1.1 Membranes

Membranes are porous polymeric filters with specific pore diameters. They act as a selective barrier to retain or to permit the passage of permeating species. Membranes retain microorganisms larger than their pore size primarily by sieving mechanism, the particles smaller than the pore size of membranes may be retained by other mechanisms like for example complexation or even diffusion.

1.1.1 Classification of synthetic membranes

In general there are two types of membranes depending on their cross-section: isotropic and anisotropic membranes (Figure 1.1).

The membranes that are chemically homogeneous in their composition are called isotropic membranes. Micro porous membranes, nonporous dense films and electrically charged membranes are examples of isotropic membranes. The pore diameter of micro porous membrane ranges from 100-5000 nm. These membranes are usually formed by the irradiation of nonporous polymeric film with heavy ions to form tracks through the films (polymer based track etched), by controlled transformation from a homogeneous polymeric solution to a solid state induced by immersion precipitation (phase inversion) or by solvent free technique where polymers are heated above the melting point and extruded into thin films followed by stretching techniques (stretched polymer films). In case of non porous dense films, diffusion driven by applied force such as pressure, concentration or electric-field gradients is the cause for transport of permeates. Electrically charged membranes can be either microporous structure or nonporous dense films which consist of positive or negative charged ions decorated on membrane walls i.e. cation exchange or anion exchange membrane respectively.

Anisotropic membranes are mainly of two types: asymmetric membranes and composite membranes (thin film, coated films, self assembled structure, mixed matrix). The asymmetric membranes are chemically homogeneous membranes similar to isotropic microporous membranes, but pore size and porosity vary across the membrane. Composite membranes are chemically and structurally heterogeneous.

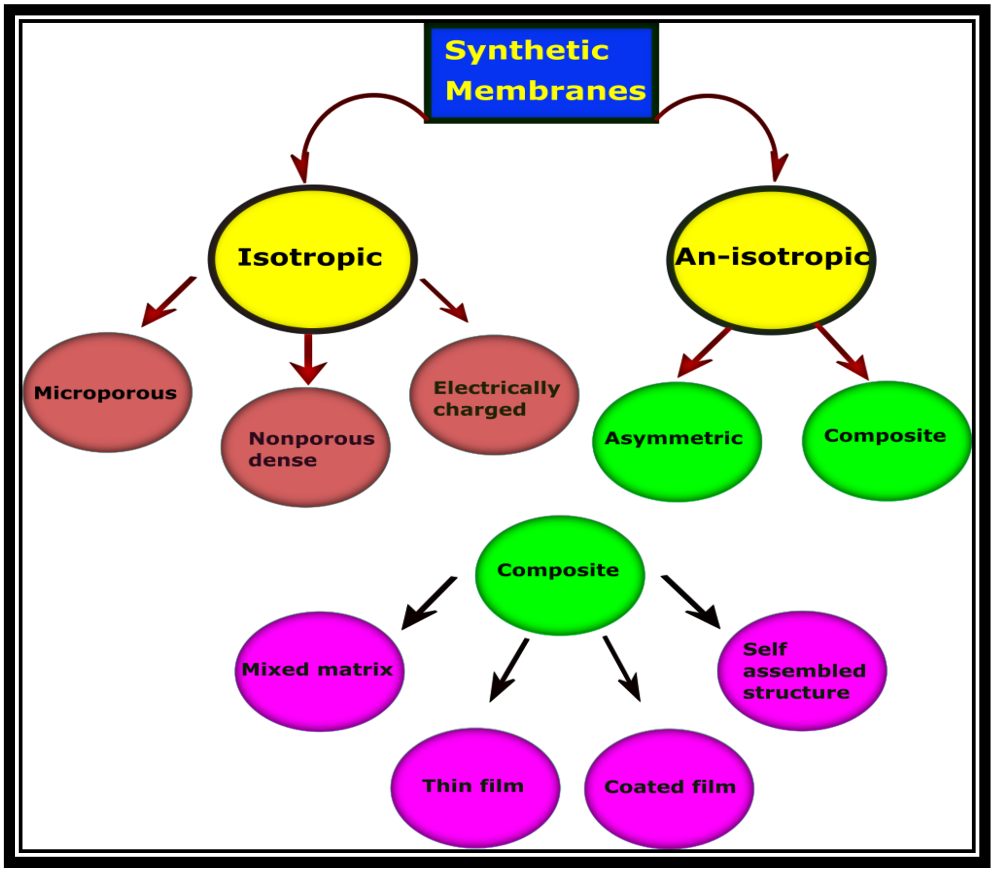

Figure 1.1 Schematic for the type of membranes

The days of early 1960s witnessed the pioneering work of Loeb and Sourirajan (1963) as the preparation of asymmetric membranes. They contain 0.1- 5 µm thick skin layer on a highly porous 100 – 300 µm thick substrate [2]. The actual selective barrier of the asymmetric substructure is known as 'skin' layer. The separation characteristic of the membranes depends on the nature of the material or pore size in the skin layer. The porous substrate layer has not much effect on the separation properties of the membranes and acts as support for the usually very thin skin later which is relatively dense [2]. The controlled structure of the dense top layer has become a serious concern in the membrane fabrication [3]. The resistance to the mass transfer is mainly determined by the surface layer [4, 5]. Pressure driven membrane processes such as reverse osmosis, ultra filtration, gas separation and sometimes microfiltration make use of mainly asymmetric membranes. The unique properties of asymmetric membranes are reasonable mechanical stability and high flux [6].

Cadotte et al had given a major breakthrough in the field of membrane separation with the invention of thin film composite (TFC) membranes in 1978.

The chemistry and hence performance of the upper selective layer and the porous support layer can be independently selected to optimize TFC membrane performance, which is the major advantage of these membranes over asymmetric membranes [7]. TFC membranes are structurally similar to asymmetric membranes as they are born out of the conventional asymmetric polymeric membranes. In TFC membranes the substrate and active layers are made up of two different polymers. The porous layer is generally formed through phase inversion and thin film is applied through interfacial polymerization or coating (dip, spin, spray) followed by cross-linking [8,9]. Polysulfone (PSf), polyether sulfone (PES), sulfonated PSf and PES, polyether ketones, Poly vinyledene fluoride (PVDF), sulfonated PVDF or Poly acrylo nitrile are the polymers which are generally used for microporous support for TFC membranes [10, 11, 12, 13]. Pore formers such as polyvinylpyrrolidone (PVP), poly (ethylene glycol) are added to casting solutions to enhance the porosity of the top layer and thus enhanced permeability of TFC membranes [14, 15, 16].

Zimmerman et al first introduced the concept of mixed matrix membrane (MMM) in the 1990’s to overcome the limitation of polymeric [17] as well as thin film composite membranes [18]. These membranes are having the advantage of ease of fabrication of organic polymeric membranes and the mechanical strength & functional properties of inorganic materials. High permeability, enhanced fouling resistance and higher hydrophilicity are the key features of mixed matrix membranes [19]. MMMs offer an opportunity for tunable water treatment membranes as well due to targeted functionalities, increased selectivity and superior mechanical, chemical & thermal stability. These membranes enrich the thermal and mechanical stability of polymeric membrane by decreasing the impact of heating and compaction of membrane. Compaction occurs during the initial stages of membrane operation which results in irreversible flux decline [20]. Addition of mechanically strong fillers to the bulk macro void region of asymmetric membranes reduces the structural losses, as the majority of compaction is known to occur in this region of membranes [21].

1.2 Polyethersulfone (PES)

There are many materials such as Polysulfone (PSf), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polyether sulfone (PES) which have been used for the polymer matrix formation. Out of these PES (Figure 1.2) is the most important polymeric material widely used in microfiltration [22-24], ultrafiltration [25-27] as well as nanofiltration [28-29] membranes which possess toughness and thermal stability [30-34].

