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Mechanism of nanofibres on removal of water pollutants - A review

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Water is polluted by the effluents discharged from various industries and some of the pollutants are acids, dyes, heavy metals and nanoparticles. The polluted water bodies lead to the lack of safe drinking water. Hence an efficient method is required to remove the pollutants from the wastewater. Membrane technology is an emerging technology used for water treatment. Among the various membrane fabrication techniques, electrospinning gained popularity because of its large surface area to volume ratio and high porosity. Many polymeric nanofibre membranes have been prepared by using electrospinning technique. Electrospun nanofibre membranes have been extensively studied for the removal of hazardous pollutants from the wastewater. This review paper tells how the electrospinning works to produce nanofibres from polymeric solution, in what ways these polymeric electrospun nanofibre membranes are modified and by which mechanism the electrospun polymeric nanofibre membranes removes or degrades the pollutants from the water.

Keywords : Adsorption, Membrane, Nanofibres, Photocatalytic process, Water pollutants

Water is the basic need for life on earth. An enormous amount of water is utilized for both industrial and domestic purposes. After utilization, the quality of the water degrades and thus generated water named as "wastewater". Wastewaters are produced from many industries such as textile, tannery, pharmaceutical, petroleum industries with various categories of pollutants. Common pollutants found in wastewater are biodegradable, volatile, and recalcitrant organic compounds, suspended solids, toxic metals, dyes, microbial pathogens, and parasites[1]. These environmental pollutants emancipated from a variety of industries are highly toxic and can cause harm to living organisms and the environment[2]. Lack of safe and clean drinking water is due to effluents discharged from many industries. The worldwide developments in industries, urbanization and frequent droughts are led to the following factors such as a great challenge in supplying clean and safe water for consumption, huge quantity of wastewater release into water resources without any treatment and water scarcity. Before discharging the wastewater, it must be treated in order to remove pollutants. Recycle or reuse of the treated water is very much appreciable, as nowadays industries are much concerned about the implementation of zero liquid discharge[3-10]. Due to all these strategies, a variety of highly effective technologies for treating wastewater is developed.

Membrane technology

A number of wastewater treatment technologies are developed and those technologies are categorized into three as physical, chemical and biological methods. Figure 1 represents the various treatment methods that are available for the treatment of wastewater[11].

Among the existing technologies, membrane technologies have gained popularity over the last few decades due to their higher efficiencies, low costs and easy operation. Membrane technology is an emerging

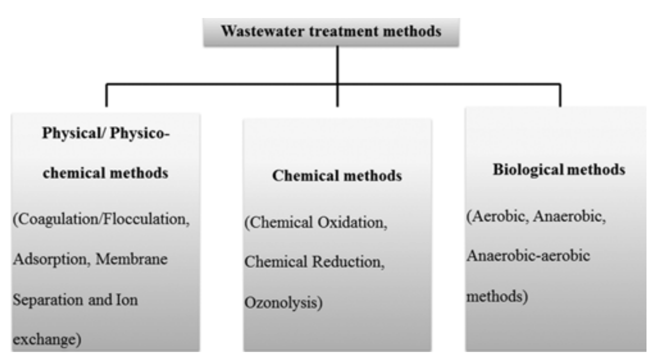

Fig. 1 — Classification of wastewater treatment methods

technology which possesses numerous applications in wastewater treatment. A membrane acts as a barrier between two phases which selectively allows particles, substances, matter from one side to the other[12]. Membranes can be classified as microfiltration, ultrafiltration, nanofiltration, reverse osmosis and membrane distillation based on pore size[13]. Microfiltration membranes can separate particles between 0.1-10 μm whereas Ultrafiltration membranes can separate particles between 0.001 and 0.1 μm in size [14]. Nanofiltration membranes have a pore size of 1-10 Å[15] and Reverse osmosis is used extensively in desalination. The above mentioned membrane processes are pressure driven process. As the pore size decreases pressure applied to the membrane increases. Thus, reverse osmosis membrane is driven at high applied pressure whereas microfiltration membranes with low applied pressure. Membrane distillation is a process driven thermally where the membrane allows only vapour to pass through its pores and retain water on one side. Membrane distillation membranes should be hydrophobic, porous and mechanically stable[16-18].

