

1.1 Polymers

The chemistry of polymers open the new platform for a bright present and an even brighter future. Polymer chemistry have attracted a great deal of research and commercial interest in the past few decades. They have a number of beneficial functions. The three major functions that must be optimized are cost, performance and durability. In addition, they have large number of conventional applications in various technological areas, such as adhesives, coatings, moisture barrier, electrical, thermal insulation, thickeners for cosmetic lotions, creams, pharmaceuticals, paints, ion-exchange, oil-recovery, paper, textile, and other industrial products etc.¹⁻¹⁰.

The polymer is classified into two types they are natural polymer (Biopolymer) and synthetic polymer (Man-Made Polymer). The natural polymers are found in living matter and they are generally considered as renewable resources such as protein, wood, rubber, resins, amber, cellulose, starch, lignin and silk fibers which are natural and are believed to be formed since the early days of the origin of living organisms on earth¹¹⁻²⁰.

Synthetic (Man-made) polymers have been studied since 1832. The first attempt on synthetic commercial polymer, a phenol formaldehyde (bakelite) polymer was patented by A. V. Baeyer and commercialized by Leo Baekel in 1910.^{21,22} The synthetic polymers with different nature have established their position in present day society through diversified applications ranging from shopping bags to aerospace technology and it shows the wide range of applications such as furniture, aircraft canopies and windows, molding powder and pellets for automobile parts and tail lamps, sanitary ware and bath tubs, optical lenses and other auxiliary items, as an emulsion and solution for paints, varnishes, coatings and adhesive applications. Still, the search is continued for improvement of the properties of polymers such as kinetics, polymer formation, molecular size, shape and mass, morphology and supramolecular structure,

There are two type of polymerization which lead to the formation of substances of higher molecular weight, (i) Addition polymerization is the reaction of linking together of molecules of monomers, it is not accompanied by the formation of byproducts and involves no change in elemental composition. (ii) Condensation reactions which involve combination of molecules having functional groups capable of condensation by the elimination of simple molecules, The functionality of the initial monomers has a great effect on the structure and properties of the resulting polymers.

Polymers with identical monomers are called homopolymers and with several types of monomeric units are called copolymers or mixed polymers. The wide range of properties of polymeric materials depend on the microscopic arrangement of the chain and the polymer may be synthesized as linear, branched or cross-linked or a mixture containing all the three. The modification of synthetic polymers are also attractive because they can be fabricated into various shapes and structure with desired features and it may be achieved by irradiation, chemical, thermal or by combination of some of these routes. Among these, the chemical route is widely practiced to obtain end polymer product with desired solubility, crosslinks, mechanical strength, inflammability, flammability etc.

The development of new polymer based material is aimed at improving the range of service of polymers to meet practical needs and the modern technological demands for materials which have desirable chemical, mechanical, thermal and electrical characteristics, high strength, light weight, flexibility, resistance to chemicals, wear and tear. As well as the progress of polymer science is widely used in various branches of technology and agriculture. Some of specific functionalized polymers merge with molecular biology and medicine which may be strictly inorganic or organic in character called as inorganic-organic polymers.

The investigation of functionalized polymeric materials by synthetic aspect is a great interest in field of polymer chemistry. The polymers with specific functional groups for intended use, are generally known as specific or functionalized polymers. The functionalized polymer can be obtained either by introducing desired functional groups on suitable monomer and polymerisation or by incorporation of the same on desired polymer matrix by appropriate modification. The main groups of the functional polymer used for surface functionalization include epoxide, carboxylic acid, hydroxyl, aldehyde, amine groups, phosphonic acid, iminodiacetic acid, amidoxime, hydroxamic acid, mercapto and dithiocarbamate etc. The functional polymers have been utilized extensively in sectors like agriculture, ion-exchange, packaging, transportation, electronic components, building materials, automobiles, biomedical and medicines etc.²³⁻³⁴. The chelate forming ion exchange polymer is of great interest in field of polymer chemistry. The chelating polymer made from functionalized polymers have proven to be resistant to the environmental and chemical degradation reactions while at the same time maintain their physical, mechanical and chemical properties.

The chelating polymer generally consists of atoms such as oxygen, nitrogen and sulfur, nitro, nitroso, azo, diazo, nitrile, amide and other groups. Oxygen atom is usually in the form of phenolic, carbonyl, carboxylic, hydroxyl, ether, phosphoryl and some other groups. Sulfur atom is in the form of thiol, thioether, thiocarbamates, disulphide groups, etc.. The use of functionalized polymers as supports in which reactive groups are introduced by covalent bond formation by sorption phenomenon has been an active area of research³⁵⁻³⁷.

The preparative method used for chelate polymers are based on the standard methods of organic polymer synthesis. They may be divided in to three categories (i) when metal ions and suitable multi-dentate monomer are linked together, (ii) those obtained by incorporation of metal ions into formed polymeric ligands having coordination sites and (iii) polymerization of coordination monomers. The useful industrial applications of some of these functionalized polymers are in such diverse fields as hydrometallurgy, desalination, waste-water treatment, permselective membranes, ion exclusion, catalyst, recovery, purification of biochemical, resisting to low level radioactive wastes, protecting potable water and reserve water.

The importance of polymer electrolytes are particularly attractive because they can lead to flexible, compact, laminated solid-state structures free from leaks and available in different geometries³⁸. The polymer electrolytes are mainly divided into several classes such as polymer/salt complexes, gel polymer electrolytes which formed by incorporating an organic electrolyte solution into a polymer matrix, polymer-in-salt/rubbery electrolytes, where the polymer fraction is a minority with respect to the salt, composite or nanocomposite polymer electrolytes, in which inorganic particles are introduced into a polymer electrolyte^{33,39-45}. In principle, the ideal polymer electrolytes for lithium-ion batteries must satisfy some basic requirements such as higher ionic conductivity at ambient temperature, virtuous thermal stability, no-leakage of electrolyte, chemical and mechanical stability, higher energy density, a lithium transport number close to unity, compatibility with the electrodes flexible geometry and improved safety hazards have drawn the attention of many researchers on the development of lithium polymer batteries^{34,46,47}.

1.2 Polymer composites and blends

In recent decades, the development of polymer composites and polymer blends and their technological importance leads to variety of industrial applications ranging from

electronic materials to load-bearing structural materials. The incorporation or composition of two or more polymers called polymer composites/blends. Each network form of polymer is linked together through secondary forces. Composites consist of a continuous phase and discontinuous phase. The difference between a blend and a composite is the size scale. Blends are mixtures of different polymer chains on a molecular level, whereas composites can be considered as mixtures on a macroscopic level. The polymer composites and blends are of fundamental importance in diverse fields such as conducting polymers for supercapacitor, sensing of nanomaterials, reinforcing, coating, 3D printing, porous material media flows and hydrodynamic lubrication⁴⁸⁻⁵².

This mixing or blended polymers can give new materials with unusual properties such as surface area, pore volume, pore size distribution and are classified as microporous and macroporous. In the case of microporous, in dry condition no measurable surface area is found. Normally, microporous polymers are prepared by using low amounts of crosslinking agents with good solvent and the macroporous polymer blend/composites are prepared with high amount of crosslinking agents and they are made with suitable solvents. The size of the porosity are usually higher in case of macroreticular than macroporous polymer. However, the swelling behavior of porous polymer depends on the amounts of crosslinking agents.