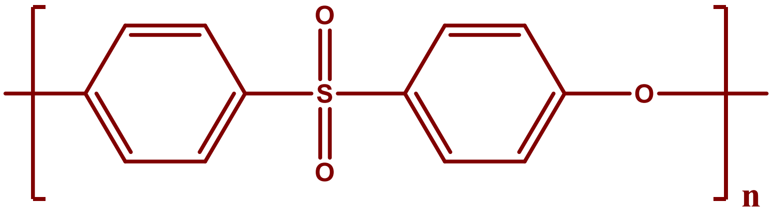

Figure 1.2. Structure of Polyethersulfone

The precursors for the synthesis of PES are bisphenol A and dichlorodiphenylsulfone which proceed the reaction via condensation polymerization through aromatic nucleophilic replacement mechanism. Polyether sulfone is a thermoplastic polymer which is typically amorphous in nature [35-

37]. PES may exhibit crystalline properties to some extent because of the existence of harder benzene ring and softer ether bond in the structure (Figure 1.2).

PES gives very good properties such as heat resistance, high glass transition temperature, environment survival and processing. Though, it is one of the important polymer for the preparation of membrane. However, its hydrophobicity controlled by PES structure leads to low membrane flux and fouling easily which greatly affect the performance and life of the membranes. Thus PES or pristine PES membrane should be modified to enhance the hydrophilicity.

1.3 Methods of modifications

1.3.1. Surface modification

To enhance the hydrophilicity of the membranes the surface modifications have been performed while keeping the polymer backbone unchanged. Contact angle is the measure of surface hydrophilicity which depends on the surface roughness, porosity and pore size distribution. Hydrophilic modifications on the surface of the membranes avoid the accumulation and attachment of organic foulants on the membrane surface. The increased roughness of the membrane surface results in higher contact angle i.e. hydrophilicity is decreased [38, 39]. Surface modification of PES membrane have been done by various techniques including blending method, plasma treatment, UV grafting and surface initiated atom transfer radical polymerization (SI-ATRP) which enhanced hydrophilicity of membrane surface by the addition of hydrophilic functional groups [40, 41].

1.3.2. Blending techniques

This is the strategy to blend the hydrophilic material into the polymeric matrix to modify the membrane surface. This may be homogeneous blending or heterogeneous blending. There may be addition of polymeric materials such as

Polyaniline (PANI) [42, 43], Polytetrafluoroethylene (PTFE) [44], β-CD Polyurethane [45], polyethylene glycol (PEG), polyvinylpyrrolidone (PVP), or (polyethylene oxide-b-polypropylene oxide-b-polyethylene oxide [46] or inorganic materials such as carbon nanotubes [47], Graphene oxide nanoparticles [48], $BaCO_3$ nanoparticles [49], ZnO nanoparticles [50], silica nanoparticles[51], titanium dioxide nanoparticles [52-56], aluminum oxide nanoparticles [57] and silver nanoparticles [58-60]. In a study, Wang et al [61] used polyaniline nanoparticles as polymeric filler in polysulfone matrix. The membranes were prepared by classical phase inversion process. These membranes were evaluated in terms of pore size, porosity, pure water flux and BSA solution permeate flux. Higher porosity and larger pore size was observed than the pristine polysulfone membrane. The pure water flux observed for modified membranes was 800 LMH which is 1.4-1.7 times higher than the polysulfone membrane. Vatanpour et al prepared acid oxidized-MWCNT/PES membrane and studied the effect of addition f-MWCNT on pore size, hydrophilicity, rejection and antifouling characteristics of membranes. Addition of 0.2 wt % of nanotubes results in increment of pore size. On further addition, pore size is decreased. The membrane surfaces have become hydrophilic which results in enhanced pure water flux. AFM studies shows that 0.04 wt% of nanotubes makes the surface of membrane smoother due to low electrostatic interactions among the MWCNTs and they are regularly collocated in the membrane. However on 0.2 wt% addition of nanotubes roughness extremely increases because of increase in pore size and agglomeration of carbon nanotubes. At values above 0.2 wt% MWCNT, combined effect of increased viscosity and lower thermodynamic stability of the blend solution takes place and by the addition of hydrophilic MWCNTs the pore size reduced again and smoothens the surface. Fouling of the membranes by BSA filtration is removed due to addition of nanotubes. The mechanism for salt rejection is Donnan exlusion which shows the membrane surface is negatively charged [62].

1.3.3. Bulk modification

In this modification, the polymer backbone is functionalized to alter the hydrophilic properties of the polymer. Functional group may be sulfone (SO_3H), carboxyl (COOH) [63], amino (NH_2) [64], hydroxyl (OH) or combination of these functional groups. The sulfonation reaction introduces negatively charged sulfonic acid group to the polyether sulfone which imparts hydrophilic properties. Sulfonic acid groups can be attached to the polymeric chain in two ways. It can be done by homogeneous reaction with pre-sulfonated monomers in polymerization reaction [65] or heterogeneous reaction using sulfonating agents [66]. The later i.e. heterogeneous reactions are found to be more facile due to low cost and ease of reaction [67]. Polyethersulfone has been sulfonated previously using different sulfonation agents such as chlorosulfonic acid [68-72], oleum [73], sulfur trioxide triethylphosphate complex [74-75], sulfuric acid [76], sulfuric acid as a solvent followed by chlorosulfonic acid sulfonating agent [77-80], sulfur trioxide [81], trimethyl silylchlorosulfate [82-85]. The sulfonation of polyethersulfone follows the electrophilic aromatic substitution mechanism in which hydrogen atom in the benzene ring of PES is replaced by sulfonic acid group and is attached to the ortho position in the aromatic ring of PES with respect to ether linkage present in the polyethersulfone.

1.4 Membrane fabrication methods

Synthetic membranes can be prepared by different techniques either inorganic materials such as Zeolites, metals, glass, ceramics or organic materials [86-87]. The method of preparation greatly depends on the materials used, the membrane morphology and the separation mechanism applied. There are different techniques such as phase inversion, stretching of films, sintering of powders, microfabrication vapour deposition, irradiation, sol-gel process, etching of films and coating etc. [88-92] out of which phase inversion process is one of the important method for the preparation of flat sheet membranes. Both symmetric and asymmetric morphology can be obtained by the phase inversion process due to the consequence of immersion precipitation (Figure 1.3) [93-100]. The transformations of polymers have taken place from liquid phase to solid phase in this process in a controlled manner. The mechanism of the phase inversion process can be understood by a polymer/solvent/non-solvent system, in terms of ternary phase diagram [101].

The Phase inversion process comprises of different methods which are described as follows:

1.4.1 Precipitation by controlled evaporation

In this technique, polymer is dissolved in a mixture of solvent and non-solvent. Here the solvent chosen more volatile than the non-solvent this evaporation leads to polymer precipitation as the content of non-solvent remains higher. The morphology of the membranes prepared from this technique is skinned membranes.

1.4.2 Thermal precipitation

In this method, polymer is dissolved in a solvent or mixture of solvents and after casting the film followed by cooling for the phase separation to occur. Generally microfiltration membranes are prepared by this technique. The thermal precipitation method leads to the formation of skinned membranes [102-105].

1.4.3 Precipitation by solvent evaporation

This technique uses the simple technique procedure to prepare the phase inversion membranes which are described as: First of all polymer is dissolved in the suitable solvent to prepare homogeneous solution (dope solution). Afterwards solution is casted on a glass plate or polymer or non-woven fabric. Finally the solvent is allowed to evaporate in an inert atmosphere such as argon, nitrogen etc. to avoid contact of moisture which gives dense homogeneous membrane [106].

1.4.4 Precipitation from the vapour phase

In this method the homogeneous membrane casting solution is placed in a vapour atmosphere which consists of a non solvent saturated with the same solvent. The high solvent concentration in the vapour phase resists the evaporation of solvent from the casted film. Thus diffusion of non solvent occurs into the casted film and membrane precipitate outs. The structure of the membranes prepared from this process is usually porous membranes without a top layer.

1.4.5 Immersion precipitation

Commonly polymeric microfiltration, ultrafiltration as well as nanofiltration membranes are prepared by this technique [107]. Membrane is prepared by this technique by casting the polymer dope solution on suitable substrate followed by immersion of casted film in the appropriate coagulation bath. Polymeric films precipitate out as a result of exchange between the non-solvent and solvent. This process is also known as dry/wet method [108]. Generally the structure of the membranes obtained from this technique is asymmetric membranes. The structure of the membrane is governed by both mass transfer and phase separation method [109].

