1.0 Introduction to Nanofibers

Fibers having diameter less than 100 nanometers are generally considered as nanofibers (as per National Science Foundation). According to nonwoven industries nanofibers should have a diameter of less than one micron. Research into production of nanofiber has been funded by the government for more than twenty years. Much of the early work was done by Darryl Reneer at the University Akron. When diameter of polymer fiber material decreases from micrometer to nanometer, the properties exhibit significant changes, such as large specific surface area, greatly improved accessibility to surface functionalities, and remarkable mechanical properties compared with any other known material forms. These outstanding properties make the polymer nanofibers optimal candidates for many different and important applications in filtration, sensors, photonics or biomedicine and nano-drug fields. Polymeric nanofibers are rapidly finding their place in nonmaterial’s technology. Generally, polymeric nanofibers are produced by an electrospinning process. When the diameters of polymer fiber materials are shrunk from micrometers (e.g. 10–100 mm) to submicrons or nanometers (e.g. 10\(^{10}\)–100\(^{10}\) mm), there appear several amazing characteristics such as very large surface area to volume ratio, flexibility in surface functionalities, and superior mechanical performance (e.g. stiffness and tensile strength) compared with any other known form of the material. While glass fibers have existed in the sub-micron range for some time and polymeric melt blown fibers are just beginning to break the micron barrier, 0.25 micron diameter electrospun nanofibers have been manufactured and used commercially for air filtration applications for more than twenty years. Nanofibers are an exciting new class of material used for several value added applications such as medical, filtration, barrier, wipes, personal care, composite, garments, insulation, and energy storage. Special properties of nanofibers make them suitable for a wide range of applications from
medical to consumer products and industrial to high-tech applications for aerospace, capacitors, transistors, drug delivery systems, battery separators, energy storage, fuel cells, and information technology [1, 2]. Electrospinning is a process that spins fibers of diameters ranging from 10nm to several hundred nanometers. This method has been known since 1934 when the first patent on electrospinning was filed. Fiber properties depend on field uniformity, polymer viscosity, electric field strength and DCD (distance between nozzle and collector). Advancements in microscopy such as scanning electron microscopy has enabled us to better understand the structure and morphology of nanofibers.

1.1 Properties of Nanofibers

Polymeric nanofibers exhibit special properties like Low density, large surface area, high porosity, and tight pore size. The comparison of a human hair and pollen particles with nanofibers has been shown in Figure 1.1.

**Figure 1.1:** Comparison between human hair, human red blood cell and nanofiber web

*Entrapped pollen spore on nanofiber web.*
1.2 Production Techniques

Polymeric fibers can be produced by using various techniques such as drawing, template synthesis, phase separation, self-assembly and electrospinning [3-9] etc.

1.2.1 Drawing

In this technique one-by-one long single nanofibers are obtained as in case of dry spinning. Polymeric Nanofibers can be mechanically drawn from viscous polymer liquids directly (Figure 1.2) [10]. The drawback of this technique is that only visco-elastic polymers are used, which can undergo strong deformations while being cohesive enough to support the stresses developed during pulling of nanofibers.

![Figure 1.2: One step drawing process](image)

1.2.2 Template synthesis

In this method a self-ordered nano-porous membrane or material like alumina is used as a template to make nanofibers of solid (a fibril) or hollow (a tubule) shape. Polymer nanofiber arrays can be released from these molds by destruction of the molds or mechanical detachment (Figure 1.3). The most important feature of this method may lie in that nanometer tubules and
fibrils of various raw materials such as electronically conducting polymers, metals, semiconductors, and carbons can be fabricated. But the limitation of this method it is not capable of producing one-by-one continuous nanofibers.

![Figure 1.3: (a) Schematic of the fabrication of polymer nanofibers using a template technique [49].](image)

1.2.3 Phase separation

In phase-separation, the gel of a polymer is prepared by storing the homogeneous solution of the polymer at the required concentration in a refrigerator set at the gelation temperature. The gel is then immersed in distilled water for solvent exchange, followed by the removal from the distilled water, blotting with filter paper and finally transferring to a freeze-drying vessel leading to a nanofiber matrix. Although the phase-separation process is very simple, it is only limited to the laboratory scale and the process takes relatively long period of time to transfer the solid polymer into the nano-porous foam.
1.2.4 Self Assembly

It is a process in which individual, pre-existing components organize themselves into desired patterns and functions (Figure 1.5). However, similarly to the phase separation the self-assembly is time-consuming in processing continuous polymer nanofibers. Thus, the electrospinning process seems to be the only method, which can be further developed for mass production of one-by-one continuous nanofibers from various polymers [11].
1.2.5 Electrospinning

In the process of Electrospinning a polymer solution or melt can be spun into smaller diameter fibers using a high potential electric field. It covers a wide range of fibers having diameter in submicron that are normally produced by electrospinning. On the basis of earlier studies, it is evident that the average diameter of electrospun fibers ranges from 100 nm–500 nm [12]. Fiber science and in textile related scientific literature; fibers are generally referred to as nanofibers with diameters in the range 100 nm–500 nm. The electrospinning process are technically simple, easy to handle and simple in construction, which consists of a high voltage electric source with positive or negative polarity, a syringe pump with capillaries or tubes to carry the solution from the syringe or pipette to the spinnerets, and a conducting collector like aluminum. The collector may be having different shape according as per the requirements, like a flat plate, rotating drums, etc. A schematic of the electrospinning process is shown in Figure 1.6.