The polymer composite materials, in most cases, fiber reinforced polymers, are generally having light weight, high specific modulus and strength are critical issues. In particular, the manufacturing of parts from thermoplastic as well as thermosetting polymers, short and continuous fiber reinforced composites are emphasized. The strength and stiffness of the polymer composite remain very much a function of the reinforcing material, but the matrix makes its own contribution to properties. The ability of the composite material to conduct heat and current, for example, is heavily influenced by the conductivity of the matrix.

Effective method for modifying polymer properties especially thermoelectric properties of polymer blends and composites by blending with small molecule, polymer or nanoparticle additives. Many small molecules and simple inorganic salts are soluble in polymer matrices and have been widely used in electronic applications, including organic solar cells, electrodes and field-effect transistors⁵³⁻⁵⁷. The polymer composites are prepared by monomer polymerization in the presence of nanoparticles, in situ reduction of inorganic salts to form particles in the presence of a polymer, or solution blending of

polymers and nanoparticles. More commonly, homogeneous and uniform dispersion of nanoparticles in the polymer matrix give optimized properties and ligand exchange or covalent modification of nanoparticles which can be used to ensure that the two components are miscible and optimize polymer with particle interactions. Moreover, the polymer-nanoparticles or crystalline-amorphous polymer interfaces create boundaries that scatter phonons, thus ensuring low thermal conductivity.

Doping with large molecules can also be used to prepare conducting polymer composites with improved mechanical properties. An effective way to improve mechanical properties of conducting polymer material is to create their composites or blends with other polymers that have better mechanical properties for the intended application. Conducting polymers like polypyrrole and polyaniline have also been explored as conductive fillers, in order to overcome the poor processability of these conducting polymers as well as to impart conductivity to otherwise insulating polymers⁵⁸.

The production of man-made bioartificial polymer blends confer unique structural and mechanical properties on the base of the specific properties of natural polymers and synthetic polymers. Bioartificial blending has been suggested to have potential for use in distinct biomedical applications and can lead to a new generation of scaffolds, bone fixation, bone replacement and tissue engineering applications⁵⁸⁻⁶⁰. Generally, biopolymers are abundant and some may be obtained at a relatively low cost however high cost is connected with the purification of biopolymers from natural sources. To develop modified materials based on the blends of a natural polymer and a man-made polymer, the two components of the blends need to be combined into one versatile material. The components can be combined in the molten state (melt mixing) and it can be dissolved in the same solvent to avoid denaturation of the structure⁶¹.

One of the most promising methods of solid-phase modification of polymers is the joint action of high pressure and shear deformation on the blend of solid components. Under these conditions, the reacting material is subjected to plastic flow with an unlimited strain.

1.3 Terpolymers

A terpolymer is a polymer by consisting of three distinct monomers incorporated in one polymer chain and such different monomers occur in a random or alternating fashion. The term is derived from *ter* (Latin) meaning thrice and polymer. The importance

of terpolymer material has increased recently because of their useful new desirable properties, such as mechanical and thermodynamic properties, which are both unique and attractive for many industrial applications.

During the past few years, a significant amount of research in polymer chemistry has focused on the development of polymerization methodology that provides the straightforward preparation of terpolymer with predetermined molecular masses, narrow molecular mass distributions, advanced architectures, tunable properties etc.,

1.3.1 Properties of terpolymer

The terpolymer exhibits various functional properties such as magnetic, dielectric, and optical, that may be significantly different from properties of other polymers. The incorporation of monomers into terpolymer matrices can improve existing properties or impart new properties such as mechanical optical, electrical, photovoltaic, thermal and barrier. Thus such incorporation opens opportunities for combining functional properties along with a prescribed morphology.

1.3.1.1 Mechanical properties of terpolymers

The terpolymeric based material displayed better mechanical properties than other pristine polymer. The mechanical properties such as tensile strength, elongation at break, modulus and work to break are very important characteristics of terpolymer and their blends (composition of two polymer) or composites. These macroscopic properties are known to very closely depend on the strain rate, thus an understanding of strain rate dependence of their deformation behavior is important for encouraging their wide use in engineering and structural applications. Strain rate has a complicated and dramatic effect on materials deformation processes because the energy expended during plastic deformation is largely dissipated as heat. This process was observed to be more prominent at higher loading rates that are associated with adiabatic drawing than during lower loading rates where isothermal drawing occurred. The mechanical properties of terpolymer blends depend on the nature of terpolymer-blends interactions and the state of terpolymer, size, concentration, shape, and dispersion state, and their architecture.

Terpolymeric materials with high ionic conductivity are important for applications such as batteries and fuel cells. The performance of these materials depends not only on their electrical properties but also on other properties such as shear modulus, permeability, etc. The mechanical properties of terpolymer electrolytes, for example, are particularly

important in secondary solid-state lithium batteries. Repeated cycling of these systems leads to dendrite formation, reducing battery life and compromising safety^{28,62,63}.

1.3.1.2 Degradation properties of terpolymers

In general, degradation is the process where the deterioration in the properties of the polymer takes place due to different factors like light, heat, mechanical etc. As a consequence of degradation, the smaller fragments do not contribute effectively to the mechanical properties. Thus, any polymer or its composite which is to be used in outdoor applications must be highly resistant to all the environmental conditions.

Thermal degradation of terpolymeric materials is characterized by two major types of transition temperature, the crystalline melting temperature (T_m) and the glass transition temperature (T_g). Many factors which contribute the thermal stability of the terpolymeric materials, some of these are primary bond strength, resonance stabilization, secondary bonding forces, rigid intra-chain structure and stable end groups on the molecules, molecular weight, heat rate, sample form, atmosphere, frequency, load and molecular weight distribution.

Photodegradation of terpolymeric material begins with the production of macro-radical in the amorphous regions of terpolymer substrate. This radical rapidly reacts with oxygen to give a macropoxy radical which abstracts a hydrogen atom from the terpolymeric backbone to produce a hydroperoxide group. The hydroperoxide group is photolytically cleaved to produce the highly reactive radicals, which continue the chain, irreversibly. The radical recombination form a non-radical product which is called crosslinking. The hydroperoxides can be cleaved both by exposure to UV light, visible light or heat.

1.3.1.3 Ion exchange properties of terpolymer resin

Ion-exchange terpolymers can be considered as high molecular weight acids or bases, which can exchange their hydrogen or hydroxyl ions for equally charged ions and thus are converted into high molecular weight salts. The mobile ions bound to the polyelectrolytes can be displaced by other ions of equal charges resulting in ion exchange.

The synthetic ion-exchange materials having appropriate functional groups are incorporated into terpolymeric structures. The structure may be based upon polystyrene, phenol and formaldehyde, or similar stable polymeric chemical structures. To function as a cation exchanger, the terpolymer resin should contain acidic groups. The anion

exchangers are obtained by introducing amino groups into a terpolymeric network. The factors such as concentration of electrolyte, pH and dosage can affect the properties of terpolymers. The solid state terpolymer resins are suitably insolubilized in high molecular weight polyelectrolytes possessing labile or mobile ions capable of exchanging ions of equal charge from the surrounding medium, without altering the general physical nature of the ion exchanger materials⁶⁴⁻⁶⁷.