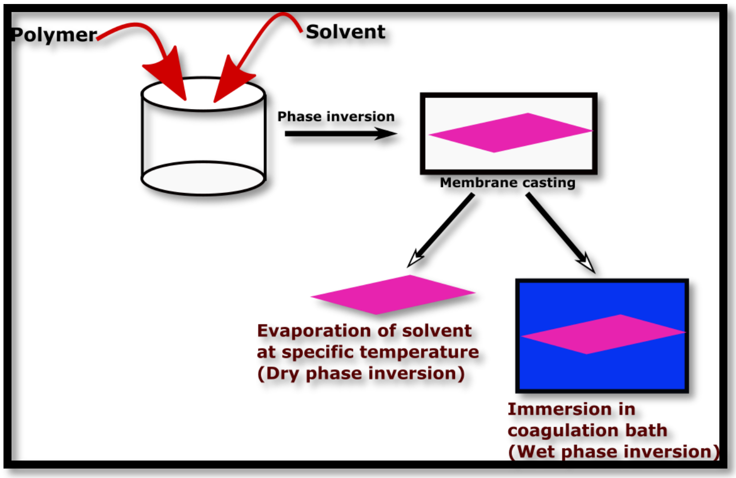

Figure 1.3 Schematic representation of Phase inversion process

1.5 Carbon nanotubes (CNTs)

Carbon nanotubes discovered by Ijima in 1991 came out as versatile materials with applications in diverse fields including membrane technology, electronics, structural integrity, biomedical engineering, tissue engineering, drug delivery, nano-injectors etc. CNTs are allotropes of carbon and having a tubular nano structure with excellent mechanical strength, thermal and electrical conductivity which makes them useful as fillers. CNTs belong to the fullerene structural family. Walls of CNTs are one atom thick sheets of carbon, called graphene (sp^2 hybridized bond). These sheets are curled at specific or discrete angles and both the rolling angle and radius decide the properties shown by nanotubes (Figure 1.4). Chemical bonding of CNT carbons are sp^2 hybridized as present in graphene. These bonds are stronger than sp^3 hybridized bonds (present in alkanes and diamonds) and provide them unique strength. CNTs can be metallic or semiconducting depending on their diameter and chirality. 'Armchair' structures have energy bands that cross the Fermi level and are therefore metallic. 'Chiral' and 'zigzag' CNTs are found to be metallic when $n-m=3I$ where I is an integer or semiconducting with an energy gap of order about 1 eV when $n-m\neq 3I$, n and m are the integers of the vector equation $R=na_1+ma_2$, where a_1 and a_2 are the unit cell vectors of a graphene sheet.

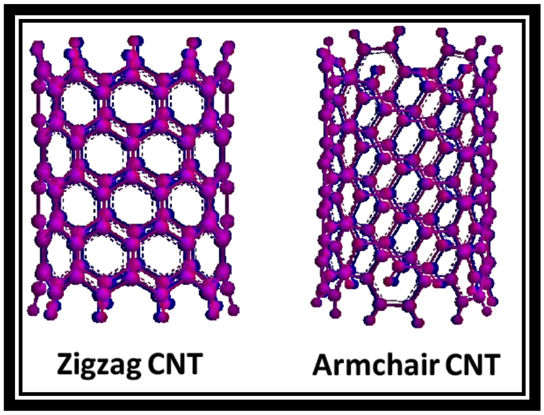

Figure 1.4 Various conformations of carbon nanotubes

CNTs are categorized of mainly 2 types; Single walled carbon nanotubes and multiwalled carbon nanotubes. Individual nanotubes are held together by weak bond known as Vander wall forces more specifically π stacking.

1.5.1 Types of carbon nanotubes

1.5.1.1 Single walled carbon nanotubes (SWCNT)

The structure of SWCNTs are formed by 2-dimensional graphene sheet cut at various angle with respect to the hexagonal lattice that has been rolled in the form of seamless cylinder (Figure 1.5). The diameter of the nanotube can be calculated from Equation 1

$$d = \frac{a}{\text{л}}\sqrt{n^2 + \mathrm{nm} + m^2} = 78.3\sqrt{(n+m)^2 - \mathrm{nm})}\ \mathrm{pm} \qquad (1)$$

The 'n' and 'm' are integers which denote number of unit vectors along two directions in the honeycomb crystal lattice of graphene. If n=m the CNTs are called armchair, if m=0 nanotubes are known as zigzag, otherwise they are named chiral.

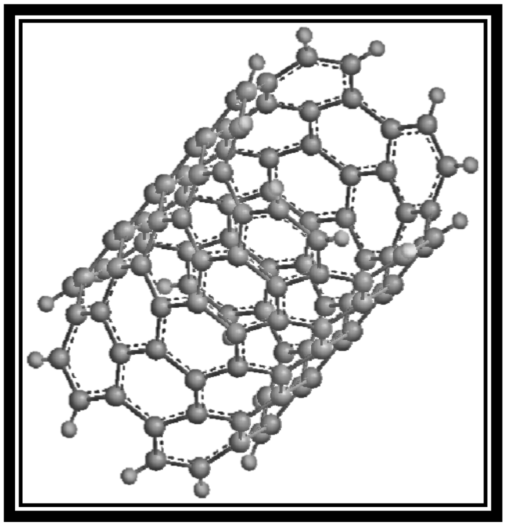

Figure 1.5 Structure of SWCNT

1.5.1.2 Double walled carbon nanotubes

Double walled carbon nanotubes were first synthesized in 2003 on a gram scale by CCVD technique, from the selective reduction of oxide solutions in methane and hydrogen. The morphology and properties of DWCNTs are similar to SWCNT except the resistance to chemical in improved (Figure 1.6). In case of SWCNTs the covalent function breaks some C=C bonds, leaving holes in the nanotubes structure thus modifying both its mechanical and electrical properties. However in case of DWCNTs only outer wall are modified leaving inner wall of the nanotubes unchanged thus no change in properties of Double walled carbon nanotubes.

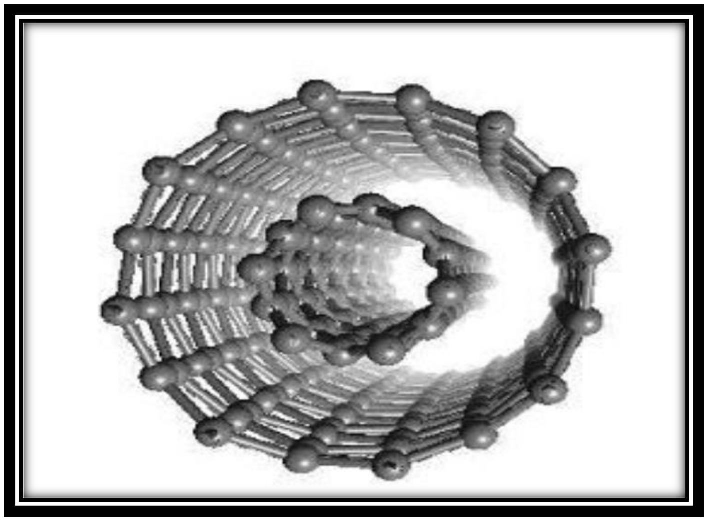

Figure 1.6 Structure of DWCNT

1.5.1.3 Multiwalled carbon nanotubes

Multi-walled nanotubes (MWNT) consist of multiple concentric tubes made of graphene, surrounding a hollow core (Figure 1.7). Its inner diameter is in the range of 1-3 nm and outer diameter is 2-100 nm having length of 5-10 micrometers. MWCNT can be divided into two categories according to the arrangements of graphene sheets. One is structure where graphene sheets are arranged in a concentric tubes and other is where one graphene sheet is rounded towards itself [110].

