dose. Both the high energy radiation and low energy UV-irradiation methods are discussed in what follows.

1.4.1 High energy radiation

High energy radiations like gamma rays or electrons interact with organic and other molecules in the polymerizing solution to create free radicals s precursors which will often chemically react in various ways. These precursor radicals thus formed results in formation of new bonds among the monomers or rearrangements in existing polymer chains. The degree of the rearrangements depends on the structure of the monomer and the conditions of treatment before, during and after irradiation. There are several advantages of high radiation grafting methods over commonly used chemical methods:

✓ Possibility of polymerizing monomers which are difficult to polymerize by conventional methods.
✓ Ease and high efficiency of polymerization with low power consumption.
✓ Purity of the initiators is not a concern because polymers form free radicals on its surface.
✓ High penetrating ability makes it appropriate for solid substrate grafting.
✓ Grafting of different monomers on different portions of the same polymer: mosaic grafting is possible.

Preirradiation, peroxidation, and simultaneous radiation are three different methods of irradiation of polymers which are briefly discussed below.
(a) Preirradiation technique

In this method the backbone of polymer is irradiated by high energy radiation in an inert gas atmosphere to form free radicals on its surface and then this is further reacted with a monomer at high temperature (Fig 1.8). As monomers are not involved during the radical generation stage, the possibility of homopolymerisation is negligible in this technique. The major disadvantage of this method is the formation of block polymers compared to graft polymers because of the scissoring of the direct polymer by using high energy radiation.

![Diagram of preirradiation method of grafting](image)

Fig 1.8 Scheme showing preirradiation method of grafting

(b) Peroxidation technique

In this the polymer is subjected to high energy radiation in the presence of air or oxygen. Formation of hydroperoxides/diperoxides depending on the nature of the polymeric backbone and irradiation conditions occurs on the polymer backbone. These stable peroxy products are then treated with the monomer at higher temperature, where the peroxides undergo decomposition to radicals (Fig. 1.9). The
radicals thus formed are made to react with the monomer to be grafted on the polymer chain.

![Diagram](image)

**Fig. 1.9 Scheme showing peroxidation method of grafting**

(c) **Simultaneous method**

This is the commonly used method and in this the polymer is irradiated simultaneously along with the monomer [203]. As both the monomer and substrate are exposed simultaneously to the radiation source, formation of active radicals occurs on both of them (Fig. 1.10). Further reaction is dependent on the generation of free radicals on the polymer/monomer in the reaction system. Homopolymer formation is favored over grafting if the monomer has high radiation yield. Radiation doses required to achieve graft polymerization in this method are lower than the other two methods described above.
Fig 1.10 Scheme showing simultaneous method of grafting

1.4.2 Photoirradiation

Grafting and crosslinking using photo irradiation i.e with UV or lasers light is one of the other methods to generate radicals. In this method radicals are generated via photochemical reaction. Photoirradiation requires very low activation energy and it provides both spatial and temporal control of the reaction since light can be directed to locations of interest in the system. In addition to this, these reactions proceed under low or room temperature and grafting can be controlled on polymeric surface unlike in high energy radiation induced grafting where surface polymerization is not possible because of the penetrating nature of radiations [204,205]. There are two pathways for photoinitiator induced grafting; one is the direct method where photolysis of the chromophoric groups present on the surface occurs whereas the other one is an indirect way where radicals are generated by the photolysis of solvent or additive molecules.

The direct method shows that apart from the graft copolymer, the unwanted homopolymer is also formed if radical A• generated by the photolysis of side groups of the polymer (| - A) is reactive towards the monomer (Fig. 1.11). The chemical nature of
the final product depends on the extent to which chain termination occurs via disproportionation versus combination. Combination of polymer chains usually leads to various crosslinks in the polymer matrix.

\[ A \text{hv} + A + M \rightarrow (M)_n \]

\( (M = \text{Monomer}; A = \text{Photoactive group}) \)

**Fig 1.11** *Scheme showing direct method of photoirradiation*

The indirect method of photoirradiation is illustrated in the following routes (Fig 1.12). Route 1 shows the attack of free radicals on the monomer whereas route 2 illustrates the reaction of electronically excited photoinitiator molecules with the functional groups of the monomer. Usually photoinitiators are required in all those cases where the monomers have a low quantum yield.

**Route 1:**

\[
\begin{align*}
[\text{PI}] & \xrightarrow{\text{hv}} [\text{PI}^*] \\
[\text{PI}^*] & \xrightarrow{\text{RH}} R_1^0 + R_2^0 \\
R_1^0 + RH & \rightarrow R_1^0 + PIH^0 \\
R_2^0 + H & \rightarrow RH + \cdot \\
\cdot + nM & \rightarrow (M)_n \\
R_2^0 + nM & \rightarrow R-(M)_n^0
\end{align*}
\]
Route 2:

![Scheme showing in-direct method of photoirradiation](image)

The primary radicals thus produced react with the monomers to form graft polymers through the initiation, propagation, and termination reactions as in the usual free – radical polymerization. In the present thesis photo irradiation method has been used to introduce the required grafted monomer chains on the polymeric backbone of polypropylene sheets. The precursor grafted membranes thus formed are treated with specific organic groups or inorganic ions so as to generate selectivity towards the targeted ions.

