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Role of Nanomaterials on the Removal of Pollutants from Water

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Abstract: ***Availability of pollutant free drinking water is a major concern in the present era. Rapid industrialization, urbanization and developments in agricultural sector have led to incorporation of various toxic as well as nanosized pollutants into the water bodies. The pollutants can vary from heavy metals to organic dyes along with various hazardous chemicals. Hence introduction of efficient techniques and their timely implementation is the need of the hour for treatment of wastewater. Nanofibres have been used in membrane technology for the purification of waste water. The technique of electro spinning has been in recent trends for the fabrication of effective membrane system. This review paper focuses on the use of electro spinning, modification of electrospunnanofibre membranes and their role in removal or degradation of pollutants from water.***

Keywords: Adsorption, Dye removal, Electrospinning, Membrane, Nanocomposite, Water, Pollutants

1. Introduction

Over the years, the global demand of water has surpassed the available supply of water[1, 2]. This has led to water scarcity on a global level. A large amount of water is put to domestic as well as industrial usage on daily basis. The quality of water post utilization becomes very degraded and unsafe for drinking purpose, which generates huge amount of wastewater. The wastewater is a composition of numerous pollutants varying in chemical and physical properties. Some common pollutants are volatile, biodegradable organic compounds, dyes, microbial pathogens, toxic heavy metals and suspended solids[3]. These contaminants are highly toxic and can cause irreversible damages to the ecosystem in long run[4]. The contamination is a result of uncontrolled discharge of effluents from various industrial and domestic sectors into the water bodies. Further the toxicities of nanomaterial pollutants on living organisms have been a topic of interest for researchers over the last many years[5]. One of the examples include the effect of carbon nanotubes on animals which results into granulomas in their lungs[6, 7]. Lack of safe and clean water is a major challenge today. The water must be treated before hand and recycle or reuse should be appreciated for the implementation of zero liquid discharge in the industrial sector.[8-15]. To avoid unfavorable repercussions, several technologies have been developed for the treatment of waste waters. Classification of technologies includes physical, chemical as well as some biological methods as stated in Table 1[16.]

Table 1: Methods for treatment of waste water

1	**Physical**	Coagulation, Adsorption, Membrane separation
2	**Chemical**	Oxidation, Reduction, Ozonolysis
3	**Biological**	Aerobic, Anaerobic

Out of all the recent developments, advancement in the membrane technologies have been quite notable and has managed to be an effective method in treating polluted water.

Membrane technology

A membrane is a selectively permeable barrier that allows movement of particles through it[17.] The process of passage is pressure driven. Depending on the pore size, classification of membranes can be done into microfiltration, ultrafiltration, nanofiltration, reverse osmosis[18]. Table 2 shows the specific pore size and uses of this membranes[19-20].

Table 2: Membranes and their pore size

	Membranes	Pore size	Uses
1	**Microfiltration**	0.1	Separates various microorganisms and other waste
2	**Ultrafiltration**	0.01	Separates larger particles and some viruses
3	**Nanofiltration**	0.001	Used to soften hard water, removes divalent ions
4	**Reverse osmosis**	0.0001	Removes all organic molecules, viruses, desalinates water

The applied pressure on the membrane is inversely proportional to size of pores present in a specific membrane system. This is the reason why reverse osmosis occurs at high pressure unlike microfiltration. Figure 1 shows the selectivity of membranes. Some membranes allow only vapours to pass, as a result of which water gets retained on the other side. This process is called membrane distillation. Such membranes are highly porus, hydrophobic and show high mechanical stability[21-23].

Fabrication techniques

Membrane fabrication plays a vital role in dictating the efficiency as well as the cost effectiveness of a pressure driven membrane system. To fabricate a membrane, methods like phase inversion, electrospinning, interfacial polymerization, and track-etching can be used depending on the type of system to be fabricated. Figure 2 gives a diagrammatic representation of the methods of fabrication. Out of these four, the technique of electrospinning has been in recent trends over the past few years as it results in availability of larger surface area and the product can be used under various conditions[24]. When a polymeric film is irradiated with energetic heavy ions, linearly damaged tracks are formed which is called Track-etching. Similarly the process of interfacial polymerizations deals with two reactive monomers present in immiscible solvents. Another process includes conversion of liquid phase to solid state. The process is called phase inversion and occurs under controlled conditions.