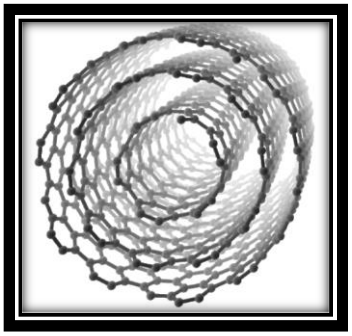

Figure 1.7. Structure of MWCNT

1.5.2 Methods for synthesizing Carbon nanotubes

Arc discharge or laser ablation method was first used for the synthesis of carbon nanotubes which are high temperature preparation techniques. But due to lack of precise control on the orientation, nanotube length, diameter, alignment, purity and density of CNTs nowadays these methods are replaced by low temperature chemical vapor deposition method. In any of the carbon nanotubes synthesis method the CNTs are associated with various impurities (other carbonaceous particle such as nano crystalline graphite, amorphous carbon, fullerenes, metals Fe, Co, Mo, Ni) that were introduced as catalyst during the synthesis [111]. These impurities raise problems in the desired properties of CNTs and interfere in the characterization and applications. Therefore, development of efficient and simple purification methods is the challenges in CNT science [112]. Most successful and used purification technique is based on acid treatment of CNTs [113].

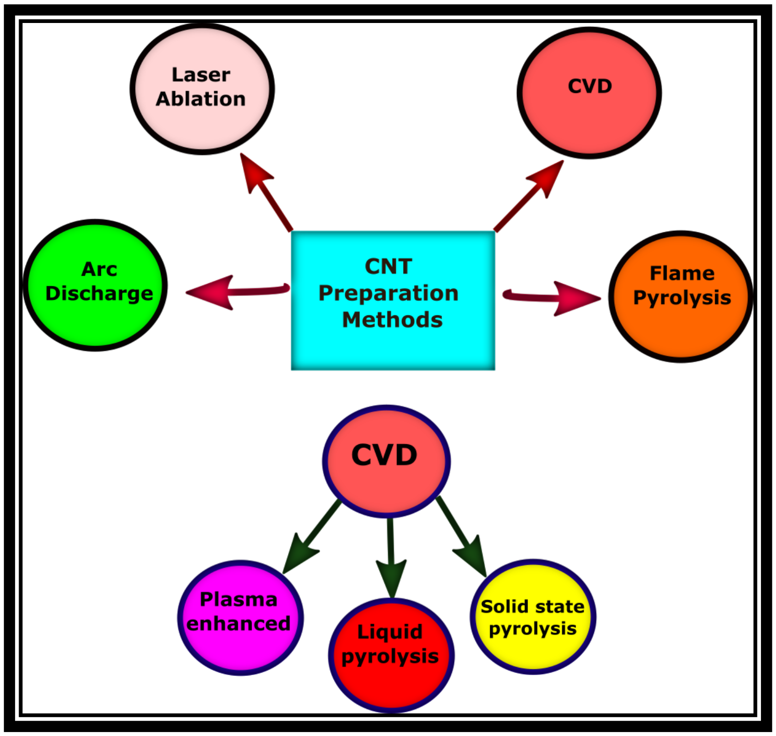

Figure 1.8 Methods for CNT synthesis

1.5.2.1 Arc Discharge method

Arc discharge method uses temperature above 1700^{o}C for the synthesis of carbon nanotubes which results in growth of CNTs with lesser structural defects compared to other techniques.

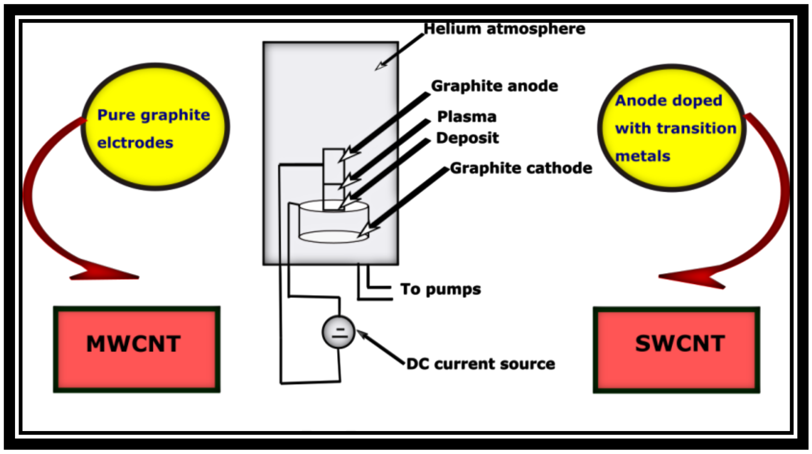

Figure 1.9 Schematic of arc discharge method for the synthesis of nanotubes

1.5.2.1.1 MWCNT Synthesis

The arc discharge method of MWCNT uses DC arc discharge between two water cooled graphite electrodes having diameters 6 and 12 mm in a chamber filled with helium and at sub atmospheric pressure. The morphology and properties of the MWCNT varied based on the use of different atmosphere and conditions. Wang et al have done DC arc discharge of graphite electrodes in He and methane. Evaporation under high pressured methane gas and high arc current, thick nanotubes with many carbon nanoparticles were obtained. However, under a methane gas pressure of 50 Torr and arc current of 20 A for anode with a diameter 6 mm thin and long MWCNTs were obtained [114]. In other work Zhao at al compared the formation of fine and long MWCNT under H_2 gas atmosphere with the He and CH_4 atmosphere. The observed that little carbon smoke was obtained in case of H_2 gas while more carbon smoke was obtained in case of evaporation under He and CH_4 gases [115]. Pulsed techniques were also reported instead of commonly used DC arc discharge. Parkanshy et al have done single-pulse arc production of near vertically oriented MWCNT deposited on the Ni/glass samples using a graphite counter-electrode in ambient air. MWCNTs with a diameter of about 10 nm and lengths of up to 3 µm were produced on the samples with a single 0.2 µs [116]. Tsai et al reported single pulse discharge in air. MWCNTs with the outer diameter of 17 nm and an inner diameter of 5 nm was obtained using a peak current of 2.5A and a discharging time of 1000 µs [117].

1.5.2.1.2 SWCNT synthesis

In arc discharge method CNTs could be synthesized with or without use of different catalyst precursor. Typically MWCNT are synthesized when no catalyst are used. On contrary SWCNT are produced when the transition metal catalysts are used. SWCNT are synthesized by Arc discharge process using composite anode, usually in hydrogen or argon atmosphere. The anode is made as a composition of graphite and a metal (Fe, Co, Ag, Pt, Ni etc.) of mixture of Co, Fe, Ni with other elements such as Co-Ni, Ni-Ti, Fe-No etc. The yield of the nanotubes is significantly improved by using metal catalysts. To achieve high efficiency the process needs to be held on a constant gap distance between the electrodes which gives stable current density and anode consumption rate. Here also side products such as MWCNT or fullerenes are usually produced.

1.5.2.2 Laser ablation

Laser ablation method was first demonstrated by Smalley’s group in 1995 and the principles and mechanisms of this method are similar to arc discharge method [118]. The only difference is that the energy is provided by a laser hitting a graphite pellet containing usually Ni or Co catalyst materials [119]. Almost in all the studies lasers used for the ablation have been Nd:YAG and CO_2. The laser properties (energy fluence, peak power, cw versus pulse, repetition rate and oscillation wavelength), structural and chemical composition of the target material, the chamber pressure and the chemical composition, flow and pressure of the buffer gas, the substrate and the ambient temperature and the distance between the target and the substrate governs the properties of the synthesized CNTs.