1.3.1.4 Sorption characteristics of terpolymers

Several features of solute structure such as chain length, ring structure, nature of polar groups and physical state in solution, their shape and size in solution have a dominant role to play in understanding the adsorption process. In a given mixture of equivalent macromolecules the larger molecules get adsorbed better. This phenomenon is particularly more observed in the higher concentration region, where as in the lower concentration region, the lower molecular weight fractions also get adsorbed. The rate of adsorption of shorter chains are greater than that of longer ones due to diffusion. So at the initial stage they are adsorbed and then displaced by larger ones depending on the thermodynamic equilibrium state. This may not happen when the adsorption bonds are stronger as in chemisorption. For a complete analysis of the results, information on the actual size of the molecules penetrating into the pores are necessary, even then it is difficult and lacks reliable dependence of the adsorption on the molecular weight⁶⁸⁻⁷⁰.

When molecules adsorbing to the surface of terpolymer undergoes a conformational change, groups are exposed and sites are created to which a second layer of macromolecules can undergo sorption. In fact, the process could be repeated forming multilayers. The potential for multilayer formation is more observed in case of compact terpolymers, which are prone to undergo conformational change upon adsorption. Steric hindrance in the polymer molecules will tend to reduce the strength of bond between polymer and the substrate. The major advantage of these kind of terpolymeric materials is the insolubility leading to filter ability which makes it possible to be recycled for reuse.

1.3.1.5 Biological properties of terpolymeric materials

The terpolymeric materials can possess outstanding biological properties for biomedical and biotechnology applications. The wide variety of literature reports has captured the imagination of both the academic and industrial communities, many reports have included environmentally responsive and biologically active terpolymers and

highlight a diverse range of biomedical applications for the efficient and non-cytotoxic delivery of drugs, genes, and active agents. Biocompatible terpolymeric materials show promising applications for the in vivo delivery of anti-cancer drugs for tumour treatment and even in the treatment of degenerative brain conditions. Terpolymeric materials with responses to pH stimulus also exhibit applications for the rapid and non-cytotoxic cellular delivery of DNA sequences, which opens the possibilities for efficient gene-delivery for the treatment of specific genetic diseases⁷¹⁻⁷⁵.

1.3.2 Applications of terpolymers

In recent years, terpolymeric material have been more and more viewed as alternative material for the removal of specific heavy metal ions from wastewater terpolymer resins are co-ordinating terpolymer possesses covalently bonded side chains which contain single or multiple donor atoms. The donor atom containing active sites acts as Lewis base, which effectively forms co-ordinating bonds with Lewis acids such as the most toxic metal ions. Functional groups such as carboxylic, amide and amine when present in the polymer structure, provide the binding sites for the removal of metal ions and organic dyes from aqueous solutions.

The relevant use of these terpolymer in photocatalytic applications, especially when the particle size of the terpolymer reaches to nanometer scale tunes their optical, magnetic, electrical and chemical (catalytic) properties. The use of terpolymer in catalysis is relevant, because of their irregular surface which is continuously reconstructed to adapt the adsorbate and their size-dependent electronic properties to optimize the photocatalytic activity. One important technique for removing industrial waste is the use of light energy. The terpolymer are sensitive to the light energy mineralize the waste which aids in the removal of dyes present in the solution.

The terpolymer composites/blends films are used as proton exchange membrane in PEMFC due to its high proton conductivity and good resistance to chemical attack. In addition, as a solid electrolyte, the cell using the solid polymer membrane is much easier to seal compared to the cells with liquid electrolyte such as that in an MCFC. Also, the better corrosion resistance compared to the other types of fuel cells.

Bioactivity of terpolymer composites/blends film used in bone tissue engineering with wide properties such as compatibility, architecture, bioactivity, mechanical property and degradability have been accepted among the tissue engineering community as key

properties for their successful use in bone tissue engineering which results in a formation of a bond between the tissue and that material

1.4 Environmental pollution

The environment and all the life forms on earth are facing a serious threat as a result of heavy metals and dye pollution. Numerous metals such as Chromium (Cr), Cadmium (Cd), Arsenic (As), Lead (Pb), Copper (Cu), Nickel (Ni), Zinc (Zn), Mercury (Hg) etc. are known to be significantly toxic. Unlike toxic organic compounds, heavy metals are totally nondegradable and hence they tend to accumulate in the environment. The effluents released from various industrial activities such as electroplating industries, refineries, tanneries, metal processing industries, batteries, manufacture of electrical equipments, paints, alloys, pesticides, mining operations, refining ores, paper and pulp industries, organochemicals and fertilizers etc., heavy metals loaded wastewater are directly or indirectly released into the environment. The effects of heavy metals in water and wastewater range from beneficial through troublesome to dangerously toxic, depending upon the concentration of heavy metal⁷⁶⁻⁷⁸. As seen in **Figure 1.1**. Shows the toxicity of heavy metals and dyes and **Table 1.1** presents the source and effect of heavy metals and dyes on human being. As seen from the figure and table several of these metals are bio-accumulative and detrimental to human health.

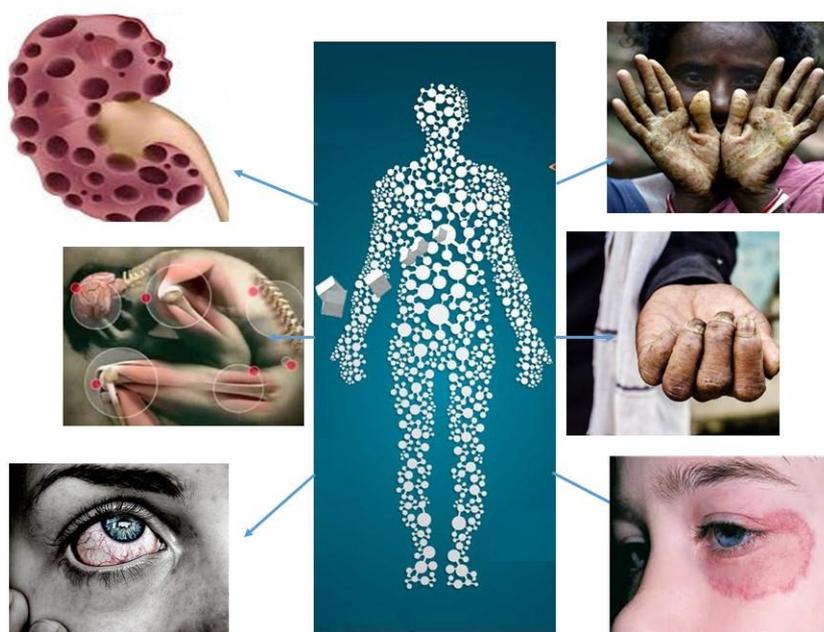


Figure 1.1. Toxicity of heavy metals of dyes

Table 1.1. Sources and effects of heavy metals and dyes on human beings

Heavy Metals	Sources of Heavy Metals and Dyes	Health Effects
Cr	Electroplating, wood preservatives, leather and tanning, pulp processing units, petroleum refining, paints, photography and textile industries etc.	Carcinogenic, epigastric pain, severe diarrhoea, dermatitis, lung tumors and longtime exposure can cause kidney and liver damage.
Cd	Mining, soft solder photoelectric cells and plastics, batteries, metal coating and plating, galvanizing, rayon and paper, pigments, ceramics and metal refining.	Cancer, cardiovascular diseases, kidney damage, hypertension and bronchitis.
Pb	Batteries, paints, dyeing and pigments, mining and smelting, leaded gasoline, alloy, coal, ceramics, automobile and petrochemicals etc.	Affects nervous and circulatory system, anorexia, brain damage, loss of appetite, constipation, diminishing IQ and cancer.
Cu	Copper plating, printed circuit boards, pulp and paper, electroplating, plastic industry, metal refining and finishing etc.	Kidney and liver damage, neurotoxicity, interstitial pulmonary lesions, dizziness and modular fibrohydine scars.
Ni	Steel & non-ferrous alloys, coal power plants, diesel oils, paint and powder, electroplating and mining, galvanization and batteries etc.	Respiratory symptoms, lung cancer, chest pain, nausea, hemorrhages, heart and liver damage
Zn	Electroplating, rayon and paper, paint, dyes, pigments, rubber industries, metal production, polymer stabilizers and alloys etc.	Cancer, skin irritation, depression, nausea, stomach cramps, anaemia and metal fume fever.
Hg	leather tanning, batteries, thermometers, adhesives and paints, coal, chlor-alkali industry, gold and silver mining, paper, pulp and pesticides industries etc.	Damage to brain and the central nervous system, coma, spontaneous abortion and irreversible brain damage in babies and death.