Membrane fabrication methods

Most commonly used methods to fabricate membranes are electrospinning, phase inversion, interfacial polymerization, stretching and track-etching. In phase inversion, a polymer solution is converted from a liquid to solid state in a controlled manner. A polymeric membrane will be formed by interfacial polymerization when two reactive monomers dissolved in immiscible solvents, the monomers diffuse at the interface and polymerizes. In stretching, a polymer solution is heated above its melting point and extruded as a thin sheet. These extruded thin sheets are stretched to introduce holes. Track etching is a process in which linearly damaged tracks are formed across the polymeric film when the polymeric film isirradiated with energetic heavy ions. Among these techniques, recently electrospinning technique gained an attention to prepare membranes[14]. Figure 2 represents the methods of membrane fabrication such as phase inversion, interfacial polymerization, stretching and track-etching.

Electrospinning

Electrospinning is a simple, efficient, versatile and cost effective process used to fabricate one dimensional nanofibre in the form of non-woven structure with diameters ranging from tens of nanometers to a few micrometers[19-22]. Electrospun nanofibrous material exhibits numerous excellent characteristics such as large surface area to volume

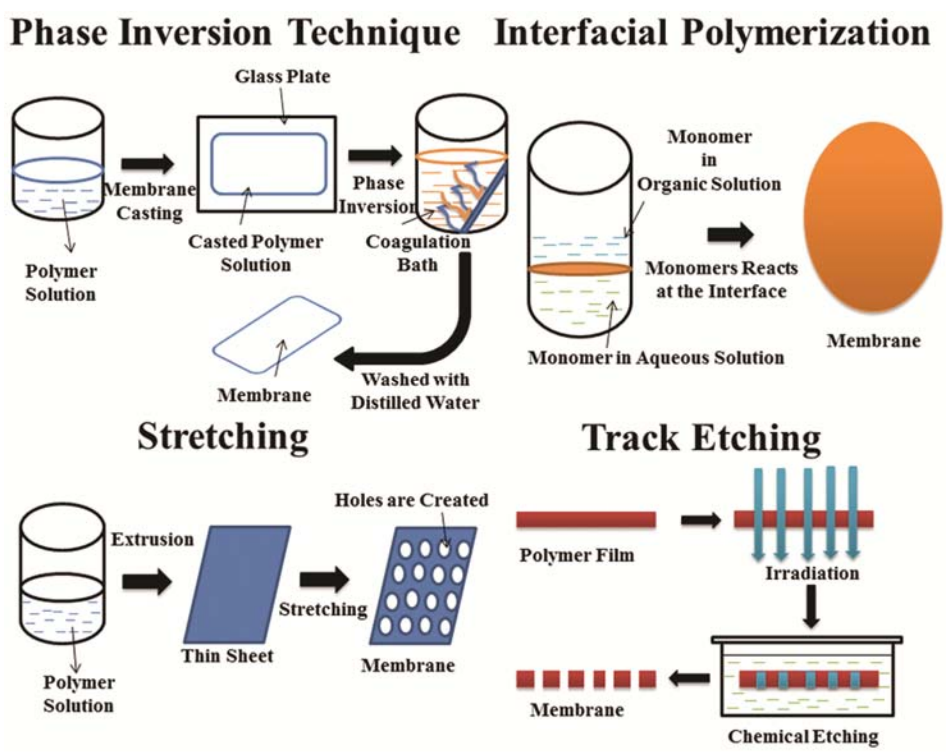

Fig. 2 — Membrane fabrication techniques

ratio, high porosity, an amazing flexibility and good enrichment ability for organic compounds[23-27]. A typical electrospinning set up comprises of three basic components includes syringe pump, high voltage power supply and collector. The syringe pump is filled with the polymer solution which is to be fabricated as nanofibres. A charge is developed when an electrical potential is applied between droplets of a polymer solution held at the end of a needle tip and a grounded target, it develops a charge to the polymer solution. This electrical potential is increased further for the formation of Taylor cone[28]. Thus applied electrical potential overcomes the surface tension of the polymer solution; a jet is ejected from the tip of the Taylor cone. The charged jet undergoes bending instability leads to the formation of randomly oriented nanofibres[29]that deposited on a collector. A simple electrospinning unit is shown in Fig. 3.