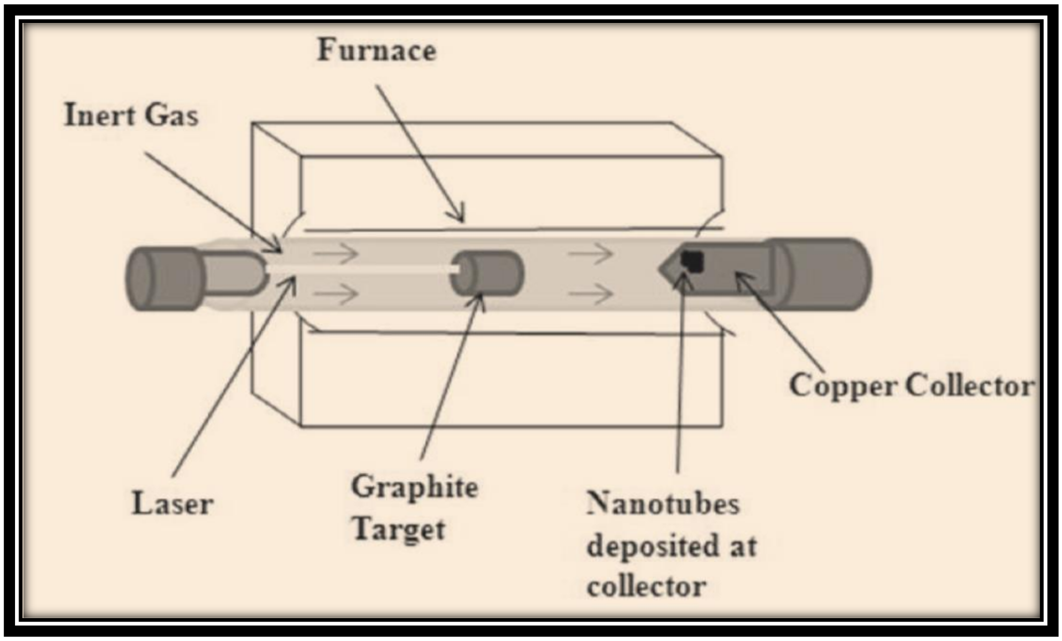

Figure 1.10 Schematic of laser ablation method for CNT synthesis [138]

1.5.2.3 Chemical vapour deposition (CVD)

The CVD process was discovered in 1950's though the discovery of CNTs by this method took place in 1993. A reactor bed is used which consist of a layer of metal catalyst such as Ni, Co, Fe or mixture of these metals [120]. High temperature annealing of substrate is performed and combination of two gases inorganic or process gas and organic gas is used as initiator for growth of nanotubes at metal particles. Inorganic or process gases are generally H_2 or N_2 and organic gases may be methane ethane or ethyne. The catalyst particles can stay at the tips of the growing nanotube during the growth process, or remain at the nanotube base, depending on the adhesion between the catalyst particle and the substrate [121]. It is an economically viable process for large scale and pure production of CNTs compared with laser ablation. The other advantage of CVD is easy control of reaction procedure [122]. The role of catalyst in the chemical vapour deposition process is the decomposition of carbon source via either heat (thermal CVD) or plasma irradiation (plasma-enhanced CVD, PECVD) and its new nucleation to form CNTs. CNTs growth depends also on the catalyst selected for the process. Thus its preparation is also a decisive step in CNTs synthesis. Flahaut et al reported the effect of conditions of catalyst preparation on the synthesis of CNTs via Catalyst Chemical Vapour Deposition. In this work, they have done combustion of ether urea or citric acid for the preparation of catalyst. They found that in case of citric acid milder combustion conditions were obtained, it can either limit the carbon nanofibre formation or increase the selectivity of CCVD synthesis towards CNTs with lesser walls which depends on the composition of catalyst [123].

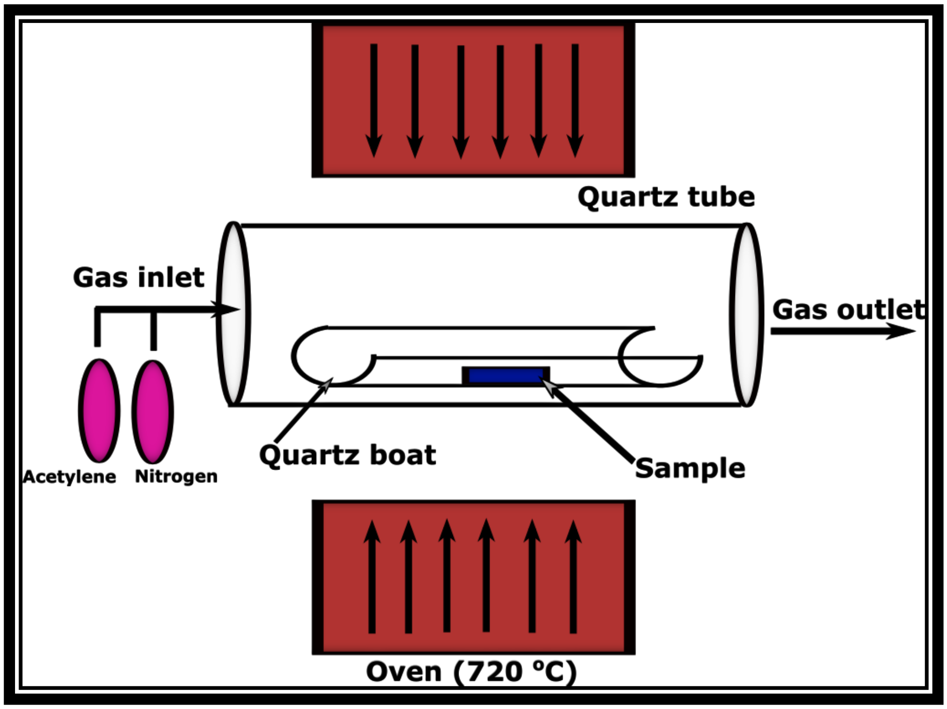

Figure 1.11 Schematic of CVD process for carbon nanotubes synthesis

1.5.2.3.1 Plasma enhanced CVD

PECVD is appropriate method for carbon nanotubes hybrid material synthesis and their surface properties modifications. Different modes can also be used in

PECVD; direct current (DC-PECVD), diffusion (DPECVD), radio frequency (RF-PECVD) or microwave (MWPECVD). Wang et al reported the preparation of vertically aligned CNTs using FeNi or Fe sputtered catalyst layers on glass substrates by RF or DC PECVD. In this work CNT growth mechanism using both methods were compared with respect to gas flow rate, plasma power and catalysts. They explained the reson of more efficient decomposition of gas molecule by RF-PECVD than DC-PECVD by plasma theory. The higher concentration of reactive materials was in the RF-PECVD than DC-PECVD. However CNTs growth was well aligned vertically in case of DC-PECVD [124].

Both in thermal CVD and Plasma enhanced CVD various catalyst types to improve the yield and the quality of CNT production are applied. Eg. Vollebregt et al used Pd as a catalyst material and prepared vertically self-aligned CNTs and CNFs. They compared two preparation methods with various conditions and catalysts (Pd, Ni, Fe, Co) as follows: PECVD at 450^{o}C to 500^{o}C and atmospheric-pressure chemical vapour deposition (APCVD) between 450 ^{o}C and 640 ^{o}C. High density self-aligned CNTs were obtained using APCVD and Pd as the catalyst, while Co and Fe resulted in random growth. TEM revealed that the CNTs grown by Pd with PECVD formed large bundles of tubes, while Ni formed large-diameter CNFs. The CNTs grown using Pd or Ni were of low quality compared with those grown by Co and Fe [125].

1.5.2.4 Flame pyrolysis

Flame pyrolysis is a new method for mass CNTs production with the ease of equipments and experimental conditions. It is presented by the research group of Liu et al. and thy named it as V-type pyrolysis flame. Heat was provided by the combustion of Acetylene/air premixed gas. Mixture of hydrogen/helium gas acted as diluted and protection gas and pentacarbonyl as the catalyst. They synthesized CNTs with less impurities (approximate diameter 10nm and 20 nm and with length dozens of microns) and high yield using carbon monoxide as the carbon source. They studied the effect of sampling time, hydrogen and helium to the CNTs growth process [126].

1.5.3 Applications of CNTs in membrane technology and literature outline

With the advancement in the field of nanotechnology, membrane based separation technology has been enriched with some feasible and valuable approaches which enhanced membrane performance with their synergistic effects for water and wastewater treatment [127]. Both single and multiwalled carbon nanotubes have been involved in the formation of mixed matrix membranes and due to their high chemical, thermal and mechanical stabilities as well as high surface area, interesting results in water treatment [128], desalination [129-130], gas separation [131-133], and some other applications have been obtained [134]. Moreover, nanotubes show excellent adsorption, catalytic and electrochemical properties which are profitable to link adsorption, catalytic or electrochemical function with membrane separation process, which makes CNT based mixed matrix membranes efficient for water treatment.

