CHAPTER 1

INTRODUCTION

Worldwide demand and supply of fresh water was discussed briefly in this chapter. Growth of industrialization, urbanization and agricultural activities discharging different types of pollutant to the water bodies and their impact on environment was also discussed. Development of photocatalytic membrane as an alternative to conventional and emergent technologies for treatment of wastewater was highlighted. Based on the literatures available the objectives was framed which is mentioned at end of this chapter.

1.1 WATER AVAILABILITY AND DEMAND

Environmental pollution is increasing and environmental components (air, land, lakes and rivers, oceans, soil, forests, etc.) are getting degraded due to rising population and increasing industrialization. Environmental pollution started with the industrial revolution of 1860 and increased rapidly as the industries grew and urbanization started at fast pace (Onac et al., 2019).

During the second half of the twentieth century, environmental pollution accelerated at a fast pace due to uncontrolled population growth, irregular urbanization, and unplanned industrial development as a result disposal and management of pollutants increasingly became a serious problem (Castillo et al., 2002; Cheng et al., 2015). This resulted in increasing pollution of air and water bodies.

Over 2/3rd of the Earth's surface is covered with water but only 2.5-3 % of the water mass is available as fresh water and out of which 0.5–0.75% is groundwater and <0.01% is surface water and rest is in the form glaciers and ice (Sánchez et al., 2011). Water distribution on the Earth is shown in Figure1.1. In spite of fresh water being an essential but scarce natural resources its consumption is increasing continuously (Mishra et al., 2020; Saeedi-Jurkuyeh et al., 2020). Its uneven distribution across the globe is creating another problem. According to World Health Organization (WHO) report, presently one-third of the world's population are already facing the challenges of water tension and by 2030 it is projected to increase by 62% (Alejo et al., 2017; Anjum et al., 2018).

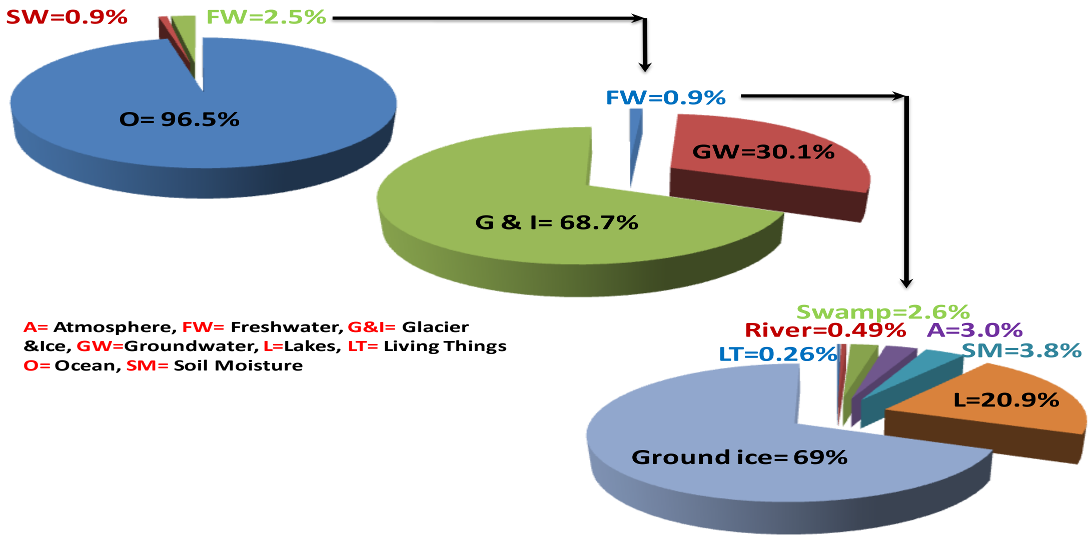

Figure 1.1: Water distribution across the world
(https://en.m.wikipedia.org/wiki/Water_distribution_on_Earth)

Increasing water pollution (due to the presence of inorganic, organic, and biological contaminants) and reducing availability of fresh water for human consumption has made it essential to treat and recycle as much as of polluted water as possible (Boliestty et al., 2019; Adetunde et al., 2010).