1.4.1 Conventional techniques for removal of pollutants

Growing environmental concern and strict government policies have directed the attention towards the elimination of heavy metals and dyes from wastewater. Several techniques are well established and have been in use for the removal of heavy metals from contaminated water includes include chemical precipitation, ultra-filtration, cementation, ion exchange, reverse osmosis, Electro dialysis, etc.^{79–84} These conventional techniques are inherently problematic in their application because of unpredictable metal ions removal and generation of toxic sludge. The various types of conventional techniques are presented in the flowchart diagram shown in **Figure 1.2** and their disadvantages are listed below **Table 1.2**.

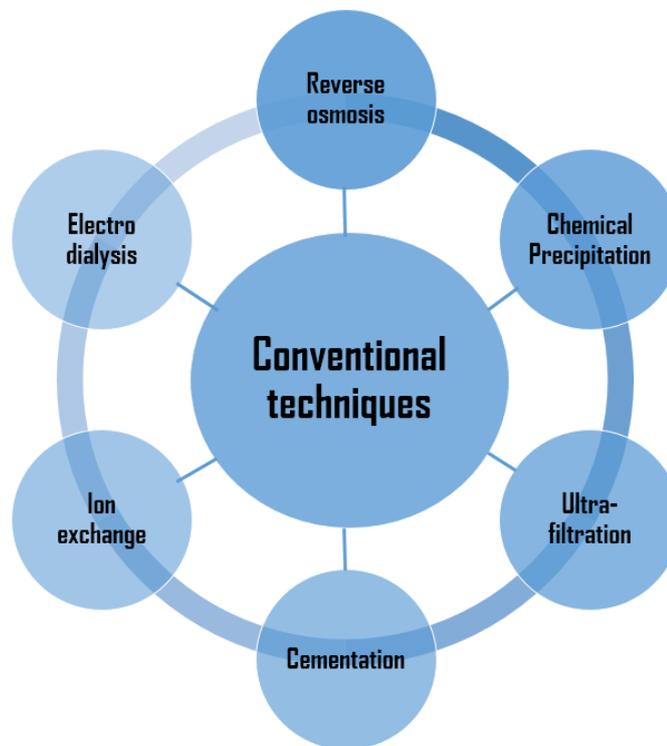


Figure 1.2. Various types of conventional techniques for removal of toxic metal ions

Table 1.2. Disadvantages of Conventional Techniques

Conventional Techniques	Disadvantages
Reverse osmosis	The promising material used for the reverse osmosis is cellulose acetate which has disadvantages of being unsusceptible to various parameters like temperature, pH and fouling. The water soluble metal ion cannot be exchanged properly and the major drawback of this process is the high power utilization due to the pumping pressures, and the restoration of the membranes.
Chemical precipitation	Transportation, and disposal of the final reaction products are slow precipitate formation, aggregation of metal precipitates, inappropriate for large solution volumes with very low concentrations of metal ions poor settling and unnecessary sludge production that requires further treatment, increasing the cost of sludge dumping and long-term environmental impacts of sludge removal.
Electro dialysis	The main disadvantages in electro dialysis include change in selectivity, formation of metal hydroxides, voltage increase and clogging of the membrane. Development is hindered by limitation on the life of membrane, the lack of economy of scale and high energy cost
Ultra-filtration	The main disadvantage of ultra-filtration is that it develops or generates the sludge
Ion exchange process	Cannot handle highly concentrated solutions and other solids in wastewater and is highly sensitive to pH of the solution. The main disadvantages of Ion exchange process are very expensive, requires continuous monitoring, long term maintenance and regular inspection
Cementation	The main disadvantages of the method are surplus sacrificial metal spending and redox potential of sacrificing metal and this process is suitable only in the small wastewater flow since long contact time required is time consuming

1.5 Adsorption

Adsorption is a process of accumulation of solute molecules from solution to the surface of solid, due to the residual surface forces is known as adsorption. These forces are merely extensions of the forces acting within the body of the material. Because of the unbalanced attraction at the surface, there is a tendency for the molecules to be pulled away from the surface. Adsorption has been an alternative and more attractive method for the removal of trace inorganics and organics from wastewaters.

The substance being concentrated at the interface is termed as 'adsorbate' and adsorbing phase is known as 'adsorbent'. The main advantages of this technique are the reusability of adsorbent, low operating cost, easy handling, high selectivity for specific metals of interest, Low operating cost, removal of heavy metals from effluent irrespective of toxicity, short operation time, Regeneration of adsorbent and no production of secondary compounds which might be toxic. The surface attachment can be physical, chemical or exchange adsorption⁸⁵⁻⁸⁷.

1.5.1 Types of adsorption

1.5.1.1 Physical Adsorption (Physisorption)

Physical adsorption is caused by Van der Waals forces and is the easiest to separate because these forces are weak in nature and separation process become cheaper. It does not include sharing or transfer of electrons and is essentially reversible. It has a low degree of specificity thus adsorbed molecules are free to cover the entire surface of the adsorbent. A physically adsorbed molecule keeps its identity and upon desorption returns to the fluid phase in its original form.

1.5.1.2 Chemical Adsorption (Chemisorption)

In chemical adsorption, strong attractive forces are operative in the formation of new bonds between the adsorbate species and active centres of the adsorbent. Chemically adsorbed species are fixed at specific sites and are linked to reactive parts of the adsorbent surface, confining the adsorption to formation of monolayer. The extent of chemical adsorption is dependent on the reactivity of the adsorbent and adsorptive.

1.5.2 Contacting Systems and Modes of Operation

In order to provide an intimate contact between adsorbent and adsorbate for the effective removal of pollutants from wastewater, various experimental techniques have

been employed by several workers. The contacting systems may be broadly divided into following two types.

(i) Batch System

In this mode of operation, a definite quantity of adsorbent is agitated with a particular volume of natural or artificial polluted water until the concentration of polluting species has decreased to a desired level. The dose of adsorbent and period of contact are adjusted according to the needs. The adsorbent is then recovered and either discarded or regenerated for reuse,

(ii) Continuous Flow System

In this type of operation, the adsorbent is always in the contact of a fresh solution. The adsorbent is added from the top and the spent adsorbent is withdrawn from the bottom. The waste water is made to flow upwards through the vertical column containing the adsorbent. However, the batch mode of operation is commonly adopted due to its easy handling and simplicity.