Vatanpour et al prepared acid oxidized-MWCNT/PES membrane and studied the effect of addition of f-MWCNT on pore size, hydrophilicity, rejection and antifouling characteristics of membranes. Addition of 0.2 wt % of nanotubes resulted in increment of pore size where as further addition of CNTs the pore size decreased. The membrane surfaces became hydrophilic which resulted in enhanced pure water flux. AFM studies shows that 0.04 wt% of nanotubes makes the surface of membrane smoother due to low electrostatic interactions among the MWCNTs and they are regularly co-located in the membrane. However on 0.2 wt% addition of nanotubes roughness increased. This observation has been explained on the basis of increase in pore size and agglomeration of carbon nanotubes. At values above 0.2 wt% MWCNT, combined effect of increased viscosity and lower thermodynamic stability of the blend solution takes place and by the addition of hydrophilic MWCNTs the pore size reduced again and smoothens the surface. Fouling of the membranes by BSA filtration is suppressed due to addition of nanotubes. The mechanism for salt rejection has been explained due to Donnan exclusion which shows that the membrane surface is negatively charged [135].

Majeed et al. have used commercially available hydroxyl MWCNT membranes incorporated in the PAN matrix in which nanotubes concentration is maintained at 0.5, 1.0 and 2.0 wt%. The membranes were characterized using FTIR, Raman, viscosity measurement, scanning electron microscopy (SEM), transmission electron microscopy (TEM), porosity measurement, contact angle measurement and water flux measurement. The highest water flux was observed for 0.5 wt% CNT which is 63% larger than the neat membranes. This enhancement in flux has been explained to be due to improved hydrophilicity of MWCNT mixed matrix membranes. At CNT concentration more than 0.5 wt% the pure water flux starts decreasing which have been attributed to the increase of thickness of the top layer in membrane. The rejection capacity of membranes is measured using 300 ppm solution of a mixture of dextrans. 0.5% CNT-PAN membranes showed 47 % rejection which is less in comparison to pristine PAN (57%), 1% CNT PAN (57%), 2% CNT PAN (56%). The reason for less rejection has been explained by two opposite effects. First, the increased hydrophilicity accounts for the higher water transport through the membranes without enhancing the permeability of dextran. Second, dragging of solute caused by higher water flux negatively affected the retention values. The reason given for lower retention is also attributed to slightly higher pore size and more interconnected pores compared to rest of the membranes with higher retention [136].

Yin et al prepared hollow fiber membrane containing oxidized MWCNT/ Polysulfone (PSU) and observed the membrane performance in terms of permeability, humic acid and procion red removal and BSA fouling. The pore size of the membrane is first increased and then decreased with increasing nanotube concentration, which is attributed to increased viscosity as well as lowered thermodynamic stability of the dope solution by incorporation of hydrophilic CNTs. At three different polymer dope concentration (15, 18 and 20 wt%) the observed pure water flux is same, while it first increases and then gradually decreases with increasing filler concentration which is consistent with membrane pore dimensions. As compared to pristine PSU membrane, mixed matrix membranes showed significant increase in pure water flux (60% to 100%), while solute rejection does not change considerably [137].

The heavy metal removal capacity of membranes with oxidized, amide and azide functionalized MWCNTs incorporated polysulfone (PSU) matrix was analyzed at varying pH and transmembrane pressure. The concentration of CNT was varied from 0.1-1 wt% in the polymer matrix, The best rejection was obtained from 1 wt% azide functionalized/PSU matrix at 0.49 MPa and acidic pH 2.6. Amide functionalized CNT/PSU membrane rejected 94.8 % Cr(VI) which is just 10.2% in case of pristine PSU membrane [138].

In another study, Vatanpour et al studied the membrane filtration properties of PES/NH_2-MWCNT membranes in terms of protein fouling, and salt rejection. The salt rejection of Na_2SO_4, $MgSO_4$ and NaCl was measured using mixed matrix as well as bare PES membranes. The best salt retention was observed for 0.045 wt% of PES/NH_2-MWCNT, which is 60% for Na_2SO_4, 45% for $MgSO_4$ and 20% for NaCl for 180 min of duration. The increase in salt solution pH caused more negative surface charge and higher retention. The more negative surface charge, lower roughness and higher hydrophilicity of mixed matrix membranes led to the significant improvement in fouling recovery ratio (FRR), during BSA filtration [139].

Interestingly, functionalized single walled carbon nanotubes (SWCNTs) are also utilized for the preparation of mixed matrix membranes within the polysulfone matrix. The charge generated on the membrane surface, was measured by zeta potential to insure the well alignment of nanotubes inside the membrane. Oxidized functionalized MWCNT/PSU membrane having 1 wt% concentration of filler gave the highest rejection of Cr(VI), AS(III) and Pb(II) as 96.8, 87.6, 94.2% respectively [140].

Recently, small angle neutron scattering (SANS) technique has been used to study the morphology of the polyether sulfone/functionalized MWCNT mixed matrix membranes, dimensions, porosity and correlation length of the membrane pores are explored using this tool. It is found that with the increase in weight percentage of nanotubes in membranes, the pore dimensions keep on decreasing up to 1wt% while the porosity of the membrane increases which is in agreement with the percentage of heavy metal removal [141].

Qui et al have described the preparation chitosan membranes for the separation of ethanol/water mixture by pervaporation. The functionalized nanotubes were dispersed with chitosan in 2 wt % acetic aqueous solution and cast on PAN UF membrane and dried under infrared lamp. Authors have investigated the sorption, swelling and pervaporation properties of membranes. The swelling degree of composite membranes increased with the addition of MWCNT content which enhances the adsorption ability of chitosan membrane towards ethanol/water mixture. The effect of operating temperature as well as MWCNT content on pervaporation is analyzed in this work. It was observed that between 30˚C-70˚C, total permeation flux increased significantly and separation factor slightly decreased due to increasing thermal energy, the free volume in the membrane matrix increased because of increased frequency and amplitude of the chitosan chain jumping. Resulting diffusion of both permeating molecules increased which leads to higher permeation flux, whereas selectivity was slightly suppressed. The membrane having low content of MWCNTs shows better pervaporation properties than the chitosan membrane [142].

Shiraji et al synthesized CNTs by CVD method using cyclohexanol and ferrocene as carbon precursor and catalyst respectively. These synthesized nanotubes are purified and treated with nitric acid to get acid modified CNTs. Membranes were prepared by incorporation of these nanotubes to poly vinyl alcohol. Surface morphology of CNT-PVA nanocomposite membrane at various nanotubes concentrations was observed by FESEM.

This study also concludes that 2.0 wt% CNT are well dispersed in the PVA matrix while further increasing the nanotubes concentration agglomeration of CNT is observed. Relation between selectivity and permeation flux of CNT-PVA membranes & CNT loading is studied at fixed operating condition 10 wt% water in IPA mixture and feed temperature of 30^{o}C for all the membranes. These membranes are used for the pervaporation application. They observed elevation in selectivity for the CNT-PVA nanocomposite membrane as compared to the pristine PVA membrane. CNT in PVA matrix acts as reinforcing bridge elements thus making PVA chains more rigid, which resulted in reduced degree of swelling with a simultaneous flux reduction. In detail, rigidification can reduce the free volume thereby giving higher selectivity and less permeation flux. Pristine PVA membrane is having highest degree of swelling and permeation flux. The values for water selectivities for the pristine PVA and 2 wt% CNT incorporated nanocomposite membranes are 119 and 1794, respectively [143].

Aroon et al have focused on the use of chitosan functionalized MWCNT (C-f-MWCNT) and raw MWCNT (r-MWCNT) for the preparation of polyimide membranes (PI) and compared with respect to gas permeability between the PI, C-f-MWCNT/PI and r-MWCNT/PI membranes. From TEM images of r-

MWCNT and C-f-MWCNT, they have described that r-MWCNT are entangled and closed loop in nature while functionalized nanotubes are well dispersed and open ended. The membrane with r-MWCNT showed low He permeability than the PI membrane and with C-f-MWCNT, showed higher He permeability than the PI membranes which was explained as resulting from open ended nanotubes [144].