1.2 WASTEWATER TREATMENT

Need for augmenting the available fresh water and recycling of polluted water has attracted global attention towards developing cost effective, efficient, and sustainable water purification and a wastewater treatment systems. Several biological, chemical and physical processes for treating contaminated and polluted water have been developed and are in use since decades. A brief account of these processes is presented here in the following coming sections.

1.2.1 Technologies available for contaminant removal

Various physical and chemical treatment techniques/method currently in use are shown in Figure 1.2. These include adsorption (Warsinger et al.,2018), electrochemical processes (Jin et al., 2016; Deghles et al., 2016) , biological operations (Angelucci et al., 2017)), coagulation/flocculation (Mella et al., 2015), chemical precipitation (Borra et al., 2014) solvent extraction (Nayl et al., 2015), filtration and membrane processes (Bao et al., 2015; Koushkbaghi et al., 2018)) . Selection of a given technique will depend on the wastewater characteristics and level of treatment required. However, out of different technologies available only few are employed by the industrial sector on technological and economic grounds. Table 1.1 enlists the pros and cons of different techniques.

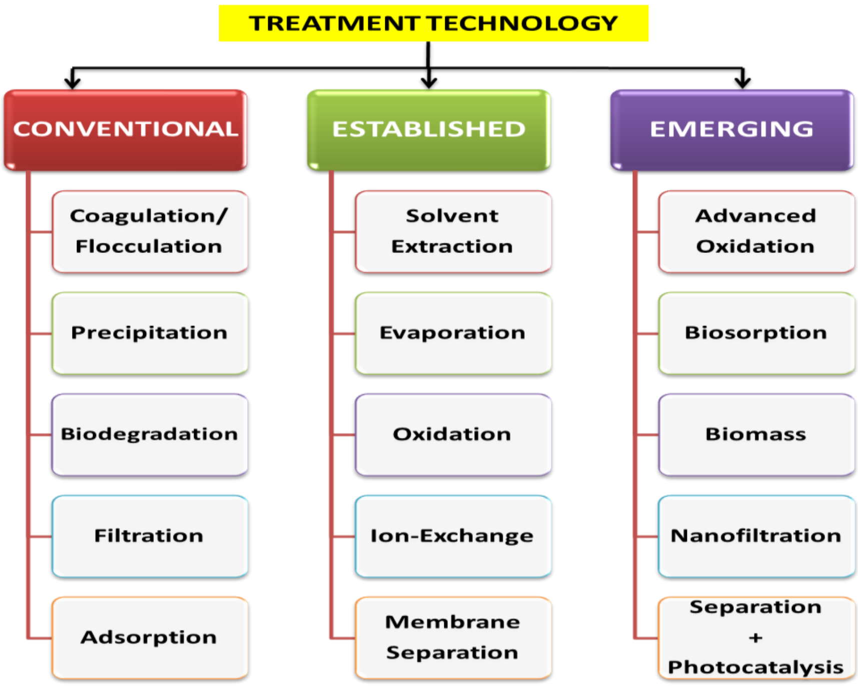

Figure 1.2: Classification of technologies available for pollutant removal

Table 1.1: Pros and cons of different wastewater treatment techniques (Crini et al., 2019)

Process	Pros	Cons
Chemical Precipitation	• Simple technology • Economically advantageous • Adaptability to high pollution load	• Ineffective metal ion removal capacity • Increased sludge volume generation • High chemical consumption
Coagulation/ Flocculation	• Simple technology • Low capital cost • Efficient removal of suspended solids and colloidal particles • Good sludge settling and dewatering characteristics • Significant reduction in the chemical and biological oxygen demand • Bacterial inactivation capability	• Increased sludge volume generation increase treatment cost • Non-reusable chemical composition is high
Chemical oxidation	• Simple, rapid and efficient process • No sludge production • Increases biodegradability of product	• Formation of intermediates • No effect on salinity • Limited effect on chemical oxygen demand
Biological methods	• Simple, economically attractive • High reduction in biochemical oxygen demand and suspended solids • Efficient removal of biodegradable organics	• Optimal favourable environment for survival of bacteria. • Complex microbiological mechanisms and slow process • Possible sludge bulking and foaming