![Electrospinning setup](image)

Figure 1.6: Electrospinning setup
The creation of fibers, by electrifying a fluid, traces back into the last years of the 1800's. In 1917, John Zeleny published a paper [13] entitled "Instability of Electrified Liquid Surfaces", which described the observation of liquid jets created by electrical forces. In 1934, Formhals patented his first invention relating to the process and the apparatus for producing artificial filaments using electric charges [14]. From 1934 to 1944, Formhals published a series of patents [15-18]. This was after research in the 1920's clearly established that polymers are long linear molecules, and at the time when the synthesis of fiber forming molecules was making dramatic progress. In 1955, Drozin investigated the dispersion of a series of liquids into aerosols under high electric potentials [18]. In 1966, Simons patented an apparatus for the production of non-woven fabrics of ultra thin and very light in weight with different patterns using electrical spinning [19]. In 1971, Baumgarten made an apparatus to electrospin acrylic fibers with diameters in the range of 0.05–1.1 microns [6]. Since 1980s and especially in recent years, the electrospinning process essentially similar to that described earlier [6] has regained more attention probably due in part to a surging interest in nanotechnology, as ultrafine fibers or fibrous structures of various polymers with diameters down to submicron or nanometers can be easily fabricated with this process.

1.3 Applications

Nanofibers due to their enhanced properties required for application in specific areas like catalysis, filtration, nano-composites, nanofibrous structures, tissue scaffolds, drug delivery systems, protective clothing, storage cells for hydrogen fuel cells, etc. have been attracting the attention of global research these days. As per the US patents representation (Figure 1.7 and 1.8), 2/3rd of all applications are related to the medical field (grafts and vessels). 1/2 of the rest are related filtration applications, and the remaining 1/2 belongs to other applications including
tissue template, electromagnetic shielding, composite and liquid crystal device [19, 20]. For filtration and composite applications, the small diameter of nanofibers is advantageous. For catalyst and drug delivery applications, high surface area of nanofibers is favorable [21, 22].

Figure 1.7: Application fields targeted by US patents on electrospun nanofibers.

Figure 1.8: Applications of nanofibers in various fields
1.3.1 Medical

Nanofibers have been using in various bio-medical fields like in tissue engineering scaffold, blood vessels, bones, muscles, skins, neural tissues, wound healing, drug delivery release control and cosmetics etc. A basic principle of the tissue engineering includes repairing, replacing, maintaining or enhancing the function of a particular tissue or organ as illustrated in Figure 1.9.

![Figure 1.9: Illustration of tissue engineering](image)

A scaffold should possess a following characteristic such as high degree of porosity with an appropriate pore size distribution, a large surface area, biodegradability with the degradation rate matching the rate of neo-tissue formation and structural integrity to prevent the pores of the scaffold from collapsing during neo-tissue formation, and appropriate mechanical properties. The scaffold should be non-toxic to cells and biocompatible, positively interacting with the cells to promote cell adhesion, proliferation, migration, and differentiated cell function. Nanofibers in this regard exhibit great performance than other biomedical materials. Along with pure PCL nanofibers, nanofibers from gelatin/PCL blend [24] and PCL composite with calcium carbonate nanoparticles and hydroxyapatite (HAp) nanoparticles [25] have been used for bone scaffolds.
Collagen nanofibers were also reported to assess the feasibility of culturing smooth muscle cell [26]. Skin works, to prevent outside intrusion, regulate water retention and heat loss. Polymeric nanofibers have been evaluated for their cytocompatibility to fibroblast and/or keratinocytes. Polymeric electrospun nanofibers exhibit good capability of supporting cell attachment and proliferation in most of the cases. Cells seeded on the nanofiber structure were guided to grow according to the nanofiber orientation and tended to maintain phenotypic shape. In these regard blends of polymeric nanofibers were also studied, and showed good cell attachment and proliferation. For example a small fraction of low molecular weight polyethylene glycol (PEG) in PLLA nanofibers increased the hydrophilicity. As a result, biological reactivity of fibroblast cells was improved [27]. Electrospun nanofibers are also considered as a good wound dressing candidate because of their unique properties (Figure 1.10). Like first-highly porous mat like structure and well interconnected pores are particularly important for exuding fluid from the wound, second- the small pores and very high specific surface area not only inhibit the exogenous microorganism invasions, but also assist the control of fluid drainage and third the electrospinning process provides a simple way to add drugs into the nanofibers for any possible medical treatment and antibacterial purposes. Controlled release is an efficient process of delivering drugs in medical therapy. A process of regenerating dermal and epidermal tissues is called as wound healing. In case of deep burns or deep ulcers, there is no source of cells remaining for regeneration, except from the wound edges. As a result, complete re-epithelialization takes along time and is complicated with scarring of the base [28]. Dressings for wound healing function to protect the wound, exude extra body fluids from the wound area, decontaminate the exogenous microorganism, improve the appearance and sometimes accelerate the healing process. For these functions, a wound dressing material should provide a physical
barrier to a wound, but be permeable to moisture and oxygen. Electrospun nanofibers obtained from Chitosan/silk, collagen/chitosan, polyvinyl alcohol/polyvinyl acetate have been reported to use as a wound healing materials [29-31]. Polymeric electrospun nanofibers have advantages in drug delivery applications also. In nanofiber drug delivery system high specific surface area and short diffusion passage length of nanofibers give higher overall release rate than the bulk material (e.g. film) using biodegradable polymers and hydrophilic polymers. Model drugs that have been studied include water soluble [32], poor-water soluble [33] and water insoluble drugs [34]. The release of macromolecules, such as DNA [35] and bioactive proteins [36], from nanofibers was also investigated.