In another study, carboxyl functionalized CNT and Ru (Fe) modified CNT incorporated polyether sulfone membrane for measuring the gas permeability and selectivity is reported. These membranes were prepared by phase transition method followed by compression molding. TEM images of membrane surface confirmed the formation of dense membranes. The CNT are randomly dispersed in the polymer matrix and metal nanoparticles are visible on the CNT surface.

CO_2 and N_2 permeability were analyzed through the prepared membranes, which showed that the gas permeation rates are higher for composite membranes than the pristine PES membrane. Up to 5 wt% modified nanotubes loading enhances the gas permeability due to the continuous free volumes between CNTs and polymer chains leading to lower gas diffusion resistance. However, agglomeration or poor dispersion occurs due to higher CNT loading which may be due the formation of discontinuous nanogaps between CNTs and polymer chains & tortuosity around the agglomerated CNTs limits further permeability increment thus deterioration in the permeation flux at loading ratio as high as 10 wt%. In case of Fe-CNT membranes, higher concentration (10 wt %) of CNT does not deteriorate the gas permeability probably due to better dispersion of Fe-CNT at 10 wt% loading. Larger sized Fe particles derived at higher temperature reduction may obstruct CNT agglomeration and generate more interfacial volume between CNTs and polymer matrix in the mixed matrix membranes. The improved gas permeability was due to the disturbed polymer chain packing caused by the addition of nanofillers. The CO_2 and N_2 gas selectivity of COOH-CNT nanocomposite membranes is same as pristine PES membranes. Membranes containing Ru modified CNTs displayed better performance on both flux and selectivity, while lower selectivity is observed in mixed matrix membranes with Fe-CNTs. Due to modification of gases, adsorption difference of gases varies thus affecting gas selectivity of composite membranes. Larger adsorption difference of CO_2 and N_2 could be introduced by Ru modification than by COOH and Fe modification [145].

1.6 Water

Water is very essential elements for the whole world. Increasing pollution, industrialization, population growth has made the lack of clean drinking water a serious issue throughout the globe. 75 % of the earth surface is surrounded by water. Although most of this water is not drinkable due to its high salinity. About 2.8% of water is locked in glaciers and polar ice. Only 0.5% water is available for human beings. Large community is dependent on rain water and stagnant water for slaking their thirst. A number of people do not get access to sufficient amount of adequate sanitation and clean water [146]. A large population suffers with many hazardous diseases which are caused by drinking impure water.

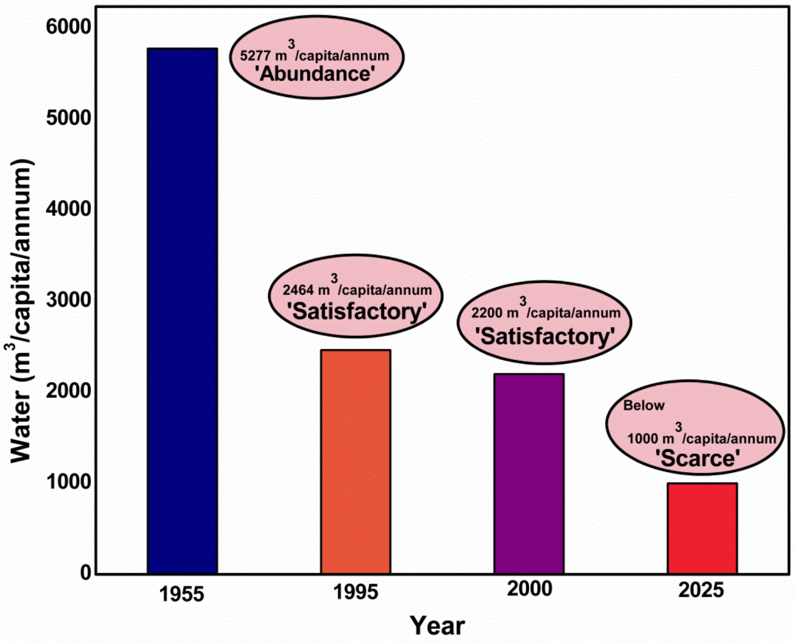

Figure 1.12 Scenario of availability of renewable fresh water in India

With the expansion of the industries and growth in technology the surface water is considerably contaminated with heavy metals. These metals are adsorbed into the soil, overspill into rivers or lakes or trickle in the ground water which is an important source of drinking water. Thus by consuming these contaminated water animals, plants as well as human tissues have been taking these hazardous heavy metals.

There is a permissible limit for different constituents (such as heavy metals, salts, organic chemicals, minerals, essentials metal ions, algae and other suspended impurities) of potable water set by World health organization (WHO). Water is not suitable for drinking with concentration above this permissible limit [147].

1.7 Noxious ions present in surface and ground water

Lead, Mercury, Arsenic, cadmium and chromium are main toxic ions. These ions are not metabolized by human or animal or plant body and accumulate in the soft tissues.

ATSDR's – 'Top 20 List of Hazardous Substances' contains the list of some ions as toxic ions identified by Agency for Toxic Substance and Disease Registry (ATSDR), Department of Health and Human Services (US) [148].

1.7.1 Sources and Health effects

1.7.1.1 Chromium

Domestic waste water, sewage sludge and different industrial processes such as electroplating, metal finishing industries and tanneries are the common sources to introduce Chromium into natural waters. It is common toxin with mutagenic effect which occurs mostly as Cr (III) and Cr (VI) in aqueous solutions. Cr (VI) is more harmful and gives greater risk due to its carcinogenic properties [149].

Keen exposure to Cr (VI) produces liver & kidney damage, internal haemorrhage, nausea, dermatitis & respiratory problems, diarrhea. However acute poisoning by Cr (III) compounds is extremely rare which shows their low toxicity to human beings.

International Agency for Research on Cancer (IARC) found the compounds of Cr (VI) cancer producing in 1980 but not yet categorized it as carcinogenic element due to insufficient evidences for its carcinogenicity to human beings. R. Sanz reported that people exposed to Cr (VI) compounds in stainless steel welding, chrome pigment production and other industrial processes can suffer various form of cancer [150].

1.7.1.2 Lead

Pyrometallurgical nonferrous metal processes, combustion of leaded fuels and coal combustion are the processes accountable for lead introduction water streams. However the primary sources of lead comprise domestic waste water, manufacturing processes and atmospheric deposition.

Lead accounts for the most of the cases of the paediatric heavy metal poisoning which targets the kidney, thyroid gland, brain and bones. It's acute poisoning is rare.

IARC classified lead into Group 3: inadequate evidences for carcinogenicity in humans and sufficient evidences for carcinogenicity in animals.

1.7.1.3 Cadmium

The main sources for contamination of cadmium in water are manufacturing processes related to chemicals and metals, smelting and refining of nonferrous metals and domestic waste water [151]. About 15% of cadmium contmination is from atmospheric deposition such as from natural sources such as volcanoes, biogenic particles and windborne soil particles.

Acute exposure to cadmium causes diarrhea, vomiting, salivation, muscular cramps and nausea in humans.

IARC has classified cadmium for carcinogenicity in humans and no evidences for carcinogenicity in animals [152].

1.7.1.4 Copper

Volcanoes are one of the main sources of copper metal [153]. Dying industries as well as nuclear generating industries are also responsible for the contamination of copper in effluent water [154].

Copper is vital nutrient to humans but if consumed in excess concentration can be resulted in liver cirrhosis, anemia, liver and kidney damage. Children exposed to higher concentration to copper can suffer with diarrhea, abdominal pain, vomiting, headache and nausea [155].

1.7.1.5 Arsenic

Plenty of minerals and ores are the source of arsenic to ground water [156]. Though the occurrence of arsenic in generally due to the domestic waste water.

Other sources are sewage sludge, smelting & refining and manufacturing processes.