1.5.3 Factors affecting adsorption

A number of factors can affect adsorption process such as nature of adsorbent and adsorbate, concentration of adsorbant and adsorbate, nature of the solvent, temperature of the system, pH of the solution, porosity of the adsorbent, presence of the foreign material, time duration allowed and the procedure adopted for the systems. The important factors are discussed below.

1.5.3.1 Nature of adsorbent

The nature of adsorbent depends mainly on the physicochemical nature of adsorbent which is responsible for the adsorption such as presence of pores, particle size, comers and cracks, edges, corners, cracks and pre-treatment and interlaminar regions. The pretreatment of the surface by etching, grinding, cleaning etc. also affects the rate of adsorption.

1.5.3.2 Nature of adsorbate

The adsorption at a solid-solution interface is highly influenced by the extent of solubilisation, ionisation, molecular size, physical state in solution, electrical charge of the adsorptive species etc. Solubility has an important role in the study of adsorption. For a

given solvent less or slightly soluble adsorbate are more strongly adsorbed than the much soluble ones. The relation between the extent of adsorption and chain length of adsorbate has been recognized for a long time.

1.5.3.3 Effect of concentration of adsorbate

Effect of concentration of metal ion solution is a major part of the study. The extent of adsorption of ionic species is highly affected by the concentration of the adsorbate species in the system. For a particular system, at a constant temperature, the relationship between the solution concentration becomes complicated owing to the formation and overlapping of mono and multilayer adsorption as well as capillary condensation.

1.5.3.4 Effect of amount of adsorbent

The effect of variation of amount of adsorbent plays an important role in standardizing the adsorption process with quantification of adsorbate solution and the adsorbate. The series of experiments with different amount of adsorbent were kept in contact with fixed volume of heavy metal ion solution of approximate concentration. The adsorbents were untreated and treated with acids and base and adsorbate are same.

1.5.3.5 Nature of Solvent

Solvent plays an important role in the adsorption study. Adsorption depends upon the interaction of solvent with the solute present in the adsorbed layer. Solvent effects are found to be important in adsorption onto polar surfaces, especially when the solvent is polar and/or contain aromatic ring. The solvent order of adsorption of lauric acid on alumina is n-pentane, benzene, diethyl ether, with carbon blacks; the polar surface sites also contribute to the solvent effect.

1.5.3.6 Effect of temperature

Temperature is one of the most one of the chief determinants and important factors which determine the extent of adsorption of given system. The system (consists of adsorbate and adsorbent) were maintain at constant temperature and was shaken continuously till the equilibrium is attained. The sample solution withdrawn at various time intervals were used for measuring the corresponding concentration remaining in the solution. The values thus obtained were employed for computing the actual amount of heavy metal ion adsorbed on the surface at that time. The experiments were repeated at various temperatures. This study is helpful in determination of the alteration in the extent

of the adsorption as well as computing the corresponding energy of activation involved in the process.

1.5.3.7 Influence of pH

The study of adsorption is very much depending on pH of the solution and prominent factor among others which affects the extent, rate and mechanism of adsorption. The pH of the solution is found to be very effective in deciding the amount of adsorption especially if the solid adsorbent are prone to surface alternation due to changes in the hydrogen concentrations, large variation have been found with metal, metal oxides and metal hydroxides as adsorbents.

1.5.4 Conventional adsorbents

There are many types of adsorbents developed and applied for various applications. Some examples of adsorbents are Activated Carbon, Silica gel, Fly ash, zeolites, clays and polymeric adsorbents etc.

1.5.4.1 Activated Carbon

Activated carbon has been the most widely used adsorbent in both granular and powdered form to remove heavy metals from wastewater because they have h It is mainly depends on the large mesoporous and microporous volume to high surface area the unique properties could be helpful to removal of undesired species by adsorption adsorption from liquids or gases in order to effect purification or the recovery of chemical constituents^{88,89}.

1.5.4.2 Silica gel

Silica gel is synthetic amorphous silica consisting of a compact network of spherical colloidal silica particles which having hydroxyl groups on its surface could adsorbe heavy metals. Silica gel functionalized with chelating groups could afford a column for the selective removal of heavy metals from aqueous solution^{90,91}.

1.5.4.3 Fly ash

Fly ash is one of the residues generated in the combustion of coal. It consists of mainly SiO₂, which is present in two forms (a) amorphous-which is rounded and smooth (b) crystalline- which is sharp, pointed and hazardous (Al₂O₃ and Fe₂O₃). Fly ashes are generally highly heterogeneous consisting of mixture of glassy particles with various

crystalline phases such as quartz, mullite and various iron oxides. It is presently used in the synthesis of geopolymers and zeolites and also in waste water treatment^{92,93}.

1.5.4.4 Zeolites

Most synthetic zeolites are aluminosilicates which could be thought of as stoichiometric blends of the two adsorbents viz., silica and alumina. Zeolites are inherently crystalline and exhibit micropores within those crystals that have uniform dimensions. The micropores present are of uniform size and uniformly distributed and these can separate identically sized molecules. As a result they have been called "molecular sieves". Applications of zeolites include gas or liquid drying, separation of oxygen from air, normal paraffin from naphtha and p-xylene from other isomers⁹⁴⁻⁹⁶.

1.5.4.5 Clays

The major content of clay minerals is metal oxide such as SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO. Depending upon the source there are five main groups of clays 1) Kaolinite 2) Montmorillonite 3) Smectite 4) Illite 5) Chlorite. Montmorillonite is having small size, large surface area and highest cation exchange capacity for the removal of heavy metals from waste water and air purification^{97,98}.

1.5.4.6 Polymeric Adsorbents

In recent years polymeric resins have been more and more viewed as alternative to adsorbents due to their tremendous balance of mechanical, thermal and chemical properties. Chelating polymers have many practical applications Compared with conventional techniques in environmental protection, chemical analysis, etc. Recently, many scientists have prepared and studied many kinds of chelating polymers containing various ligands and have used these polymers for removal and recovery of heavy metal ions from industrial wastewater. It is composed of a synthetic polymer and ligand, wherein the metal ions are bound to the polymer ligand by a coordinate bond. A ligand contains anchoring sites like nitrogen, oxygen or sulfur obtained by the polymerization of a monomer possessing a coordinating site. The synthetic organic polymers are their high capacity, wide applicability and great versatility and low cost relative to the removal of toxic heavy metal ions⁹⁹⁻¹⁰².

1.6 Terpolymer as adsorbent

Adsorption on terpolymer has attracted much attention in recent decades. Terpolymer in its broadest sense includes a wide range of processed polymer based materials. Terpolymer have a highly developed surface area which is involved in the removal of toxic metals from wastewater in trace quantities, based on metal binding site of the terpolymer has directed the attention to adsorption. The growing importance of adsorption (e.g. in separation technology, industrial catalysis and pollution control) has resulted in the appearance of an ever increasing volume of scientific and technical literature on novel adsorbents and catalysts.

Hence, the usage of conventional techniques for metal removal are often restricted due to technical and economic constraints such as incomplete removal, expensive equipment, need high energy and reagents, generate toxic secondary pollution and require disposal unit. During few decades, adsorption by terpolymer have gained the attention in research for the treatment of waste water. The adsorption by the terpolymer technologies have major advantages compared to conventional methods and some of them are listed below:

- Removal process can be carried out in the contaminated site
- They are emerging advantages like attractive, highly efficient economical and cost effective materials.
- Selection of metal: The selection of metals depends on different types of biomass, mixture in the solution, preparation and physicochemical treatment. Each one is more or less selective in nature.
- Regeneration of terpolymer: After the metal is recycled, the terpolymer can be reused.
- No sludge generation: they do not form secondary pollutant like sludge with the terpolymer adsorption.
- Possibility of metal recovery: In case of metals, they can be recovered after being sorbed from the solution.