Figure 1.10: Nanofibers for wound healing application

1.3.2 Composites

Various materials such as traditional (micro-size) carbon, glass, and Kevlar fibers have been using in composite development as reinforcement [37]. The composite materials can provide better mechanical and structural properties such as high modulus and strength to weight ratios, which generally cannot be achieved by other materials alone. So nanofibers find important applications in making nano-composites, because of having even better mechanical properties than micro fibers of the same materials, and hence the superior structural properties of nano-
composites can be achieved. Nano-composites may possess some additional merits than traditional (microfiber) composites. The difference in refractive indices between fiber and matrix, results in opaque or non-transparent composite due to light scattering. This problem can be overcome by using the nanofibers having smaller diameter than the wavelength of visible light. For example; nano-composite using electrospun Nylon-4,6 nanofibers non-woven membranes and an epoxy matrix has been reported in literature [38].

1.3.3 Catalyst and enzyme carriers

Electrospun nanofibers have been effectively used as catalyst carrier due to the extremely large surface area that could provide a huge number of active sites and thus enhancing the catalytic capability (Figure 1.11). The well-interconnected small pores in the nanofiber mat warrant effective interactions between the reactant and catalyst, which is valuable for continuous low chemical reactions or biological processes. The catalyst can also be grafted onto the electrospun nanofibers surface via coating or surface modification. It is found in the literature, that catalytic activity of the Palladium (Pd)-loaded poly(acrylonitrile-acrylic acid) (PAN-AA) loaded nanofibers for selective hydrogenation of dehydrolinalol was measured, to be about 4.5 times higher than that of Pd/Al₂O₃ catalyst [39]. To immobilize enzyme on electrospun nanofibers, many approaches have been used, including grafting enzyme on fiber surface, physical adsorption, and incorporating enzyme into nanofiber via electrospinning followed by cross-linking reaction. To graft enzymes on nanofiber surface, the polymer used should possess reactive groups for chemical bonding. Polymer blends containing at least one reactive polymer For example, α- chymotrypsin was used as a model enzyme to bond chemically on the surface of electrospun PS nanofibers [40, 41].
Now a day’s need of new and more energy efficient materials for water purification is becoming an important issue for environmentalist, due to the fast population growth, energy use concerns and increasing environmental crisis. The pollutants like heavy metals in drinking water can cause bladder, lung, kidney, liver and skin cancer. Filtration is a necessary for industry as well as to keep a clean environment for a healthier life. The materials to be used for water filtration should essentially have high efficiency, high durability, low operating pressure (low energy), low cost, and the ability to fabricate using environmentally friendly processes [42, 43]. For example, ultra-fine cellulose nanofibers with small diameter, high surface-to-volume ratio, easy surface functionality, good mechanical properties and good chemical resistance have been used for water filtration [44]. Bio-fouling and virus penetration are two major problems in water treatment associated with membrane filtration [45]. Filtration systems may be improved by the use of nanofibrous materials having light weight, high permeability and small pore size which make them appropriate to remove unwanted particles smaller than 0.3 µm [46]. Filtration system containing nanofibrous material may be having different thickness, fiber diameter and
distribution, representative pore size, porosity, and tortuosity factor (indicating geometry and interconnectivity of pores) depending on the type of polymer used [47]. Nano-materials like metal nanoparticles, antibiotics and bacterial agents, can be incorporated in the polymer matrix and converted into nanofibers using electrospinning technique. These nanofibers are synthesized by a new and efficient fabrication process, namely electrospinning technique. For removing solid substances from air or liquid, filtration process has been widely used in both households and industries. Donaldson Company produced a air filter which is based on polyamide electrospun nanofibers (Figure 1.12).