Arsenic is on number 1 in the “Top 20 List of Hazardous Substances” created by ATSDR. It is the most common source of acute heavy metal poisoning in humans. It can also affect the gastrointestinal tract, skin and respiratory tract of humans. Chronic intoxication can cause muscular weakness, loss of appetite, neurological disorders, nausea, and skin disorders such as hyper-pigmentation and keratosis.

IARC classified inorganic arsenic in group 1: Inadequate evidences for carcinogenicity in animals and sufficient evidence of carcinogenicity in humans. The consumption of arsenic contaminated water causes skin pigmentation especially in rural areas. Further contamination of arsenic can lead to leprosy or other highly communicable skin disease [157-158].

1.8 Techniques for water purifications

1.8.1 Chlorination

Chlorination is used to remove microbes from the water by treating it with either elemental chlorine or sodium hypochlorite. Further after maintaining the concentration of chlorine or sodium hypochlorite up to 3 ppm or less, water can be consumed. Chlorination is effective against bacteria, few algae and virus but the major drawback of this process is that chlorine reacts with hydrocarbon present in the water resulting in the formation of chlorinated hydrocarbon which are highly carcinogenic.

1.8.2 UV Treatment

In UV treatment a typical wave length in the range of 240 - 280 nm is used for the photolysis of DNA. By this method water can be well purified as the genetic information contained in the microbial DNA is destroyed due the photochemical reaction [159]. UV treatment is having 3 main limitations: poor activity in presence of turbidity and suspended particles, water flow rate in the UV tube is also a key factor that affects the efficiency of the process and transmittance of ultraviolet rays is greatly affected by turbidity as well as suspended particles.

1.8.3 Chemical precipitation

Chemical precipitation method can be used for the removal of iron and aluminium from sewage water and for the removal of zinc, nickel, iron, tin, copper and cadmium from the effluents of metal finishing industry [160]. Generally heavy metals are precipitated as their hydroxides using lime or sodium hydroxide. Lime is frequently chosen for precipitation due to its low cost and excess of lime can be used as adsorbent for the removal of other metal ions [161]. The major drawback of chemical precipitation process is sludge production [162].

1.8.4 Ozone treatment

Ozone treatment is an efficient process to remove the contaminants for impure water. But it is not used widely due to high cost. The production of ozone consumes high energy and the process is carried out by an electric discharge field in ozone generators. Furthermore, ozone is a highly reactive gas with half life of 3-4 days at room temperature which shows unpleasant effects on humans at concentration above 100 ppb.

1.8.5 Electro-deposition

This method uses insoluble anodes to recover the metals present in the waste soulutions such as the cleaning of copper with sulfuric acid gives spent solutions in which copper sulphate maybe present with residual acid. In this case high quality copper cathode can be electrolytically deposited while free sulphuric acid is regenerated [163].

1.8.6 Electro dialysis

Electro dialysis is a efficient technique for surface and ground water treatment which can be utilized upto 5000 ppm. This process works under the influence of electric current and split ions from water resulting in drinkable water. There is one joint project DRDO and Rajasthan state government known as SUJALAM, in which 64 water desalination plant has been installed in extreme desert areas of the state to provide pure water to the population [164].

1.8.7 Xanthate process

Xanthate process involves the use of cellulose or starch xanthates which are commercially available for the treatment of wastewater to make it potable. Metal ion such as chromium, lead, iron and nickel are present in waste water, when this waste water is treated with cellulose xanthate it resulted in minimum level of residual metals in the pH range 6.5 to 9.5 [165]. The limitation of this technique is high operational and capital cost, complex handling and disposal problem of the residual metal sludge.

1.8.8 Ion exchange resins

Ion exchange resin is an insoluble matrix, generally having diameter in the range of 1-2 mm, in the form of small beads fabricated from organic polymer substrate. These resins have sites with easily trapped and released ions. Simultaneous trapping and releasing of other ions takes place till the equilibrium is reached. These resins are functionalized with chelating ligands which enhances its efficacy due to complex formation in favourable conditions. These modified resins can also adsorb the non specific adsorbents. Thus ion exchange resins can be used very efficiently for the removal of heavy metals from water and industrial waste wastewater [166].

1.9 Limitations of these processes and advantage of membrane technologies

The above mentioned techniques are used only for specific applications during water filtrations for example: Ozone treatment, chlorination and UV techniques are used to sterilize micro-organisms however they cannot be used for the reduction of organics. Carbon filters are very useful in the removal of organic contaminants, taste and odor though it cannot be able to remove micro-organisms.

Ion-exchange technique could be used for the demineralization and desalination of impure water [167].

Membrane technology has gained much attraction in the field of water purification as it can remove all the contaminants in the water such as organic materials, particulates as well as microorganisms. Membrane processes have many applications in separations of fluids as well as liquids due to ease of operation and energy conservation [168]. Membranes can be formed by polymer, ceramic, glass, zeolites and metal substrates though polymeric membranes are having low cost and robustness. These polymeric membranes are resistant to wide range of physical and chemical conditions. There are mainly two types of membrane separation processes (1) Pressure driven (2) Electrically driven. Hydraulic pressure is the driving force to compel water molecule through the membranes in pressure driven membrane process. Contaminants are retained and concentrate in the feed water which is known as reject stream. The water which is passed through the membranes is pure water and called as permeate stream. Electric current is used to travel ions across the membranes leaving purified water behind. The water retained in the feed stream is pure water.

Membrane based separations is based on sieving as well as adsorption mechanism in case of fluid separation. The pressure driven membrane separation technologies are subdivided into following categories: reverse osmosis [169], ultrafiltration [170-171], nanofiltration [172-173] and microfiltration [174] according to size of the separable contaminants.

1.10 Pressure driven membrane processes

1.10.1 Microfiltration

The size ranges of contaminants are 0.1 to 10 µm in the microfiltration process. Generally particulate contaminants, pathogenic organisms like bacteria etc are the impurities which could be removed using this process. Microfiltration process very prone to fouling thus reduction the permeate flux. This process operates on a constant pressure. This technique is generally employed in the electronic industries for ultrapure water.

1.10.2 Ultrafiltration

Ultrafiltration membranes are used for the removal of micro particles from colloids as well as viruses. The range of pore size of these membranes falls between 10-1000Å. UF membranes can be combined with NF and RO process for pretreatment of fluids. These membranes could not be able to separate ions from the contaminated water. Ultrafiltration membranes are used at low pressure difference across the membrane surface as the high molecular weight ions are rejected using these membranes.

1.10.3 Nanofiltration

Nanofiltration membranes are used for the rejection of low molecular weight ions, removal of hardness and dissolved organics etc [175-176]. These membranes can be operated in 50-150 psi pressure. Nanofiltration membranes have wide and numerous applications towards the rejection of impurities such as industrial effluents, sea water desalination, dairy purification, dairy and whey production etc. [177].

1.10.4 Reverse osmosis

Reverse osmosis membranes employs the flow of solvent from concentrated side to dilute side through semi permeable membranes by applying external force. Thin film composite membranes are generally termed as RO membranes. Different researchers have used RO membranes for the desalination applications [178-179]. These membranes are employed for the removal of Cr, Pb, Cu, Zn, Ni and Fe from effluent water [180]. This process is successfully used in industries and domestic scale for water purification.

1.11 Literature summary

NF and RO membranes have been used very effectively in the separation science though the prime limitation of these membranes is that the formation of membrane is quite complicated with lower pure water flux and lesser fouling resistance [181]. Thus, the idea of membranes having both polymeric substrate as well as inorganic filler came in existence, which can overcome the above mentioned limitations to a large extent. There are different studies having various fillers Fe_3O_4 nanoparticles [182-186], oxidized multiwalled nanotubes [187-189], TiO_2 nanoparticles [190-194], functionalized MWCNT [195-199], silver nanoparticles [200-202], modified silica nanoparticle [203-204], chitosan/zinc oxide nanoparticles [205-207], beta cyclodextrin-polyurethane [208], graphene oxide [209-211], manganese oxide and alumina nanoparticles [212-213], zeolites [214-215], attapulgite [216], fumed silica [217-219] which have served good results.