The morphological structure and efficiency of electrospun nanofibres depends on many parameters which are categorized as solution, system, process and ambient parameters[25,14].

Solution parameters: solution concentration, solution viscosity, surface tension, electrical and thermal conductivity and dielectric constant[30].

System parameters: Molecular weight and molecular weight distribution of polymers and architecture of polymers such as linear, branched or block polymers.

Process parameters: Applied voltage, rate of flow, needle diameter, tip to collector distance, type of collector and rotational speed of collector.

Ambient parameters: Temperature, humidity and air velocity in spinning chamber[20,14].

Electrospinning process can also be adopted for hollow nanofibre synthesis by two ways includes co-axial electrospinning and single nozzle co-electrospinning. In co-axial electrospinning, two coaxial capillaries in a spinneret containing different solutions are used to produce core-shell composite fibers. The core fibers are removed by extraction or calcinations at high temperature in order to obtain a hollow fibers[20,31]. Single nozzle co-electrospinning involves the formation of core shell composite when phase separation happens between two immiscible polymers dissolved in the solvent during electrospinning. Hollow fibers are obtained after removing the core[32,33]. Composite mats can be constructed by electrospinning a polymer solution mixed with nanoparticles to provide additional functionalities[34]. In multi-nozzle electrospinning, different combinations of polymeric nanofibres are fabricated into one hybrid mat[35]. This technique combines the properties of different polymers to provide a synergistic property effect on the hybrid mat[36].

One of the most interesting feature of electrospinning technique is the tailoring a new class of membranes that possesses extensive applications[37]. Electrospun nanofibres found innumerable applications in water purification, wound dressing, tissue engineering, drug delivery, biomedical engineering, protective clothing, catalysis reactions, sensors and energy[38–55]. Low density and interconnected open pore structure of non-wovennanofibre membranes made them as a good candidate for filtration applications[30,56-59] such as microfiltration[60], ultrafiltration[61], nanofiltration[62]and reverse osmosis[63]. Low compaction resistance of the electrospun nanofibre membrane is the major disadvantage because low compaction resistance may result in lower hydraulic permeabilities at high pressure[64].

Applications of electrospunnanofibres

Electrospun nanofibres are used extensively in various fields for different applications. In this review paper, we have demonstrated how an electrospunnanofibre can be modified and used for a particular application. And also explained the mechanism on which electrospun fibers and modified electrospunnanofibres works to remove, recover and degrade the pollutants that are present in the water. When it comes to water pollution, the wastewater contains various chemical compositions.

Among which certain chemicals are costly and hence it has to be recovered and reused in the process. And some other chemicals are highly hazardous hence it has to be removed and degraded in order to save the life on

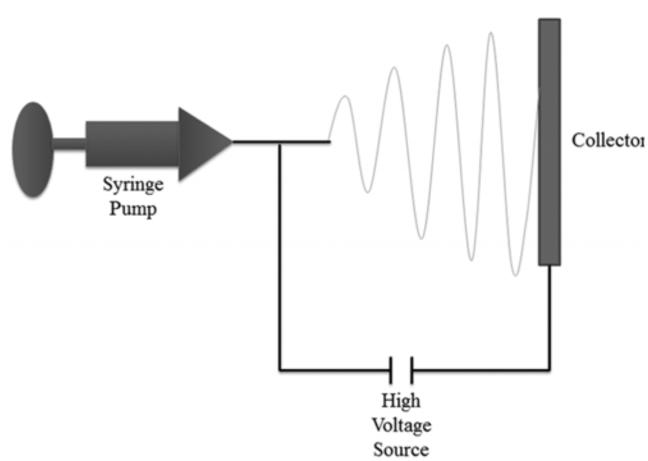

Fig. 3 — A simple electrospinning set up

the earth and the environment. Electrospunnanofibres and modified electrospunnanofibres uses various mechanisms to recover, remove and degrade various pollutants from the water will be explained in detail (Fig. 4).