Adsorption/filtration	• Simple technology • Excellent quality of the treated effluent • Efficient removal of turbidity and suspended solids	• Non-destructive and non-selective process • Regeneration is costly and results in loss of material • High investment (cost of excellent adsorbent is high)
Ion exchange	• Rapid, efficient process and produces a high-quality treated effluent. • Recovery of valuable metals	• Non-destructive process • Large treatment volume requires large columns • Rapid saturation and clogging of the reactors • Initial cost, maintenance and regeneration costs are high. • Performance is adversely affected by the effluent pH
Electro-coagulation (EC) Electro-flocculation (EF)	• Recovery of valuable metals • Effective removal of suspended solids, metals, oil & grease • Adaptation to different pollutant loads and different flow rates	• Efficiency is affected by the sludge deposition on the electrodes as it inhibit the electrolytic process in continuous operation • Increased cost due to treatment of sludge • Initial cost, maintenance and regeneration is cost is high.
Membrane Separation	• Small space requirement • Highly efficient, simple and rapid process • Produces a high-quality-treated effluent • Little or no chemicals consumption • Minimal solid waste	• Non-destructive separation • Problem of membrane clogging • Initial investment, maintenance and operation cost is high. • Energy requirement is high

	generation	
Photo-catalytic Oxidation	• No consumption of expensive chemicals • Excellent removal of organic contaminants • Successfully applied both in slurry and immobilized reactor	• Recovery of photo-catalyst is difficult • High recombination rate of electron and hole pair
Advanced Oxidation Process	• No consumption of chemicals • No sludge production • Fast degradation • Excellent reduction in Chemical and total oxygen demand	• High pressure and energy intensive process • Sensitive to pH of the solution • Low throughput and formation of by-products

Above mentioned processes are used in a particular sequence depending upon the need. Some are suitable for pre- and primary treatment whereas some are used for further treatment or grouped either under secondary and/or tertiary treatment. Most biological processes are secondary treatment processes. Tertiary treatment (or advanced treatment) includes mostly chemical and physical processes. The membrane based treatment processes are included under tertiary treatment processes. Basic information on membrane based processes is presented in the following sections.

1.3 MEMBRANE TECHNOLOGY

In recent decades membrane based separation processes have gained wide acceptability due to their several attractive features. These treatment processes have much smaller footprint than conventional treatment processes, permit easy scale-up, and provide high quality product. In view of these advantages membrane separation is preferred over conventional separation like gravity separation, coalescence, flocculation, coagulation technique (Otitoju et al., 2016). Simple operation, high efficiency, cost effectiveness, no harmful by-product formation, modular nature and easy to scale up, no phase change, and no need of chemical additives are their advantages (Kang and Cao 2014). In view of above mentioned advantages the membrane separation processes are currently being used on large scale in several industries such as water and wastewater treatment, product recovery, desalination (Safarpour et al., 2014), pharmaceutical industry (Zaviska et al., 2013), gas purification, etc. The research and developmental activity focussed on membranes also has increased steadily. According to Scopus as shown in Figure 1.3 over the past decade research and development activity related to use of membrane technology in the area of water and wastewater treatment alone has increased nearly 10 fold since 2008 (Abdullah et al., 2019). The figure clearly depicts that in early years of 2008 the number of publications related to membrane separation were less than 5000. However with passing of each year a steady increase in number of publication was observed and reaching to a value of 9000 in year 2018. This data clearly justifies that research activities in membrane area is increasing rapidly.