![Figure 1.12: Commercial air filtration cartridge using nanofibers filter media[48]](image)

For military purposes, garments and isolating bags have been used to decontaminate aerosol dusts, bacteria and virus. Another example is the respirator that requires efficient filtration ability, similar to some fabrics used in the medical area. There are various parameters such as uniformity of fiber, matrix structure, thickness, pore size, fiber surface electronic properties, and
its surface chemical characteristic (e.g. surface free energy) that affects the filtration efficiency. Besides this filtration efficiency is also dependent on pressure drop and flux resistance. Various Functional nanoparticles such as fullerene, carbon nanotubes, metals and semiconductors can release into the environment and may act as another type of pollutants, which can make special environmental concerns [49]. As per literature metal and metal oxide nanoparticles and carbon nanotubes are cytotoxic in nature and can cause granulomas in animal lungs [50, 51]. For this purpose electrospun nanofibers used in filtration applications can be an optimum solution for addressing the present environmental concerns. Electrospun nanofibers having high length (even up to hundreds of kilometers long) are one of the safest nono-materials that never become airborne and diffuse into the body. Additionally, a very high surface area, large porosity (up to over 90%) and the possibility of using safe nanofibers (excluding functional polymers), nanofibers as the scaffolding materials can significantly improve separation efficiency, that is, a better capability to remove pollutants from gas and liquid environments, accompanied by a higher permeability i.e. a lower energy consumption.

Figure 1.13: Nanofibers in Filtration application
1.4 Common contaminants in water

The problem of drinking water pollution is one of the most important environmental issues in the world now a day. Organic pollutants in water, causing adverse effects on the human and wildlife, have received great attention. Drinking water from all the sources contain some naturally occurring contaminants. When the water flows in streams, sits in lakes, and filters through layers of soil and rock, it dissolves or absorbs the substances that it touches. Water transforms in composition and in physical parameters according to its exposure. Water is generally contaminated by biological, toxic, organic, and inorganic pollutants and unsafe for human consumption as well as for other activities, such as irrigation and industrial needs. The degraded quality of water can lead to water scarcity for both human use and for the ecosystem. Central Pollution Control Board (CPCB) in 1995 identified severely polluted stretches on 18 major rivers in India. Severe contamination near urban areas indicates that the industrial, domestic and Agricultural activities contribute to water pollution. Besides this a groundwater problem has affected as many as 19 states, including Delhi. Various contaminants such as salinity, iron, fluoride, and arsenic have affected groundwater in over 200 districts spread across 19 states. Water is regenerative and its quality remains unaffected up to certain level of contaminants. Water contains following contaminants like Microorganisms, Disinfectants, Disinfection Byproducts, Inorganic Chemicals, Organic Chemicals, Radio-nuclides (Figure 1.14).
Figure 1.14: Common contaminants’ present in water

Out of all these contaminants listed above, the pollution of heavy metal ions in water sources is a critical problem all over the world. As defined by the United State-Environmental Protection Agency (US-EPA), the natural as well as anthropogenic contamination of the environment with metallic elements, are of major concern because of their toxicity, bio-accumulating tendency, and threat to human life and environment [52, 53]. Heavy metals are non-biodegradable and hazardous to the environment and human being. They can seriously cause various diseases like; headaches, nausea, vomiting, abdominal pain, insomnia, forgetfulness, neurological disorders and liver damage [54]. Thus, the removal and recovery of theses heavy metals is one of the most important issues of environmental research. To overcome this problem, there is need to develop more efficient and low cost water purification techniques. The most common metallic elements responsible for human poisoning include; mercury, cadmium, lead, arsenic, chromium, copper and zinc etc. Out of them arsenic, mercury and lead are more carcinogenic and hazardous to human health. US-EPA has set the lowest discharge limit of aresnic and mercury (10ppb) in waste water [55]. Arsenic (As) and mercury (Hg) contamination in water has been reported all over the world, and it has led to massive epidemics of arsenic and mercury poisoning. As has the property of both metal and non-metal so it is considered a metalloid. It is highly toxic and cause
neurologic, cardiovascular, gastrointestinal and hepatic, and dermal disorders in human beings.