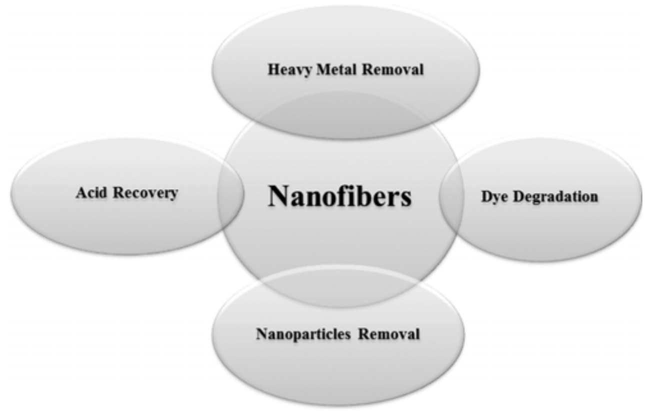

Fig. 4 — Applications of nanofibres in wastewater treatment

Modifications of Electrospun Polymeric nanofibres and their mechanisms

Nanofibres made from the polymeric solution by electrospinning are as prepared electrospun polymeric nanofibre membranes without any modification. These as prepared electrospun polymeric nanofibre membranes can be used to remove the pollutants from the wastewater by adsorption process. The pollutants are adsorbed onto/into the as prepared electrospun polymeric nanofibre membranes due to their high surface to volume ratio and porosity but lacks specificity. Hence the surface of the electrospun polymeric nanofibre membranes can be modified to adsorp a particular pollutant thus promotes selectivity of the adsorbent. The surface of the electrospun polymeric nanofibre membranes can be modified by plasma treatment, wet chemical methods, irradiation and chemical surface functionalization. These methods introduce a functional group onto the surface of the electrospun polymeric nanofibres to which the specific pollutant binds and thus removed from the wastewater whereas in the case of diffusion dialysis, a cationic charge is introduced on the surface of anion exchange membrane. The other way to modify the membranes for the degradation of pollutants is incorporating the material into the electrospun polymeric nanofibres which is capable to degrade the pollutants present in the water.

Diffusion Dialysis Mechanism

Recovery of acids used in a variety of industries is essential since the acids are expensive. Acids from the wastewater are separated by the process called diffusion dialysis[65]. Diffusion dialysis is the membrane process based on ion exchange in which the driving force is concentration gradient between the two liquids. Anion exchange membranes are a positively charged polymeric membrane which is used for recovery of acids from the wastewater[66-68]. The mechanism of the process is given in Fig. 5.

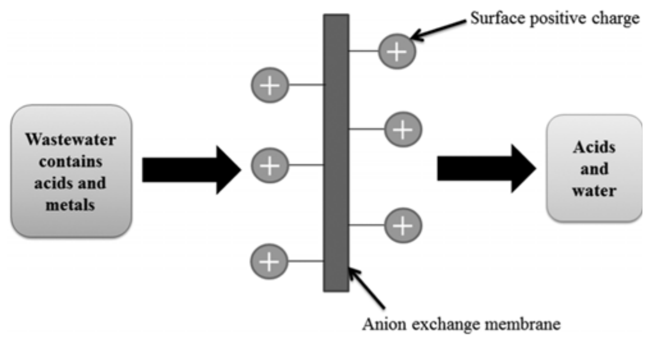

Fig. 5 — Mechanism of Diffusion dialysis for the recovery of acids from wastewater

The wastewater contains an acid and the metals which are fed from one side of the membrane and the other side of the membrane is fed with water. The anions pass through the membrane whereas the cations are not allowed to pass since they are positively charged ions but the exceptional cation is hydrogen because of its smaller size. Thus the acids are separated from the wastewater. Consider the following equation as an example in which hydrochloric acid is used

$$H^+Cl^- + \mathrm{Metal} \rightarrow H^+Cl^- + H_2O$$

In which hydrochloric acid and metals are present in the wastewater are passed through the membrane, as it passes the hydrochloric acids are allowed through the membrane whereas the metals are repelled due to the positive charge of an anion exchange membrane. Thus the acids are recovered from the metals and used back in the process.