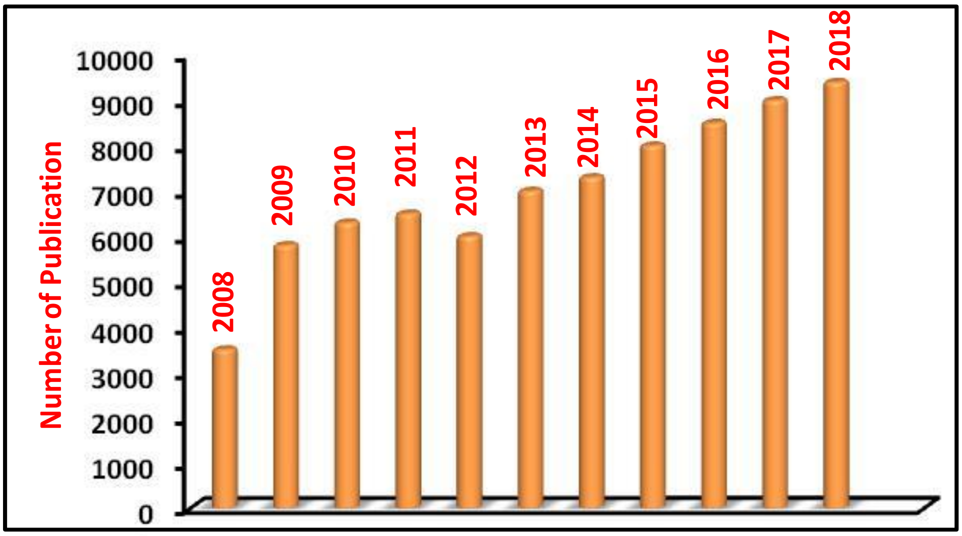

Figure 1.3: Number of publications from 2008-2018 on the membrane technology for wastewater treatment.

1.3.1 Membranes and Membrane Technology

For any membrane separation technology, membrane is the prime material that strongly affects process efficiency and its suitable application. Membrane is defined as a thin semi- permeable film that separates two phases and is selectively allows one component to pass through it. The basic principle for most of the membrane separation technique is selective filtration through pores of different sizes. Figure 1.4 depicts the separation performances of membranes based on the size ranges and operating pressure.

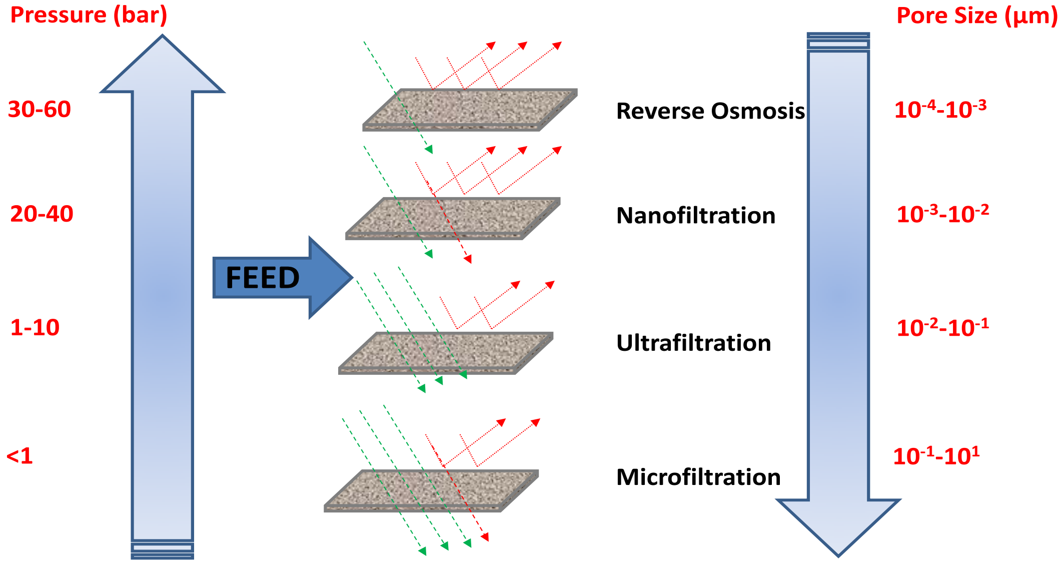

Figure 1.4: Membrane separation process classification based on their pore size and pressure.