1.7 Review of literature

The literature survey part reveals the review about the work carried out by various researchers on polymer chemistry especially in terpolymers and their applications in various fields of materials science and life sciences.

Azarudeen et al.¹⁰³ synthesized successfully novel anthranilic acid and 2-amino pyridine with formaldehyde (AAPF) terpolymer resin by solution condensation technique. The structure of the resin was clearly confirmed by spectral and elemental analysis. From the SEM images, the resin was found to be very amorphous and porous in nature; hence it was responsible for the excellent metal ion uptake capacity by the resin. From the ion-exchange studies, the results revealed that the terpolymer resin was a better cation exchanger than the commercially available phenolic and polystyrene resins. Further, the resin was reused for few cycles for the adsorption process. The order of the kinetics was also determined and the adsorption followed first order kinetics which showed that physisorption may be involved in the ion-exchange process.

Patle et al.¹⁰⁴ prepared chelating resin from polymerisation of p-hydroxybenzaldehyde and biuret with formaldehyde in hydrochloric acid medium by condensation technique. Melting point data revealed that the terpolymer has good thermal stability. The semicrystalline nature of the p-HBBF terpolymer was confirmed by the SEM studies and revealed that the terpolymer can act as an effective ion exchanger for various trivalent and divalent metal ions such as Fe^{+3} , Cd^{+2} , Cu^{+2} , Zn^{+2} , Ni^{+2} and Pb^{+2} ions. Since p-HBBF terpolymer contains alcoholic group, it plays a key role in the ion exchange phenomenon. Thus p-HBBF terpolymer has immense applications as an ion exchange resin in waste water treatment, metal recovery and for the identification of specific metal ions.

Ahamed and co-workers in a series of papers^{70,105,106} reported the synthesis of terpolymer materials by condensation technique in acid medium. 2-Amino-6-nitro-benzothiazole and thiosemicarbazide with formaldehyde (BTF) terpolymer resin was synthesized from 2-amino-6-nitrobenzothiazole and thiosemicarbazide with formaldehyde. The prepared terpolymer was quite simple and inexpensive and it was thermally stable. The cation-exchange property of the terpolymer was determined by batch equilibrium method with the effect of pH, contact time and electrolytes. The SEM and

XRD studies proved that the terpolymer can act as an effective ion-exchanger for various cations. Similarly, metal ion binding capacities of an anthranilic acid-salicylic acid-formaldehyde (ASF) and 2-amino-6-nitro-benzothiazole and semicarbazide with formaldehyde (BSF) terpolymer resin were reported. The results of batch adsorption studies for ASF and BSF terpolymer revealed that the separation of the selected metal ions from the aqueous solution by the terpolymer was found to be excellent compared to the available commercial resins. The order of the distribution ratio of metal ions for the ASF terpolymer was found to be $Pb^{2+} > Zn^{2+} > Cu^{2+} > Mg^{2+} > Ba^{2+}$. The order of metal ions uptake at higher concentrations by the BSF terpolymer at lower pH was $Cu^{2+} > Ni^{2+} > Fe^{2+}$ and at lower concentration at higher pH was $Zn^{2+} > Co^{2+} > Pb^{2+}$. These terpolymers act as excellent ion exchangers and their separation behavior may have the capacity to do well against the environmental pollution especially the water pollution.

Tarase et al.¹⁰⁷ studied the formation of 2,4-DHPOF-II terpolymer based on the condensation reaction of 2,4-dihydroxypropiophenone and oxamide with formaldehyde in the presence of acid catalyst. It was used as a selective chelating ion exchanger for Fe^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} and Hg^{2+} metal ions. The terpolymer resin showed their selectivity with respect to pH. With increase in pH, the -vely charged nature of sorbent surface increased leading to increase in electrostatic attraction between charged metal ions and -vely charged terpolymer which results in increase in exchange metal ions.

Burkanudeen et al.¹⁰⁸ carried out kinetics of thermal decomposition and antimicrobial screening of AUF-I, II, and III terpolymer resins synthesized from anthranilic acid and urea with formaldehyde by solution polymerization technique. The AUF terpolymer resins were thermally stable even at high temperature. The order of the reaction for thermal decomposition was nearly one, and the activation energy was found to be less for the decomposition. The AUF terpolymers established a phase boundary (contracting cylinder) decomposition model. The resin had a moderate activity against *A. flavus*, a mold type fungal strain which may invade arteries of the lung or brain to cause infections and also produces a toxin and the terpolymer had moderate inhibition for *A. niger*, *Penicillium* species and also resins had noticeable inhibition effect against this fungal strain.

Masram et al.¹⁰⁹ have efficiently removed trace impurities and toxic metals from industrial waste water by using a novel salicylic acid, diamionaphthalein and formaldehyde terpolymer prepared by the condensation. The chelation ion exchange properties have also been studied for Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions employing a batch equilibrium method. The study was carried out over wide pH range and in a media of various ionic strengths. The terpolymer showed higher selectivity for Fe^{3+} , Cu^{2+} , and Ni^{2+} ions than for Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions.

Zhang et al.¹¹⁰ successively prepared the terpolymer containing diketopyrrolopyrrole and benzothiadiazole side chain with enhanced photovoltaic properties via the stille coupling polymerization. The effect of power conversion efficiency was investigated. The random terpolymer exhibited a promising application in BHJ solar cells due to the broad spectrum and deep-lying HOMO energy level. PSCs were fabricated using as-synthesized terpolymer as donor and PC61BM as acceptor. Compared with the reported polymer PBDPP- 2, the terpolymer exhibited improved power conversion efficiency.

Karunakaran et al.¹¹¹ have synthesized new chelating terpolymer resin using 2,2'-dihydroxybiphenyl with thiourea and formaldehyde in presence of HCl as catalyst and proved to be selective chelating ion-exchange resins for certain metal ions. Chelating ion-exchange properties of these terpolymer were studied for Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions. A batch equilibrium method has been employed in the study of the selectivity of metal ions uptake involving the measurements of the distribution of a given metal ions between the polymer sample and a solution containing the metal ions. Chelating properties of the polymer with various metal cations were found to be pH dependent. The terpolymer showed higher selectivity for Fe^{3+} , Cu^{2+} and Ni^{2+} ions than for Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions. Therefore the terpolymer can be used as an ideal metal ion exchanger in effluents and other type of waste water.

Veleva and Co workers¹¹² have prepared a methacrylate-based terpolymer consisting of hexylmethacrylate (HMA), methylmethacrylate (MMA) and methacrylic acid (MAA) using an equimolar mixture of acetone and ether as the solvent by electrospinning. The terpolymer had well-defined, orientation and random fiber architectures. In vitro endothelial cell culture and functional analysis via cell attachment,

proliferation, and viability measurements demonstrated that electrospinning significantly improved the cytocompatibility of the surfaces to endothelial cells, especially for those substrates with random fiber distribution of endothelial cells cultured on terpolymer surfaces. This finding results showed that the HMA, MMA, and MAA terpolymers have the potential to be used in fabricating small diameter blood vessel replacement.