Electrospinning

It is a membrane fabrication process in which the polymer melt under the effect of electrical force gives out non-woven nanofibres having diameter in order of some hundred nanometers to few micrometers[25-27]. The method is relatively easy and has versatility along with cheaper costs of manufacture[28].

Materials which undergo electrospinning show specific characteristics such as high porosity, amazing flexibility, and larger surface area for greater degree of adsorption[29-33]. The technique comprises of three basic components which work together as one system: a syringe pump forming the polymer melt, high voltage power supply to draw out the polymer melt into nanofibres a collector to accumulate the nonwoven fibres. Figure 3 gives representation of an electrospinning unit. The electrical potential applied across the drop held by the needle tip and the collector results into formation of Taylor cone[34]. This in turn ejects a charged jet which undergoes bending and apparently forms randomly oriented nanofibres[35].

The nanofibres produced by electrospinning can vary in shape, structures and even efficiency depending upon some parameters. Solutions, system processes, and ambient parameters are categorized as important parameters for studying the morphology and predicting the performance of nanofibres[31, 19].

Table 3: Parameters for performance of nanofibres

1	**System**	Molecular Weight and molecular weight distribution of polymers (branched, linear)
2	**Solution**	Solution concentration, solution viscosity, electrical and thermal conductivity, surface tension
3	**Process**	Rate of flow, distance between tip and collector, type of collector, needle diameter, applied voltage
4	**Ambient**	Temperature, humidity, air velocity in spinning chambers

Synthesis of hollow nanofibre can also be obtained by electrospinning. The process includes co-axial and single nozzle co-axial electrospinning. In order to obtain a hollow fibre the core fibrous part is removed by calcinations or extraction at higher temperature[37-39]. Further to produce composite mats, a polymer solution mixed with a defined amount of nanoparticles can be electrospun which can provide additional functionalities[40]. For varying combinations of polymeric nanofibres, muti-nozzle technique of electrospinning can be used as a result of which one hybrid mat is obtained[41].

Membranes produced as a result of electrospinning have extensive applications in tissue engineering, water purification, drug delivery, wound dressing, biomedical engineering, sensors and various energy applications[42-60]. Major advantage of electrospunfibre is the relatively lower density and interlinked pore structure which makes them available for numerous filtration[61-64] processes like microfiltration[65], ultrafiltration[66], reverse osmosis[67] and nanofiltration[68]. Many a times lower hydraulic permeabilities higher pressure can prove to be a major disadvantage[69]. This is actually because of the low compact resistance present in the fibres obtained from electrospinning.

Applications of electrospinning

Fibres obtained from electrospinning finds use in variety of fields. In case of water purification the nanofibres are used according to specifically defined mechanisms along with certain modifications, if required. This review focuses on the use of electrospunnanofibres to remove, reuse, recover and degrade the contaminants through various processes like adsorption, dialysis through diffusion and other dye removal methods.

In order to remove pollutants from water, it is very important to understand the class of pollutant present in the sample. Some pollutants might be certain costly chemicals which should be recovered where as others might be hazardous chemicals or organic dyes that need proper degradation to keep up the good quality of ecosystem. Specific application of waste water purification includes heavy metal removal, acid recovery, degradation of dyes and removal of nanoparticles.

Modifications in membranes

Nanofibres produced by electrospinning are molded into membranes which can be used for purification purposes through adsorption. Pollutants can be captured onto the surface of nanofibres in appreciable quantity as they provide larger surface areas and high porosity but at the same time may lack selectivity. These membranes can be made selectively permeable by certain modifications when dealing with a specific class of pollutants. Some effective methods to modify the surfaces of such membranes are plasma treatment, irradiation, wet chemical methods and functionalization of surfaces.

The basic aim of such modifications is to add functional groups on the surface of nanofibres which increases the adsorption capacity and results into selective binding of pollutants with the membranes and hence can be removed selectively.