Different pressure driven membrane separation process are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Better permeate flux can be achieved by using a well-designed membrane having high porosity and permeability. For industrial and commercial applications membrane should have high flux, high selectivity, high mechanical and thermal stability, antifouling property and low manufacturing cost.The principle parameter affecting the performance of membrane includes pore size, porosity, surface charge, degree of hydrophilicity, and flow rate

1.3.2 Mechanism of Membrane Separation

Membrane is a barrier that selectively allows certain constituents to pass through it, retaining others. The efficiency of membrane is defined by its flux and selectivity. A brief account of various removal mechanisms is given below:

Size exclusion or steric hindrance mechanism: The membrane pore size and target contaminants size control the mechanism. Generally, solutes smaller than the membrane surface pores will pass through while bigger size solutes will be retained on/above the membrane surface.

Donnan exclusion (charge–charge repulsion): It involves a non-sieving rejection mechanism. The repulsion between charged particle and membrane surface governs this mechanism. Solution pH is the important aspect for this mechanism to ensure maximum rejection (Maher et al., 2014)

Selective adsorption capability towards specific contaminants: In order to enhance the property of membrane, fillers are often added. Due to the presence of active functional groups these additives impart selective adsorptive characteristics to the membrane surface. In general, the adsorption of metal ions occurs in four steps: (1) Bulk diffusion of metal ions and penetration into membrane pores, (2) Surface complexation on the outer sites of adsorbents within the membrane structures (3) Transfer and adsorption of metal ions on the interface of adsorbent and (4) Equilibrium stage. Hence, the rate-controlling step is the chemisorptions on the sites of adsorbents and rate-limiting step is the transfer of metal ions onto the adsorbent interface (Abdullah et al., 2016).

Membranes made of inorganic and organic polymeric materials are widely used. Each have their own advantages and disadvantages. Inorganic membranes are known for their high chemical and thermal stability however their processing is very difficult and operating cost is very high. The polymeric membranes on other hand have low cost, easy and simple process of preparation, and good performance (Owlad et al., 2009).

However, polymeric membranes suffer from poor strength and fouling problem (foulant deposition over/on the membrane surface) that adversely affect the performance of membrane. This necessitates frequent cleaning and and/or replacement of membranes (Li et al., 2017). To overcome these drawbacks it has become crucially important to fabricate multifunctional membranes with excellent flux and anti-fouling property in order to enhance the efficiency as well as ensure cheaper and safe reclamation of water.

The another major drawback related to the use of membrane technology in wastewater treatment is the generation of retentate (reject) that is highly concentrated hence additional step/ process is required to treat it before discarding into the environment thus adding to the total cost of treatment. A possible solution to overcome these drawbacks is the surface modifications to produce membranes with low fouling behavior and high flux. The modification of polymeric membranes to improve its properties involves ultraviolet irradiation (Pieracci et al., 2002), blending with hydrophilic materials (Wilhelm et al., 2002), graft polymerization (Kim et al., 1999), and plasma graft (Steen et al., 2002). At the same time it must be remembered here that the surface modifications not only damages the membrane structure but significantly deteriorates the rejection and mechanical properties. Use of filler is another way to improve the membranes performance without damaging the membrane structure. However use of traditional fillers like calcium carbonate, talc, mica, silica, and alumina need to be loaded in larger amount to get prominently improved performance (Chrissafisa and Bikiaris, 2011) which again increases the processing cost. To overcome these problems, the traditional fillers are now being replaced by nano fillers as they are easily miscible with polymer and are capable of overcoming the limitations of conventional fillers. Membranes embedded with nano-particles are termed as "nanocomposite membrane". Property of nano-composite membranes are considerably different from those of the normal pure polymeric membranes.

1.3.3 Nanocomposite membranes

Nanocomposite membranes are prepared by incorporating nanoparticles into porous polymeric or inorganic membranes (Zang et al., 2013; Liu et al., 2011). Nanoparticles can be defined as a particles having size less than 100 nm. Nano-sized material are gaining interest in several fields of research because of their unique properties i.e. large surface area per unit volume and appreciably improved like catalytic activity, mechanical strength, conductivity, thermal stability and antibacterial property compared to those for bulk material (Cuenya 2010, Palza 2015).