Several diseases in human being, such as ‘Kai Dam’ in Thailand, ‘Bell Ville’ in Argentina, ‘Black Foot’ in Taiwan, tummy bug, cancers of lungs and skin, are caused by the consumption of As contaminated water [56]. As exist in natural water both in inorganic and organic forms. In natural water, it exists in two oxidation states, arsenite (As III) and arsenate (As V). The inorganic As is considered as 70 times more toxic than organic species, and within this class, As(III) is ten times more toxic than As (V) [57, 58]. It enters in the environment and water through geochemical reactions, industrial waste discharge, etc. The long-term consumption of As contaminated water has harmful impacts on human beings. According to the European Commission and US-EPA, the permissible maximum limit of As in drinking water is 10 mg/L.

Minamata bay tragedy in 1950 caught the world aware about Hg toxicity even among the general public [59]. Hg contamination through various sources like air, water, food, pharmaceuticals, cosmetic products etc. pose serious concern because it persists in the environment and accumulates in the food web. Hg exists in inorganic, organic and elemental form out of which the organic form is most toxic as it passes the blood brain barrier owing to its lipid solubility. Hg (II) is a highly reactive ion which binds to the amino acid cysteine proteins. It is considered to be a carcinogen causing embryocidal, cytochemical, and histopathological events.[60]. It is converted into methyl mercury and its compounds, can affect the human beings even at very low concentrations [61, 62]. The maximum contaminant level goal for lead in drinking water has been set at zero by EPA because lead is a toxic metal that can be harmful to human health even at low exposure levels. Lead is persistent, and has a tendency to bio-accumulate in the body over time. A low dose of lead in water may have little effect on an adult but it significantly affect child up to 6 years of age, the fetus and pregnant women being the most susceptible [63]. Lead
toxicity results in damage to the central and peripheral nervous system, learning disabilities, shorter stature, impaired hearing, and impaired formation and function of blood cells [64].

1.5 Heavy metal removal techniques

Heavy metals pollutants in water are always an issue because they can cause serious ailments such as dehydration, stomach ache, nausea, dizziness and/or lack of coordination in muscles, destroying the nervous systems of young children, lung irritation, eye irritation, skin rashes, vomiting, abdominal pain, lung insufficiency, and liver damage [65-67]. The conventional techniques, used for heavy metal removal include precipitation and coagulation, ion-exchange, solvent extraction, membrane filtration (electrochemical separation, reverse osmosis) and adsorption [68-73] etc.

1.5.1 Chemical precipitation

In this technique water containing heavy metal ions react with certain chemicals to form insoluble precipitates. The precipitates can be separated from the water by sedimentation or filtration. The treated water is then decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation and sulfide precipitation. Chemical precipitation is effective and by far the most widely used process in industry because it is relatively simple and inexpensive to operate [74]. Limitation of hydroxide and sulfide precipitation include generation of large volumes of relatively low density sludge resulting in dewatering and disposal problems [75], amphoteric nature of metal hydroxide, presence of complexing agents in the wastewater that may inhibit metal hydroxide precipitation, sulfide precipitants in acidic conditions can result in the evolution of toxic H₂S fumes, therefore be performed in a neutral or basic medium, metal sulfide precipitation can also cause some separation problems in either settling or filtration processes.
1.5.2 Coagulation

In this process the colloid particles are neutralized to keep them apart by using the following coagulants such as aluminum, ferrous sulfate and ferric chloride, resulting in the formation of amorphous metal hydroxide precipitates. Coagulation is one of the most important methods for wastewater treatment, but the main objects of coagulation are only the hydrophobic colloids and suspended particles. Poly-ethyleneimine grafted sodium xanthogenate group is reported to be used as amphoteric polyelectrolyte to remove both soluble heavy metal and insoluble substances efficiently by coagulation [76]. At lower pH, the colloidal substances with negative charges can be coagulated, but the cationic ion cannot be removed very well. And at higher pH, the turbidity removal decreases, and the cationic removal is favored.

1.5.3 Ion-exchange process

It is generally employed to remove both cationic and anionic impurities from water. It has many advantages, such as high treatment capacity, high removal efficiency and fast kinetics [77]. Ion-exchange resin may be of either synthetic or natural solid resin. Synthetic resins are commonly preferred as compared to natural resin as they effectively to nearly remove the heavy metals from the solution [78]. The cation exchangers are strongly acidic resins having sulfonic acid groups (-SO₃H) and weakly acid resins with carboxylic acid groups (-COOH). Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. As the solution containing heavy metal passes through the cations column, metal ions are exchanged for the hydrogen ions on the resin with the following ion exchange process:

\[ nR- SO_3H + M^{n+} \rightarrow (R-SO_3^-)_nM^{n+} + nH^+ \]

\[ nR- COOH + M^{n+} \rightarrow (R-COO^-)_nM^{n+} + nH^+ \]
The uptake of heavy metal ions by ion-exchange resins is rather affected by certain variables such as pH, temperature, initial metal concentration and contact time [79]. Ionic charge also plays an important role in ion-exchange process. Besides synthetic resins, natural zeolites, naturally occurring silicate minerals, have also been widely used to remove heavy metal from aqueous solutions due to their low cost and high abundance. Natural zeolites exhibit good cation-exchange capacities for heavy metal ions under different experimental conditions. Clinoptilolite is one of the most frequently studied natural zeolites that have received extensive attention due to its selectivity for heavy metals [80]. Though there are many reports on the use of zeolites and montmorillonites as ion-exchange resin to remove heavy metal, they are limited at present compared with the synthetic resins. And the application of zeolites is on the laboratory experiments scale.