Table 4: Examples of modifications with experimental results

Sr. no	Modified material	Pollutant removed	Adsorption capacity	Reference
1	Rhodanine/ploymethylmethacrylate	Ag^{+}	125.7 mg/m^2	Lee et al (2013)
2	Rhodanine/PMMA	Pb^{+2}	140.2 mg/m^2	Lee et al (2013)
3	PVA/imino-acetic acid	Cu^{+2}	101.28 mg/g	Yang et al (2017)
4	Vinyl-modified mesoporous (poly9acrylic acid)/SiO_2	Malachite green	240.49 mg/g	Xu et al (2012)
5	Mesoporous polyvinyl pyrrolidone (PVP)/SiO_2	Cr^{+3}	97 mg/g	Taha et al (2012)

Adsorption

It is a process which involves binding of adsorbate molecules onto the surface of adsorbent. It is often referred to as a surface phenomenon and plays vital role in removal of pollutants from wastewater. It is endothermic in nature. Two major classes of pollutants which have been a matter of concern for the scientists over the past few years are heavy metals and nanoparticles. Various dyes and acids are also removed from water with the help of adsorption.

Nanopartciles finds major applications in food, medical, cosmetic and pharmaceutical industries but unfortunately, post usage they themselves serve as a major source behind water pollution and may lead to health issues and environmental degradation[70-78]. So adsorption is used preferably to remove such impurities from wastewater. Adsorption can be mainly classified into two types based on the type of interaction between adsorbate and adsorbent. When the adsorption occurs as a result of van der waals forces, it is called as physical adsorption or physiosorption. Whereas when adsorbate binds to the adsorbent as a result of any chemical bonding, its is termed as chemisorption. Physiosorption is multilayer process and reversible in nature whereas chemisorptions is monolayer and irreversible in nature.

To understand the nanoparticle and nanofibre interaction at equilibrium, two models are studied which are Freundlich isotherm[79] and Langmuir isotherm[80]. Usually, the Langmuir isotherm is used in the case of monolayer adsorption assuming no interaction in between adsorbates. Similarly for multilayer adsorption or heterogeneous surfaces, Freundlich isotherm is used.

The electrospunfibres serve as a great adsorbent but at the same time depending upon the type of pollutant, certain modifications are required to be made. In field application, the major issue that pops up during removal of pollutant through adsorption is that the water to be treated might also contain contaminants that could degrade the efficiency of the process. Sometimes separating adsorbate from adsorbent post adsorption also becomes a challenging task. Electrospunnanofibres overcome such problems and make the post process a lot easier. Along with that other parameters like pH, temperature, etc. should also be kept under check. The prominent advantage of adsorption is that it requires lesser cost, comes with appreciable efficiency and can be easily regenerated.

Dye Removal

Dyes are the substances that can impart color to materials it is combined with. Today, dyes find vast application in food, textile, plastic and pharmaceutical industries as a result of which every year a large percentage of colored waste is discharged into the water bodies. Dyes like azo dyes containing N=N groups, mehtylene blue and many others are difficult to degrade, so it is very important to remove and dispose these pollutants to preserve living organisms and the environment[81-94].

Removal of dyes can be done through different methods like coagulation, biodegradation, adsorption, ion-exchange, photocatalytic reduction[95, 96]. Adsorption is the most widely used technique and variety of adsorbent like fly ash, peat, wood, sawdust, have been the center of attention because these are available at cheap cost. The adsorbent material for removal of dye pollutant must be thermally resistant since wastewater streams are generally in hot conditions. Membranes made of electrospunnanofibres needs incorporation of an external agent be it a photocatalyst, or a functional group in order to degrade pollutant dyes.

In photocatalytic process, electrospunnanofibres are incorporated with a photocatalyst and then irradiated with UV light radiations. The electrons are excited upon radiaton and the electrons present in conduction band undergo reduction as thy react with atmospheric oxygen to form superoxides. Whereas, holes in valance band undergo oxidation and react with water molecules to produce hydroxyl ions at the end. More widely and frequently used photocatalysts are actually semiconductors since they can facilitate movement of both electron and holes and are available at relatively cheap prices.

Diffusion dialysis

Sometimes acids discharged into water streams are quite expensive and should be recovered to cut down expenditures. So industries use the technique of diffusion dialysis in order to separate acids from wastewater[96]. It is a membrane process significantly based upon the ion exchange mechanism which facilitates under the driving force of concentration gradient across two liquids. On such example is anion exchange membranes which are actually positively charged and used for recovery of acids from wastewater[98-100].

Acids and metals are present in wastewater filled on one side of the membrane whereas the other side is fed with water. Cations aren't allowed to pass through these membranes as they have positive charge except hydrogen because of its small size.