1.5 Scope of the Thesis

Development of new separation methods for removal of targeted species is a very fascinating field in analytical chemistry. Though there are many existing separation methods as explained in the previous sections, a lot of scope exists in improving the sensitivity of existing methods and for developing better methods. The greatest of the scientific and technological challenges in removing toxic ions from different aqueous matrices lies in finding a technology that gives a net positive balance in terms of their
selective removal and the other is their cost of production. Following factors has to be taken into account for developing any method for removing targeted ions from natural waters.

- The method should be capable of treating large volume of contaminated water.
- The sorbents should have high sorption capacity and kinetics.
- Chemical composition of the matrix to be treated cannot be altered therefore; sorbent has to be designed keeping in mind the targeted analyte.
- Sorbent production should not involve complicated synthetic route and the developed sorbent should be reusable making it more economical.

Functionalized inorganic-organic hybrid polymeric membranes are the new entrant in the field of membrane processes for water purification as discussed in the previous sections. Permeation selectivity of the membrane towards competing ions is an important factor for selective preconcentration of the target ions from the multicomponent aqueous feed. Generally, the selectivity is achieved by anchoring the target ions specific functional groups (receptors) in the membrane. The functionalized membranes are prepared by either physical containment or covalent attachment of the functional groups in a suitable organic or inorganic-organic hybrid matrix. The intrinsic multifunctional character of these membranes makes them potentially useful in multiple fields especially in water treatment as discussed above.

Keeping in mind the theme of the thesis, a different approach for the tailoring of existing organic polymers has been used to synthesize fixed site functionalized inorganic-organic polymeric sorbents. The fixed-site sorbents have been synthesized for the separation and
preconcentration of fluoride, boron and mercuric ions from variety of aqueous matrices especially the ground-water and seawater. The mechanism of transport of ions across these fixed-site sorbents involves “ion jumping” from one site to the next. Facilitated diffusion of targeted ions in such sorbent can occur only if the “chained” carriers (fixed sites) are reasonably close to each other and have some limited mobility. Therefore, grafting/crosssinking of a desired monomer on the existing fixed-chains of a polymer base matrix was carried out. The advantages of using these fixed-site sorbents are: (1) the stability is improved; and (2) the transport of analyte is actually enhanced as these membranes are generally hydrophilic with a high functional group density.

The ion carrier complex formation involved in mass transfer of ions from aqueous to membrane matrix should have fast reaction kinetics. To achieve this, two types of the polymer base matrices: microporous and fibrous poly(propylene) sheet has been selected. The use of the fibrous base having larger void spaces within the fibers helped in providing higher accessibility of binding sites to the targeted ion.

These fixed-site membranes are most successful when ions interact with membrane through electrovalent interactions. However, the permeation selectivity of the target ions across the membrane cannot be achieved by only electrovalent interactions. The target ions should have covalent interactions with the fixed sites in the membrane for achieving desirable selectivity in facilitated transport of the target ions from aqueous phase to membrane phase. Therefore for fluoride, boron and mercury (II) sorption, study involves anchoring of optimized chemical composition of the hydrogel in the microporous poly(propylene) matrix and their further functionalization with various inorganic/organic
groups for achieving desired selectivity. In addition to the fixed site-polymeric sheet sorbent for fluoride removal, a highly super-paramagnetic polymer sorbent has also been synthesized and optimized for various parameters under simulated groundwater and seawater conditions.

Similarly, the part of thesis focused on mercury uptake involves scanning of different types of functionalized membrane sorbents and optimizing their chemical composition in terms of sorption kinetics, capacity and selectivity in real water samples. The choice of poly(propylene) membrane base for the entire study was based on its inherited advantages as listed below.

- Reproducible geometrical form, simplicity and amenability to large volumes.
- Incorporation of functional groups by chemical bonds: Uniform material with high accessibility of binding sites.
- Non-interfering matrix and hence direct quantification using EDXRF.
- Applicability in wide pH range and salt concentration.

Comparison of all the sorbents synthesized in the present research work with the existing sorbents in terms of the key parameters that affect the sorption uptake of the desired analyte has been made. Along with the development of newer sorbents, the detection and monitoring of toxic elements at ultratrace concentrations in natural and waste waters is important. Therefore the last part of the study involves synthesis of a visual optode membrane based sensor for on-site detection of mercuric ions in natural waters. The flat sheet polymer sorbents having fixed binding sites are amenable for scaling up for water