Adsorption process

Two major pollutants to be removed from wastewater are nanoparticles and heavy metals. Researchers are highly concentrating on the removal of nanoparticles and heavy metals. Nanoparticles are the particles in the size range between 0 to 100 nm

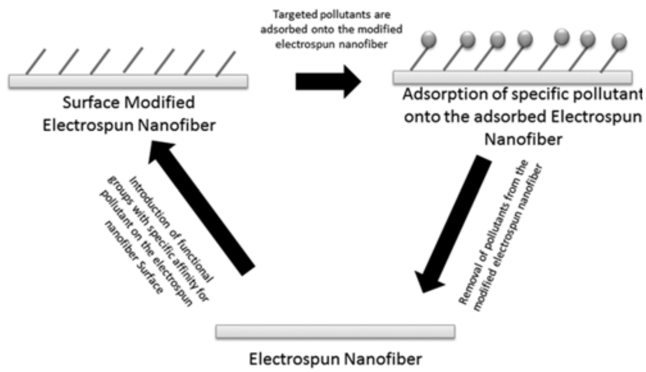

Fig. 6 — Illustration of adsorption of pollutants onto the electrospun nanofibres

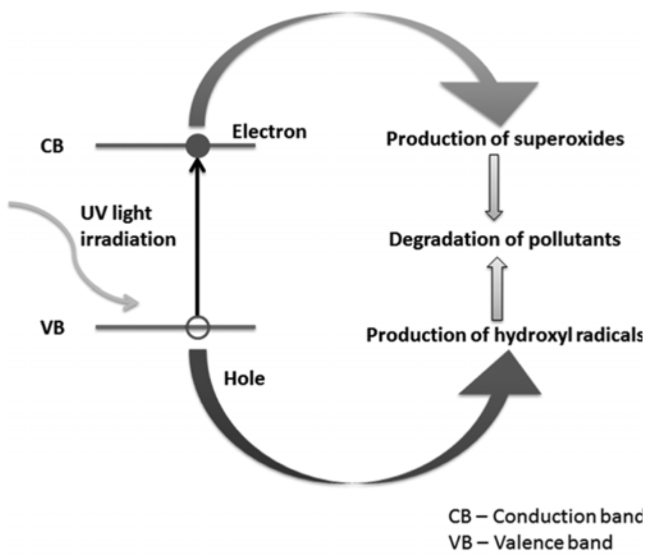

Fig. 7 — Photocatalytic mechanism of TiO_2

and exhibits high surface area to volume ratio, unique optical, thermal, mechanical and electrical properties. Hence the nanomaterials are used for the removal of heavy metals from the water and also nanoparticles are extensively used in medical, pharmaceutical, food and cosmetic industries. After employing the nanoparticles in the different applications, they turn out to be another source of pollution which may cause serious health problems due to their accumulation in the specified organs[69-77]. Hence it's a highly challenging task to remove nanoparticles from the wastewater.

Nanoparticles and heavy metals are removed from the wastewater by adsorption. Adsorption is the process in which adsorbate is adsorbed onto the surface of adsorbent, here adsorbate is the pollutant. Adsorption is basically divided into two types which are physical adsorption or physisorption and chemical adsorption or chemisorption. Physical adsorption are multilayer adsorption process occurs by van der waals attraction, hence they are reversible in nature whereas chemical adsorption are monolayer adsorption process occurs by chemical bonding, hence they are irreversible in nature. Adsorbate and adsorbent are made to contact with each other for a period of time, so that equilibrium is attained. This equilibrium condition is known as adsorption isotherm. The most commonly studied adsorption isotherms are Langmuir isotherm and Freundlich isotherm where Langmuir isotherm describes monolayer adsorption with no interaction between the adsorbates and Freundlich isotherm describes heterogeneous surfaces. Adsorption process occurs at four steps as given in Fig. 6. They are

1. Adsorbate in the wastewater transfers to the surface film of the adsorbent.
2. From the surface film of the adsorbent, the adsorbate transfers to the exterior surface of the adsorbent.
3. From the exterior surface of the adsorbent, adsorbate diffuses into the adsorbent. This is the rate limiting step.
4. Then the interaction between the adsorbate and adsorbent occurs via physical adsorption or chemical adsorption.