Shape-memory bioresorbable sirolimus incorporated poly(L-lactide-*co*-glycolide-*co*-trimethylene carbonate) terpolymer composite with antirestenotic drug has been proposed by Jaworska et al.¹¹³ The terpolymer was synthesized by ring opening polymerization (ROP). The mechanical test of terpolymer revealed that addition of the sirolimus influenced polymer strength; stress value of the composite decreased, the stiffness of the composite and neat polymer was comparable. It was explained by the notch effect caused by filler aggregation which was observed using optical microscopy. On the other hand, incorporation of drug molecules did not change shape-memory properties of terpolymer: similar shape-memory property of terpolymer and terpolymer sirolimus were observed at 37°C. The degradation was stable and even for both materials. Weight loss and M_n changes were very similar for both polymeric materials. The developed materials present potential for biomedical and pharmaceutical applications.

Baojin Chu et al.¹¹⁴ have prepared relaxor ferroelectric poly(vinylidene fluoride/trifluoroethylene/ chlorofluoroethylene) terpolymer for energy storage capacitors. It was found that the high dielectric constant (>50 at 1 kHz) and high reversible polarization in the terpolymer lead to a high electric energy density $\sim 10 \text{ J/cm}^3$, achieved under an electric field of more than 350 MV/m. The high dielectric constant also caused the polarization saturation at fields much below the breakdown field and whereby the discharged energy density increased nearly linearly with applied field, distinctively different from the low dielectric constant, linear dielectric polymers whose energy density rised with square of the applied field. The strong frequency dispersion and nonlinear polarization response (polarization saturation) of the relaxor terpolymer resulted in a low effective capacitance at the beginning of the discharge and the effective capacitance increased with time during the discharge.

Tanveer et al.¹¹⁵ reported the anti-corrosive properties of poly (2-pyridylamine-*co*-aniline-*co*-2,3-xylidine) terpolymer obtained by chemical oxidative polymerization. The

terpolymer was chemically deposited on mild steel specimens using N-methyl-2-pyrrolidone (NMP) as solvent via solution evaporation method. The anticorrosive properties of terpolymer coatings were investigated in major corrosive environments such as 0.1 M HCl, 5% NaCl solution, artificial seawater, distilled water and open atmosphere by conducting various corrosion tests which include: immersion test, open circuit potential measurements, potentiodynamic polarization measurements, and atmospheric exposure test. The terpolymer exhibited excellent protection against mild steel corrosion.

Chong Cheng et al.¹¹⁶ have extensively studied the pH-sensitivity and antifouling property of terpolymer poly(styrene–acrylic acid–N-vinylpyrrolidone) blended polyethersulfone hollow fiber membranes. The hollow fiber membranes exhibited a pH-responsive behavior with very large water flux change as the pH value was changed from nearly 38.64 to 0.64 ml/(m² h mmHg). Meanwhile, the influence of the occurred macro and micro-phase separation on water contact angle, pH sensitivity and antifouling property revealed the enrichment of the hydrophilic segments of the terpolymer at the membrane surface. A rough surface resulted from the poor miscibility of the blend proved that the phase separation would increase the pH sensitivity. Furthermore, the ultrafiltration experiments indicated that the phase separation had great effect on the pure water flux but little influence on the protein anti-fouling property after the blending of the terpolymer and the modified membrane showed good protein antifouling property.

Feng Xia et al.²⁸ observed high electromechanical response in a poly(vinylidene fluoride-trifluoroethylene chlorofluoroethylene) terpolymer. The results showed that proper selection of the third monomer effectively reduced the all-trans conformation in the polymer; the terpolymer containing 1,1-chlorofluoroethylene (CFE) as the third monomer significantly improved the electromechanical responses compared with other modified P(VDF-TrFE)-based polymers.

Yiwei Ren et al.¹¹⁷ proposed synthesis of lignin–DMDAAC–AM terpolymer by grafting copolymerization of both dimethyl diallyl ammonium chloride and acrylamide onto lignin. The corrosion inhibition properties of the terpolymer showed that the highest corrosion inhibition percentage was over 95% in 10% HCl acid medium at 25 °C and 80 °C. Adsorption of lignin terpolymer on the mild steel surface of chemical adsorption obeyed Temkin's isotherm. The surface adsorption capacity of lignin terpolymer on the

mild steel surface reduced at high temperature. The effects of corrosion inhibition had the comprehensive synergistic effect through the graft reaction among lignin, AM and DMDAAC.

Chauhan et al.¹¹⁸ synthesized 4-APOFA terpolymer using a series of sequential monomers 4-acetylpyridine oxime, formaldehyde and acetophenone in 1:5:1 molar proportion. Isoconversional analysis of TGA plots indicated the variation in activation energy of the degradation process with respect to degree of conversion. The application of generalized master plot to this system indicated the thermal degradation mechanism for the terpolymer. The presence of self-crosslinking changes the thermal degradation from three-dimensional diffusion (D3) to random nucleation with one nucleus on the individual particle (F1). Pathogenic bacteria viz *Bacillus subtilis*, *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa* were used for the study of antibacterial activity of the terpolymer. Pathogenic fungi viz. *Alternaria solani* and *Fusarium oesysporum* were used for antifungal activity studies. The antimicrobial experiments indicated that the antimicrobial activities of the terpolymer resin was significantly higher than that of standard drug. It could be used to produce implants and biomedical devices with greater resistance to microbial adhesion and biofilm formation. In addition, it could provide significant advances in many fields such as food packaging, textiles and coating of catheter tubes.

Singru et al.¹¹⁹ have synthesized p-Cresol (p-C)-melamine (M)-formaldehyde (F) (p-CMF-II) terpolymer by the condensation in the presence of 2 M HCl as catalyst with 2:1:3 molar ratio of reacting monomers. The thermal stability test showed that the p-CMF-II resin started degradation at high temperature, indicating that this polymer resin was thermally stable at elevated temperature therefore may be used in industry where thermally stable polymers are needed. The electrical property of p-CMF-II polymer was measured over a wide range of temperatures (313–423 K) and found that electrical conductivity of resin increased with increase in temperature. Hence, this polymer may be ranked as semiconductor. The chelating ion-exchange property of this polymer was studied for seven metal ions. The chelating ion-exchange study was carried out over a wide range of pH, shaking time and in media of various ionic strengths. The experimental results showed that the p-CMF-II resin was a selective chelating cation exchange polymer resin for certain metals and the uptake capacities of metal ions by the polymer resin was pH dependent.

From TGA, measurements the energy of activation evaluated from the Sharp–Wentworth and Freeman–Carroll methods were found to be nearly equal.

Shin et al.¹²⁰ prepared ion-exchange membrane using styrene/hydroxyethyl acrylate/lauryl methacrylate (Sty/HEA/LMA) terpolymer via post-sulfonation. The sulfonic groups were introduced into the membrane structure using sulfuric acid as the sulfonating agent and silver sulfate as an initiator. The ion-exchange capacity (IEC), water uptake (WU) and electrical property of the membranes were verified and the resulting membrane showed an ion-exchange capacity of 0.812 meq/g and an electrical resistance of 0.3 Ω cm². Water uptake of the prepared membranes increased with the degree of sulfonation and the reaction time. The surface morphology obtained by AFM clearly showed an increase of roughness with sulfonation reaction time. The elongation of the Sty/HEA/LMA ion-exchange membranes improved with the increasing LMA content compared to sulfonated polystyrene membrane.