This way acid get separated from the polluted sample. This saves a great deal of expenditure for the industries.

2. Conclusion

Treatment of water is very necessary considering the scarcity of safe drinking water around the globe. Several methods have been opted via different countries and researchers are constantly looking for more efficient techniques. Electrospunnanofibre have proved to be one of the most reliable medium to treat water as they provide larger surface areas, have high porosity and can be fabricated easily. Sometime to improve the efficiency and make them selectively active towards a particular pollutant, modifications are done by mixing two polymers, plasma treatment, wet chemical methods etc. All electrospunnanofibres can remove pollutants like dyes, acids, heavy metals and nanoparticles via. Adsoprtion is the most widely used process to remove nanoparticles and heavy metals whereas acid recovery is done via diffusion dialysis process. Dyes needs proper degradation, hence photocatalytic degradation is used. Electrospunnanofibres shows reduced efficiency on repeated usage. Efforts are being made to produce such functionalized membranes that can keep up with the desired efficiency even on multiple usages and thus an improved life span.

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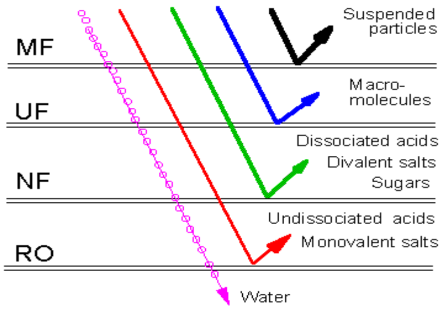

Figure 1: Selectivity of membranes.