1.5.4 Membrane filtration technologies

They show great promise for heavy metal removal for their high efficiency, easy operation and space saving using different types of membranes. The membrane process may include the following techniques like ultrafiltration, reverse osmosis, and electrodialysis. In Ultra filtration (UF) technique low transmembrane pressures for the removal of dissolved and colloidal material is used. Because the pore sizes of UF membranes are larger than dissolved metal ions containing hydrated ions or as low molecular weight complexes, these ions would pass easily through membranes. High removal efficiency of metal ions could be achieved using micellar enhanced ultra-filtration (MEUF) and polymer enhanced ultra-filtration (PEUF). The micelles containing metal ions having smaller pore size than a UF membrane can be retained by a UF membrane, whereas the untrapped species readily pass through the UF membrane. An anionic surfactant, Sodium do-decyl sulfate (SDS), is often selected for the effective removal of heavy metal ions in
MEUF. PEUF uses water-soluble polymer to complex metallic ions and form a macromolecule, having a higher molecular weight than the molecular weight cut off of the membrane. The macromolecular will be retained when they are pumped through UF membrane. After that, retentate can be treated in order to recover metallic ions and to reuse polymeric agent. In PEUF the main complexing agents used to achieve selective separation and recovery of heavy metals with low energy requirements are polyacrylic acid (PAA) [81], polyethyleneimine (PEI) [82] and humic acid [83] etc. The main drawback of this method is that, it has not widely spread to industry yet.

In Electrodialysis (ED) the separation of ions across charged membranes from one solution to another using an electric field as the driving force is achieved. Ion-exchange membranes (cationic and anionic) are mostly used in ED processes. It has been widely used for the production of drinking water and process water from brackish water and seawater, treatment of industrial effluents, recovery of useful materials from effluents, salt production and for heavy metal wastewater treatment.

In reverse osmosis (RO) process uses a semi-permeable membrane is used which allows the fluid that is being purified to pass through it, while rejects the contaminants. Wide range of dissolved species from water can be removed by RO. It accounts for more than 20% of the world’s desalination capacity [84]. RO is an increasingly popular wastewater treatment option in chemical and environmental engineering. The major drawback of RO is the high power consumption due to the pumping pressures, and the restoration of the membranes.

1.5.5 Adsorption

Adsorption is considered as one of the best methods for the removal of toxic heavy metal ions in an aqueous solution as compared to methods discussed above that are either ineffective or very
expensive and even removal of heavy metals from dilute solution is difficult [85-87]. Adsorption can be achieved either by electrostatic interaction (ionic interaction between positively charged metal ions and negatively charged matrices) or by chelation (donation of the lone-pair electrons of the matrices to metal ions to form co-ordinate bonds). Low-cost, easy recovery of metals and the possibility to reuse the adsorbent are the other greatest advantages of this method [88]. Adsorption is basically a mass transfer process in which a substance is transferred from the liquid phase to the solid phase, and bounded by physical and/or chemical interactions [89]. Sorption process generally involved three main steps (i) movement of the pollutant from the bulk solution to the surface of the adsorbent (ii) adsorption on the adsorbent surface and (iii) transport within the adsorbent molecule. A variety of adsorbents have been reported for the removal of heavy metals like materials derived from agricultural waste, industrial by-product, natural material, or modified biopolymers, have been recently developed and applied for the removal of heavy metals from metal-contaminated wastewater. Activated carbon is the most popular material and has been widely used in the removal of heavy metal. It also requires complexing agents to improve its removal efficiency for inorganic matters and becomes highly costly, so cannot be used on large-scale [89, 90]. Carbon nanotubes (CNTs) as relatively new adsorbents have been proven to great potential for removing heavy metal ions such as lead, cadmium, chromium, copper, and nickel from wastewater [91]. CNTs discovered by Iijima in 1991 have been divided into two types: (1) single-walled CNTs (SWCNTs) and (2) multi-walled CNTs (MWCNTs) [92, 93]. But the excess usage of CNTs would be discharged to the water environment and poses a risk to humans. Activated carbon fibers (ACFs), carbon nanotubes (CNTs), carbon nanoparticles, and carbon microspheres have also been used as adsorbents for the aqueous phase removal of phenol and metallic ions, including Pb\(^{2+}\). In recent years attention
has been focused on the various adsorbents having metal-binding capacities and removing unwanted heavy metals from contaminated water at low cost. Because of their low cost and local availability, various natural materials classified are as low-cost adsorbents such as chitosan, zeolites, clay, fly ash, coal, and oxides etc. Natural materials, available in abundance, or waste products from industrial or agricultural industries like sugarcane bagasse, rice husk, sawdust, coconut husk, oil palm shell, neem bark and fly ash etc show great potential as low cost adsorbents [94]. They can be easily disposed of without using costly regeneration process. As per literature various kind of bio adsorbents can be derived from three main sources such as a, non-living biomass like bark, lignin, shrimp, krill, squid, crab shell, etc; b, algal biomass; c, microbial biomass like bacteria, fungi and yeast [95].Other non-living plant material such as potato peels, sawdust, black gram husk, eggshell, seed shells, coffee husks, sugar-beet pectin gels and citrus peels etc., have been reported for heavy metal removal [89]. Rice husk ash obtained from heating rice husk at 30°C has been shown to show higher adsorption for gold-thiourea than the conventionally used activated carbon [96].