Li et al.¹²¹ prepared thermosensitive N-isopropylacrylamide–N–propylacrylamide–vinyl pyrrolidone terpolymers by varying feed ratios with free radical copolymerization method. These polymer exhibited a noticeable thermo-responsive behavior. The transition temperature, transition time and rheological properties of terpolymer were strongly dependent on the composition ratios and the addition of radiopaque agent. The in vitro evaluation of the transport and embolization of terpolymer showed that PNINAVP will be appropriate as an embolic material for further animal experiments. As a thermosensitive embolic material, the PNINAVP polymer hydrogel, especially 5wt% 16:16:1H PNINAVP aqueous solution, has optimum characteristics including embolic stability, better biocompatibility, nonadhesiveness, compatible to general microcatheters.

Pendergast et al.¹²² presented nanoporous membranes with vertically aligned nanopores formed from a poly(isoprene-*b*-styrene-*b*-4 vinyl pyridine) (ISV) triblock terpolymer via a hybrid self-assembly/nonsolvent induced phase separation process. The successful membrane structures consisted of a well-ordered, self-assembled selective layer atop an open macroporous substructure. The porous layer appeared to form between the skin layer and macrovoid substructure; perhaps, a partially ordered kinetically trapped layer was formed as the membrane formation process transitions from evaporative self-assembly to nonsolvent induced phase separation. The result showed that the obtained

membranes represent a possible route towards more precise particle and macromolecular separations, which are of interest across many industries.

Phillip et al.¹²³ have proposed a novel triblock terpolymer based hybrid films. The terpolymer was synthesized from poly(isoprene-*b*-styrene-*b*-4-vinylpyridine) by anionic polymerization. The polymer film structure comprised a thin selective layer containing vertically aligned and nearly monodisperse mesopores. The solvent flow and solute separation experiments demonstrated that the terpolymer films were stimuli-responsive and consisted pores with a nearly monodisperse diameter and have permeabilities comparable to commercial membranes. The hybrid triblock terpolymer film opened new paths to produce high-performance graded membranes for filtration, separations, nanofluidics, catalysis, and drug delivery.

Bhadja et al.¹²⁴ prepared poly(acrylonitrile-*co*-styrene sodium sulfonate-*co*-*n*-butyl acrylate) based terpolymer for water desalination via electrodialysis. The efforts were directed to obtain cation exchange membrane with suitable mechanical properties and stability in aqueous medium by adjusting the terpolymer composition. The membrane highlighted the properties and desalination performance of terpolymer-based CEM prepared by avoiding the post sulfonation reaction.

Chatterjee et al.¹²⁵ reported the preparation of a new type of anion exchange membrane from a random terpolymer of poly *n*-butyl acrylate (PnBA), polyacrylonitrile (PAN) and poly(2-dimethyl aminoethyl)methacrylate (PDMA) through quaternization and cross-linking. The terpolymer showed the low degree of water uptake along with the absence of freezing bound water in the membrane and rapid desalination with high cation exchange. The selection of polymer components and their optimized composition were crucial factors for the preparation of high performance ion exchange membranes for energy efficient applications.

Li et al.¹²⁶ prepared remarkably enhanced thermosetting terpolymer composed of benzoxazine, cyanate ester and epoxy resin prepared via co-curing reactions. The curing procedure for the ternary blends involved several steps and the higher crosslinking density of the terpolymer led to the higher glass transition temperature indicating the better thermal stability of the terpolymer at service temperature.

Liguori et al.¹²⁷ put considerable efforts toward synthesis of borate containing resins and macroporous monoliths via free-radical bulk copolymerization. The polymerization mixture was tailored to obtain swellable materials for use as insoluble carriers of single-site heterogeneous catalysts. The parent macroporous monolith was also prepared for direct use in continuous flow applications showing excellent hydrodynamic properties and high chemical and mechanical stability.

Chauhan et al.¹²⁸ prepared bio-based terpolymer derived from vanillin oxime, formaldehyde and p-hydroxyacetophenone by condensation method. The terpolymer was characterized by FT-IR, ¹H NMR, GPC, DSC and TG-DTG analysis. The activation energies for the thermal degradation of VOFHA in nitrogen obtained using the FWO method was 13.7 kJ/mol. The analysis of the results obtained using the Craido method and master plots method showed that the degradation mechanism of terpolymer in nitrogen was a D₂ process. The antimicrobial activity of the synthesized terpolymer was determined by *in vitro* well method and poisoned food technique method against a variety of bacteria and fungi. The terpolymer showed excellent antibacterial activity, some of the properties affected their antimicrobial activity such as molecular weight, spacer length between active site and polymer, functional group and concentration.

Zhang et al.¹²⁹ devoted considerable scientific effort to the synthesis of poly (3-(triethoxysilyl) propylmethacrylate) -blockpolystyrene -block -poly(2-vinylpyridine) (PTEPM-b-PS-b-P2VP) terpolymer by reversible addition fragmentation chain transfer (RAFT) mediated radical polymerization. The obtained terpolymer was prepared by novel sandwich-like organic/inorganic hybrid nanoplates with a crosslinked silica layer sandwiched by PS-bP2VP diblock polymer layers. The present nanohybrids supplied a planar scaffold on which one may perform adaptable functions and further modification which supplied versatile ways to tune elaborate structure of the planar polymer nanoobjects.

Mai et al.¹³⁰ proposed a sequential synthesis of glucose functionalized amphiphilic random terpolymer using a two-step chemoenzymatic synthetic route. The behavior of the functionalized terpolymer was promising for delivering two different chemotherapeutic agents to tumors simultaneously with an enhanced cytotoxic activity but a reduced drug dose.

1.8 Scope and objective of the present work

In the past few decades, national and international bodies are responsible for the health and become increasingly stringent in fixing the discharge of industrial effluents. The contamination of water by heavy metals causes effect to public health owing to its hazardous effects. Most of the textile effluents contain dyes and hence their harmless discharge would demand a great deal of effort and resources. So the removal of toxic heavy metals and dyes from industrial waste water become highly essential. The adsorption technique seems to be highly effective and efficient for the removal of dyes.

A careful literature survey reveals that most of the reported studies concern about the biological and environmental impact of terpolymers. Hence new terpolymer materials with lesser toxicity, low cost, wider operational window, renewable surface, stability in various solvents, longer lifetime and low background current are still needed to the treatment of industrial waste water. Thus, the present investigation has been planned to meet the following objectives:

- ❖ To design and synthesize novel terpolymers by using suitable polymerization method.
- ❖ To synthesize new PVA blended terpolymers with enhanced mechanical properties.
- ❖ To characterize the synthesized terpolymers for their chemical, spectral, structural and morphological properties before and after adsorption of toxic metals and dyes.
- ❖ To carry out the adsorption study with several parameters including concentration of electrolytes, pH, times of adsorption, dosage and desorption/reusability by batch adsorption technique.
- ❖ To understand the degradation reaction pathway of pollutants (heavy metals and dyes) and propose the possible mechanism
- ❖ To remove heavy metal ions such as Pb, Cd, Cr, Cu, Zn, Ni, Hg, Mn and organic dyes from waste water
- ❖ To evaluate the visible light photoactive properties of the terpolymers
- ❖ To optimize the reaction parameters to achieve maximum adsorption efficiency.
- ❖ To study the biological activities of the terpolymers.
- ❖ To employ the terpolymer as membrane for direct methanol fuel cell and study its performance.

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