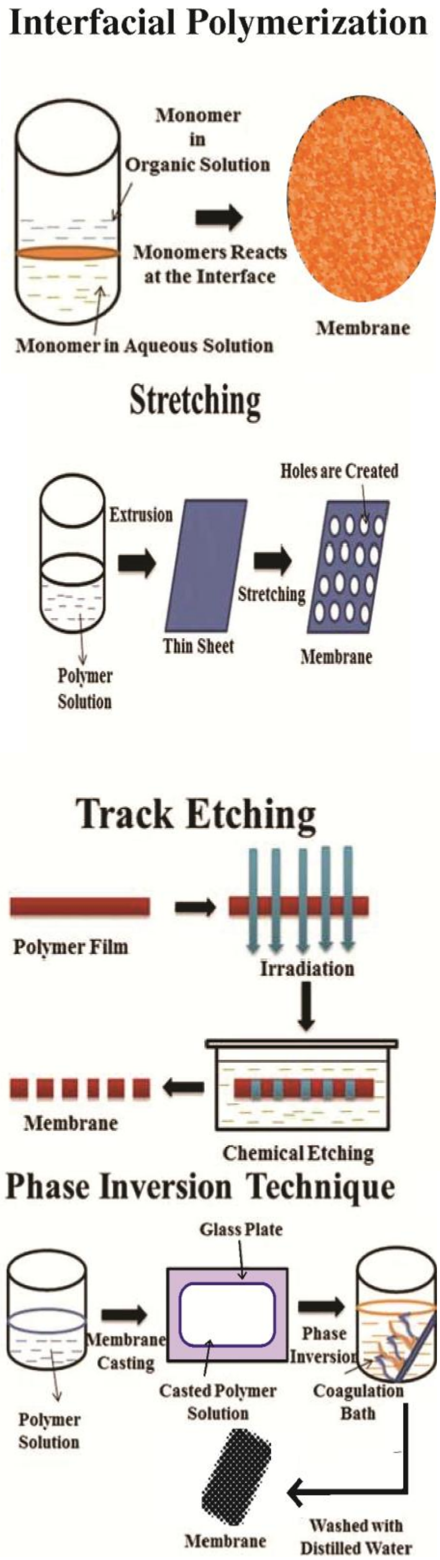

Figure 2: Fabrication techniques

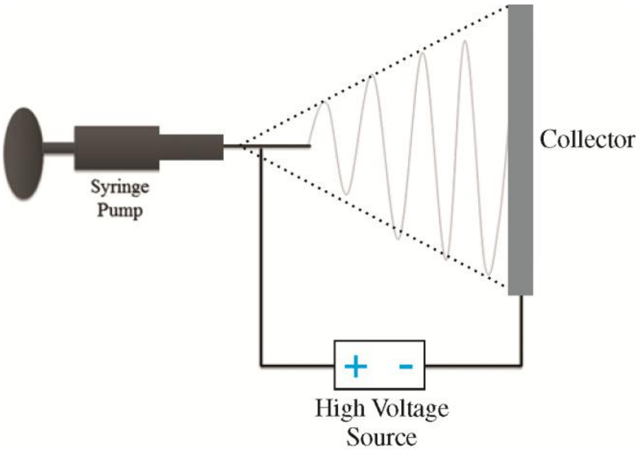

Figure 3: An electrospinning unit

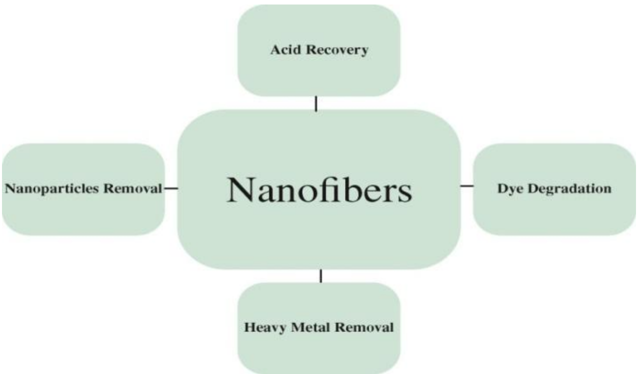

Figure 4: Applications of nanofibers

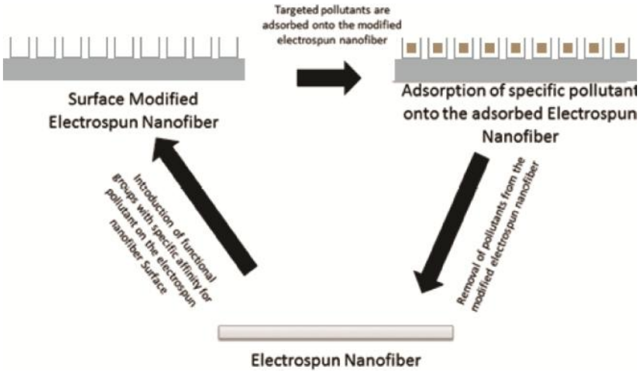

Figure 5: Adsorption of pollutants on nanofibre membranes

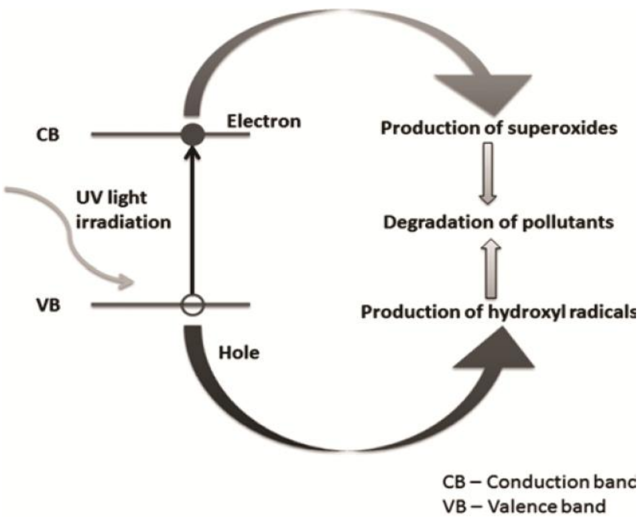

Figure 6: Photocatalytic Reduction

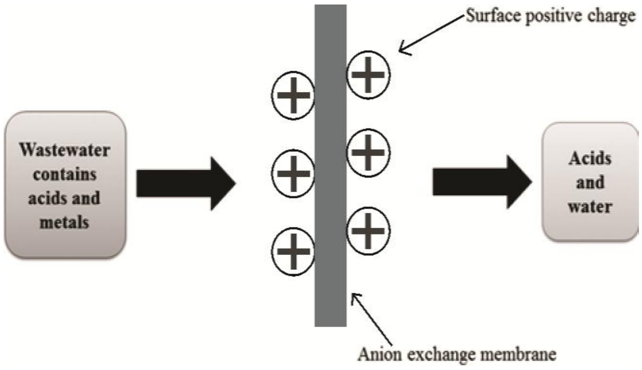

Figure 7: Representation of diffusion dialysis technique