Advantages of adsorption are cost effective, higher efficiency and easy regeneration. The main disadvantage is the separation of adsorbent from the water after the adsorption of adsorbate into the adsorbent. If the adsorbent is in powder form then it's highly difficult to separate the adsorbent from the water. To overcome this disadvantage, electrospun nanofibres are used from which adsorbents are easily separated from the water without affecting the other advantages of adsorption process. To remove a specific pollutant from the wastewater, the surface of the electrospun nanofibre should be modified by incorporating a particular functional group that gives rise to functional electrospun nanofibres.

Photocatalytic process

Dyes are chemical compounds that are used to impart colour to various materials. Many industries such as dyestuffs textile, additives, paper and plastics, foodstuffs, laser materials, leather, etc. are generating colored wastewater that are highly toxic, carcinogenic, mutagenic even at very low concentration. Annually, approximately 0.7 million tons of dyes are generated across the globe and 10-15% of which are discharged into water bodies. Among the dyes, Azo dyes contain N=N and are extremely challenging to degrade them into harmless products. Hence removal of dyes from the wastewater is crucial to preserve living organisms and the environment[78-90].

Electrospun nanofibre degrades a pollutant by incorporating the photocatalyst into a polymer solution. Photocatalysts are the materials which accelerate the photoreaction. Most widely used photocatalytic materials are semiconductors due to their band gap, capability to produce electron and hole pairs, easy availability and low cost. When an UV light is irradiated, the photocatalyst incorporated in the electrospun nanofibres are excited, thus creates electron and hole pairs. An electron in the conduction band reacts with oxygen in the atmosphere to produce superoxides which are further reduced to produce hydroxyl radicals whereas a hole in the valence band reacts with the water molecules to produce hydroxyl ions. Thus produced hydroxyl ions react with the pollutant and degrade them into harmless products. There are two types of reaction takes place such as reduction and oxidation. Reduction reaction occurs at the electron in the conduction band whereas oxidation reaction occurs at the hole in the valence band as shown in Fig. 7. The reactions are as follows

$$\text{Electrospun nanofibre incorporated with photocatalyst} + \text{UV light irradiation} \rightarrow \text{Elecron (CB)} + \text{Hole (VB)}$$

$$\text{Electron} + O_2 \rightarrow \text{Superoxides (Reduction reaction)}$$

$$\text{Hole} + H_2O \rightarrow \text{Hydroxyl ions (Oxidation reaction)}$$

The advantage of incorporating photocatalyst in nanofibres offers easy recovery of photocatalyst and lack of leaching when compared to the process which uses bare photocatalyst in degradation process.

Conclusion

Electrospun nanofibrous membranes (ENM) have been used extensively for the removal of environmental pollutants due to its advantages such as large surface area, porosity, ease of fabrication. Efforts have been made to improve the pollutant removal efficiency of the electrospun nanofibrous membrane by modification of its properties. This modification was generally done by mixing two or more polymers, incorporating a material into a polymer solution, plasma treatment, wet chemical methods, irradiation etc and thus gives rise to functional electrospun nanofibers. All the modified and bare electrospun nanofibres remove the pollutants such as acids, dyes, heavymetals and nanoparticles by using any of the following processes (i) diffusion dialysis (ii) adsorption and (iii) photocatalytic processes. Therefore the functional electrospun nanofibrous membranes are used as a best pollutant removal membrane but the repeated usage of electrospun nanofibrous membrane is very limited. Hence new functional electrospun nanofibrous membranes have to be prepared with a maximum number of repeated usages without affecting its pollutant removal efficiency. This increased repeated usages and improved efficiency will improve the life span of the membrane.

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