1.6 Justification of the proposed work

Most of the conventional methods currently used in water purification as discussed above possess one or the other limitations. Precipitation and coagulation techniques include generation of large volumes of relatively low density sludge resulting in dewatering and disposal problems. Ion exchange process and membrane flirtation processes are quite expensive and pose economic issues. The major problem associated with the reverse osmosis is use of high electricity consumption due to high pressure pumping and restoration of membrane used in RO. In adsorption process, a variety of materials as an adsorbent have been reported for the removal of heavy metals like charcoal and activated carbon, CNTs, zeolites, clay, fly ash, coal, metal oxides
and metal nanoparticles etc. Most of the conventional adsorbents are expensive and cause side effects as in case of nanoparticles. They also focus on removing the higher concentration of heavy metal at ppm level while removing low concentration of heavy metals at ppb level is quite difficult in case of these adsorbents. During adsorption process adsorbent is separated with help of ultra-centrifugation which is another drawback of such materials. Almost, all the materials require electricity so they cannot be used in remote areas where there is a problem of energy generation.

However the proposed work focuses on applications of polymeric composite nanofibers. The nanofibers can have different morphologies, such as porous-surface nanofibers, core-sheath and side-by-side structures. Electrospun nanofibers have attracted considerable attention because of their unique properties, ease of fabrication and functionalization, and versatility in controlling the fiber diameter and morphology. The extremely fine electrospun nanofibers make them very useful in a wide range of advanced applications. Due to these unique properties, there are so many scopes of polymeric nanofibers in various fields. According to the application/utility nanofibers can be modified by various inorganic materials that can have specific applications. In the present work polymeric composite nanofibers were fabricated using two different matrices like CHT and PAN by electrospinning technique. Electrospinning technique helps to obtain the continuous and uniform nanofibers. These electrospun nanofibers were further modified with Ce, Zr and Zr-phosphate (Zr-P) to improve the properties of electrospun nanofibers. The Ce (III) having smaller ionic radii, high electric charge and higher potential energy helps to improve the adsorption behavior of PVA/CHT composite nanofibers. Zr nanoparticles with desirable characteristic properties such as good electrical conductivity, chemical inertness, low thermal conductivity and high melting temperature which makes polyacrylonitrile (PAN) suitable for the
removal of heavy metal as good regenerable adsorbent. Since PAN is having high strength, high thermal stability and good solvent properties.

1.7 Objectives of the proposed work

Broad Objectives

The proposed work has been taken up with the following objectives:

- To develop fast and efficient method for the removal of heavy metal ions from water.
- To solve the problem of removing heavy metal ions from water, when present in very low concentration.
- To solve the problem of sludge formation during removal process and also to develop a material that can be easily separated during adsorption process.
- To purify the water containing heavy metal ions in remote areas where there is a problem of electricity.
- To develop materials based on polymeric composite nanofibers with enhanced stability and efficiency in heavy metal removal application.
- To prepare polymeric nanofibers that are bio-compatible, biodegradable, non-toxic and light weight by electrospinning technique.

Specific Objectives

- To develop polymeric nanofibers based on two different matrices PVA/CHT and PAN.
- To modify the PVA/CHT nanofibers with Ce and use it for the removal of As and Hg.
- To modify PAN nanofibers with Zr and apply it for the removal of As and Hg.
- To further modify PAN/ZR to PAN/Zr-P and use it for the removal of Pb.
- To study the kinetics and adsorption isotherms for developed materials for removal of heavy metals from water.
- To carry out interference study for the developed materials.
- To study the reusability of the developed materials.
- To propose the possible mechanism involved between heavy metal ions and surface of prepared materials during adsorption process.