Nanocomposite membranes can be classified as matrix and thin film nano-composite membranes. The matrix nano-composite membrane are synthesized by dispersing the nano-particles into polymer solution before the casting of membrane whereas in thin film nano composite membranes self-assembly of nanoparticles is carried out onto the surface and pores of the membrane using dip coating process (Jainesh and Murthy, 2016). Different techniques for the synthesis of membrane include conventional techniques such as phase inversion: non-solvent induced phase separation (NIPS) process and thermally induced phase separation (TIPS) (Liu et al., 2011), interfacial polymerization, electro spinning, stretching and track-etching (Otitoju et al., 2016), vapor induced phase separation (VIPS), evaporation-induced phase separation (EIPS) (Kochkodan, 2013), and solution casting.

The nanocomposite membranes are considered as excellent alternative for getting over the problems associated with the normal polymeric membranes. The addition of NPs changes their surface properties affecting the separation efficiency, flux, rejection against foulant and induces antifouling property. Also it is well known fact that a trade-off-effect exists between permeability and flux but use of nano-composite membranes could eliminate this issue because presence of particles affects the polymer cross-linking and provides adequate pathways to solvent rather than solute. The addition of NPs has resulted in the development of new characteristics like photo-catalysis through the presence of NPs (semiconductor material) that is not observed in the traditional membranes.

1.4 DEGRADATION AND SEPARATION OF HEAVY METALS USING NANO-COMPOSITE MEMBRANES

Heavy metals are considered as the most harmful pollutants as they are dangerous to humans. They are defined as the elements having atomic weights between 50.5 and 200.6 and a density > 5 g per cubic centimetre (Barid, 1995).

1.4.1 Chromium and its removal

Chromium, a highly toxic heavy metal exists in two valence states trivalent Cr (III) and hexavalent chromium [Cr (VI)]. Cr (III) is an essential element and is necessary for glucose metabolism in human body and is comparatively less toxic than Cr (VI). The major target organ of human body is the respiratory tract that is adversely affected by Cr (VI). Short term exposure to Cr (VI) leads to acute whereas and its long term exposure leads to chronic effects. It was well established that inhaled chromium (VI) is carcinogenic to both humans and animals (Lunk, 2015). Thus its removal and/or conversion to Cr (III) form is done to reduce its level below the permissible limit.

(a) Sources of chromium in wastewater

Several industrial activities generate large volumes of wastewater bearing appreciable amount of Cr(VI). A few typical examples are listed below:

- Steel and alloys,

- Chrome plating,
- Leather and wood preservation- Cr(VI) salts due to their toxicity used for preservation of wood (e.g. ‘Chromated Copper Arsenate’ (CCA) to protect timber from fungal decay)
- Foundry (refractory materials): high heat resistivity and high melting point makes it suitable for refractory applications for e.g. blast furnaces, cement kilns
- Leather tanning- chrome tanning of leather
- As catalysts for processing of hydrocarbons.
- As corrosion preventing agent.

(b) Health Effects of Chromium

Hexavalent chromium (Cr (VI)) is much more toxic than chromium (III), for both acute and chronic exposures. Some of the adverse health effects of Cr (VI) are listed below:

- Chromium (III) is an essential element in humans metabolism and 50 to 200 μg/d intake of Cr(III) is recommended for adults.
- The inhalation exposure of Cr(VI) results in shortness of breath, coughing, and wheezing at a very high concentrations of chromium trioxide.
- Very high concentrations of Cr(VI) cause gastrointestinal problems and abdominal pain, vomiting, and hemorrhage and neurological problems. Chromium (VI) exposure in humans affects the respiratory tract that may lead to perforations and ulcerations of the septum, bronchitis, asthma, and nasal itching.
- Exposure to high levels of Cr (VI) by inhalation or oral intake affects liver, kidney, gastrointestinal and immune systems

The maximum permissible limit according to World Health Organization (WHO) in surface and potable waters is 0.1 ppm and 0.05 ppm respectively (Kazemiet al., 2018).