1.8 Work done

The work carried out for development of the Polymeric nanofibrous materials can be classified into three parts:

Fabrication of PVA/CHT/Ce composite nanofibers

1. Chitosan and polyvinyl alcohol (PVA/CHT composite nanofibers were prepared by electrospinning technique. The ratio of PVA to CHT were varied (1:10 and vice versa) to obtain the uniform and continuous nanofibers at optimized electrospinning parameters.

2. Ce (III) was loaded in PVA/CHT solution to obtain PVA/CHT/Ce composite nanofibers and concentration of Ce (III) in PVA/CHT was varied from 1-6 wt. % to get uniform beadles and continuous nanofibers during electrospinning process.

3. Thermal behavior of PVA/CHT and PVA/CHT/Ce composite nanofibers was analyzed by Thermo-gravimetric Analysis (TGA) to check the effect of Ce on PVA/CHT nanofibers.

4. The determination of pH_{PZC} for PVA/CHT and PVA/CHT/Ce were conducted to determine the zero point charge on the surface of composite nanofibers using potentiometric titration method.

5. Batch adsorption experiments for PVA/CHT/Ce composite nanofibers were performed for the removal of heavy metal ions from water. And effect of various parameters on adsorption process was also analyzed like pH, time, % of Ce in PVA/CHT, initial
concentration of heavy metal ion solutions using Atomic Adsorption Spectroscopy (AAS).

6. The interference study was conducted for various other metal ions and their effect on adsorption process was also checked using tap water as well as well water spiked with known concentration of individual other metal ions like Pb, Cr, Mn and Co etc.

7. Regeneration study was performed for PVA/CHT/Ce composite nanofibers by treating the adsorbed composite nanofibers with Hydrochloric acid to check the reusability of nanofibers as adsorbent for repeated cycles.

8. PVA/CHT/Ce composite nanofibers were characterized before and after the adsorption of metal ions by SEM and EDAX, FTIR, XRD and XPS.

Fabrication PAN/Zr composite nanofibers

1. Uniform and continuous nanofibers from PAN were obtained by electrospinning technique.

2. Modification of PAN was done by Zirconia (Zr) nanoparticles to produce PAN/Zr composite nanofibers and content of Zr in PAN matrix was varied from 1-6 wt. %

3. Thermal behavior of PAN and PAN/Zr composite nanofibers was conducted by TGA and DSC to see the effect of Zr nanoparticles on PAN matrix.

4. Determination of pH\textsubscript{pzc} of PAN and PAN/Zr composite nanofibers were carried out using Mass titration method and point zero charge on the surface of composite nanofibers were determined.

5. Batch adsorption experiments were carried out using PAN/Zr composite nanofibers for the removal heavy metal ions from water. And various parameters were studied for
adsorption process like pH, time, % of Zr nanoparticles in PAN matrix, initial concentration of heavy metal ion solution using AAS.

6. Effect of other metal ions on adsorption process in tap water as well as well in water spiked with known concentration of individual other metal ions like Pb, Cr, Mn and Co etc. was also studied by carrying out the interference study of PAN/Zr composite nanofibers.

7. Regeneration of metal loaded PAN/Zr composite nanofibers was conducted using Hydrochloric acid. Adsorbent was further reused for various cycles for adsorption of heavy metals.

8. PAN/Zr composite nanofibers before and after the adsorption were finally characterized by SEM and EDAX, FTIR, XRD and XPS.

**Preparation of PAN/ZrP composite nanofibers**

1. PAN/Zr composite nanofibers were further hydrothermally modified with Ortho phosphoric acid to produce PAN/ZrP composite nanofibers.

2. Thermo-gravimetric analysis of PAN/Zr and PAN/ZrP composite was carried out by TGA and DSC to see the effect of ZrP nanoparticles on PAN nanofibers.

3. Batch adsorption experiments using PAN/ZrP composite nanofibers were conducted and remaining concentration of lead was determined by UV.

4. Lead loaded PAN/ZrP composite nanofibers were regenerated and further used for various adsorption cycles.

5. Characterizations of PAN/ZrP composite nanofibers before and after the adsorption study were carried out using SEM and EDAX, FTIR, XRD and XPS.
1.9 References


[16] F. Anton, Artificial thread and method of producing same, Google Patents, 1940.


[19] Z.-M. Huang, Y.-Z. Zhang, M. Kotaki, S. Ramakrishna, A review on polymer nanofibers by electrospinning and their applications in nanocomposites, Composites science and technology 63(15) (2003) 2223-2253.


[71] M. Monier, D. Ayad, Y. Wei, A. Sarhan, Preparation and characterization of magnetic chelating resin based on chitosan for adsorption of Cu (II), Co (II), and Ni (II) ions, Reactive and Functional Polymers 70(4) (2010) 257-266.


[77] M. Rahimizadeh, A. Liaghatb, Biosorbents for adsorption of heavy metals: A review.