Among different treatment technologies, membrane technology integrated with photo-catalytic reduction is an efficient and environment-friendly method because it not only removes Cr (VI) ions from water but also reduces it to non-toxic form Cr(III). Therefore in this work focus was on the development of a membrane-TiO_2 due to following reasons. Firstly, no additional chemical requirement promotes recycle of water back to the process. Secondly high selectivity makes membrane technology very attractive for the separation of Cr (VI) from wastewater.

Thus in the present work an attempt has been made to integrate membrane separation with photo-catalysis to overcome the problem of poor reusability of powdered photo-catalyst as well as reduce the problem associated with poor performance of membrane. The proposed treatment scheme is shown in Figure 1.5.

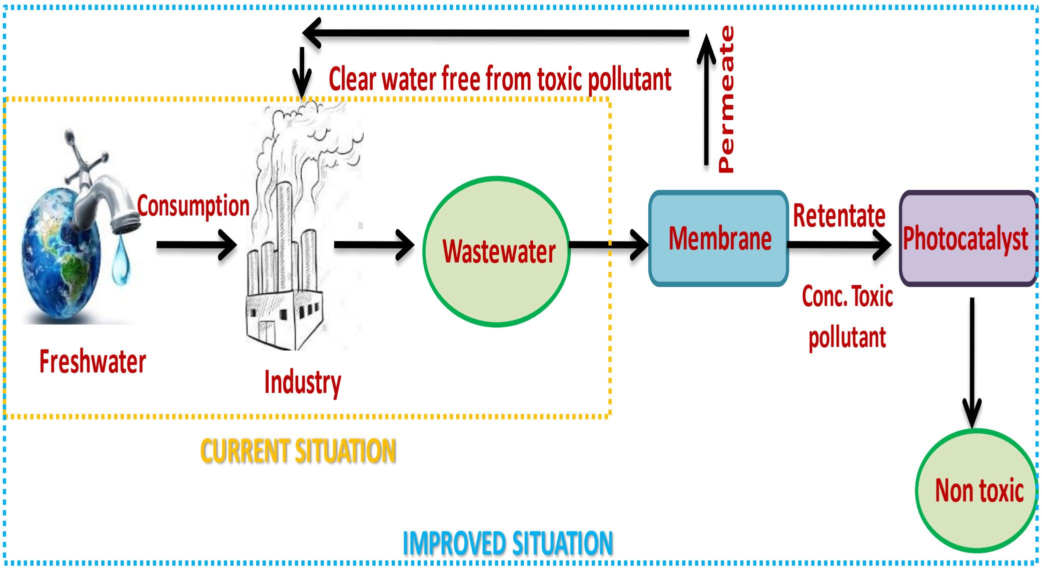

Figure 1.5: Current and proposed treatment method for removal of heavy metal

The concept of heavy metal removal using membrane-based method was started earlier in the 1970s when Bhattacharyya et al. (1978) reported a study on charged ultrafiltration (UF) membrane for the treatment of electroplating water containing ions such as Cu(II), Ni(II), and Zn(II) based on Donnan exclusion mechanism.

Photocatalyst

Use of nanoparticles (semiconductor) dominated photo-catalytic research. Photo-catalysis is defined as excitation of electron from the valence band to the conduction band in a semiconductor in presence of a light. The electrons generated during the reaction will be involved in the photoreduction of Cr (VI) (Fraile et al., 2017).

1.5 BROAD OBJECTIVES OF PRESENT WORK:

In view of the possible advantages of nanoparticle embedded membranes and photo-catalytic activity of TiO_2 the present work has been with following broad objectives in mind-

- Synthesize nano-TiO_2 particles using a green route and use it to prepare PVDF-TiO_2 nano-particles composite membranes,
- Evaluate anti-bacterial, antifouling, and catalytic behaviour of the prepared membranes.
- Efficacy of prepared membranes in removing chromium from synthetic and industrial wastewaters.

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