Nanotechnology for water purification: electrospun nanofibrous membrane in water and wastewater treatment

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ABSTRACT

The need for beneficial innovations in filtration expertise has lead to little consideration of cutting-edge materials, such as nanofiber membranes for water distillation. The presence of organic matter and traces of organics accumulation in wastewater poses a major problem and current technologies such as coagulation/flocculation and chlorine technology are unable to yield satisfying results. The extra volume of sludge generated by these technologies needs further processing and disposal. Nanotechnology has outstanding potential for filtration applications due to its capability to create precise structural controlled materials for such requirements. Electrospun nanofibrous membranes (ENMs) are cutting edge membrane technology that offer substantial high flux and high rejection rates compared to conventional membranes. ENMs present a revolution in water and sewage purification by offering a lightweight, cost-effective, and lower energy consumption process compared with conventional membranes. ENMs possess high porosity, generally approximately 80%, while conventional membranes have 5–35% porosity. Nano-engineered membranes have great potential in water treatment due to their exotic properties. In this connection, electrospinning membranes are emerging as a versatile technique with promising features for water treatment. This work highlights the application of ENM in wastewater treatment and surface modification of nanomembranes in order to address fouling issues and wastewater treatment from Tabuk Sewage Treatment Plant, Saudi Arabia.

Key words | electrospinning, nanoporous membrane, water filtration, water treatment

INTRODUCTION

The world is facing numerous problems due to a lack of clean and fresh water: approximately 1.2 billion people have inadequate access to fresh potable water, 2.6 billion have very little or no hygiene, and millions of people die every year from sicknesses communicated through hazardous water or human excreta (Montgomery & Elimelech 2007; Shannon *et al.* 2008). With the human population

and associated environmental degradation continuing to increase, the scarcity of a clean and portable water supply constitutes a major concern considering the present state of the world's water resources. Water crises are expected to worsen in the coming years, with water scarcity occurring globally due to droughts, population growth, and urbanization. Addressing these prevalent problems requires significant investigation into novel approaches to water treatment with economic benefits and minimum energy expenditure, as well as reducing the use of chemicals and influence on the environment. Intestinal parasitic infections

and diarrheal diseases caused by waterborne bacteria and enteric viruses have become a major concern regarding malnutrition due to poor digestion of food by people sickened by water (Lima et al. 2000; Shannon et al. 2008). In developing and industrialized countries, large numbers of contaminants are entering municipal water supply systems through human activities, thereby increasing public health and environmental concerns. More effective, low-cost, technologically superior and robust methods to disinfect and decontaminate waters from the source to point-of-use are urgent requirements, without harming the environment or endangering human health during treatment (Shannon et al. 2008). The growth in population, urbanization, and drastic changes in life styles are the fundamental drivers for energy and water demand along with the excessive amount of wastewater generation due to human activities (Ramakrishna & Shirazi 2015). According to some estimations, the world population will be around nine billion by 2050 and approximately 75% will face fresh water shortages by 2075 (Tlili et al. 2006; Kargari & Shirazi 2014).

The necessity of beneficial breakthrough filtration technology has led to attention being focused on advanced materials, such as nanofiber membranes for filtering devices. Given the importance of fresh water supply to people in both industrialized and developing countries, and considering the current supply scenario of meeting the increased demand for water, there is an obvious need for innovative technologies to address the water crisis.

Numerous technologies such as distillation, treatment with chemical disinfectants, sand filtration, reverse osmosis, and membrane filtration have been used in the past to purify water. Among these technologies, membrane filtration is a relatively new method, having some advantages such as scalability, low power consumption, free from chemicals, and low operational temperature (Tlili et al. 2007). A membrane is a semipermeable medium that allows only certain molecules and compounds to pass through and hinders the passage of others. Membrane filtration system can be further improved by incorporating nanofibrous media. Nanofibers possess high porosities and well-connected pore structures, good permeability and, therefore, they are ideal candidates for water purification (Timoumi et al. 2008a, 2008b). Electrospinning is a new and versatile technique to fabricate nanofibers. Electrospun nanofibers with high filtration efficiency, small pore size, high permeability, and low cost are the material of choice for filtration application. The structure of electrospun nanofibers is very promising in terms of permeability, selectivity, and low fouling. Consequently, the demand for technological innovation to allow desalination and water treatment cannot be overstated (Ahmadi et al. 2016).

Nanotechnology for water treatment

The impact of nanotechnology in the advancement of methods and techniques for water treatment will be more promising in the years to come. With the fast depletion of fresh water resources, it is expected that engineered nanomaterials will play an important role in more efficient seawater desalination, water recycling, and water remediation. Nanotechnology has been recognized as a technology that could play a significant role in addressing many problems associated with water purification (Timoumi et al. 2007, 2008a, 2008b; Tlili et al. 2008, Sa'ed & Tlili 2015; Khan et al. 2019). Nanotechnology entails the creation and utilization of particles and materials, systems, and devices at atomic and molecular level (nanoscale), in cutting-edge fields such as engineering, industry, physics, materials science, biology, and chemistry (Afridi et al. 2018a, 2018b). Nanotechnologies refer to technologies at nano level associated with the conception of materials and particles termed nanomaterials and nanoparticles; they are characterized by unfamiliar and interesting proprieties lacking in other conventional substances and materials. Nanotechnology is concerned with structures or processes that can deliver benefits developed from substances at the nanoscale, i.e., 10^{-9} m (Almutairi et al. 2018). In the last three decades, many researchers and engineers have focused on water management and desalination, which has been of great interest to decision makers. Recently, many developments in nanomaterials investigation for wastewater treatment, based on nanofiltration for biologically treated sewage from deprivation of organic colorants tissue and the paper industry by means of manganese-doped ZnO nanoparticles, have been creating promising results. Nanotechnology has the potential to contribute towards long-term water quality, availability, and viability. The deployment of numerous kinds of membranes such as nanofiltration (NF), reverse

osmosis (RO), microfiltration (MF), and ultrafiltration (UF) has been required for water purification (Theron *et al.* 2008; Khan *et al.* 2018a, 2018b, 2018c, 2018d, 2018e). RO has the potential to provide the highest water purity; however, nanofiltration membrane has been exploited as a new technique these days for purification of water. The macro size molecules and colloids are eliminated by ultrafiltration (UF) membranes if water is allowed to flow between them. The pore dimension of ultrafiltration membranes varies between 2 and 100 nanometers. For several years, the elimination of micron-range particles or biological entities has been carried out by microfiltration (MF), which is a low pressure separation process capable of separating particles with diameters extending from 0.1 to 10 μm. That is why MF remains the most applied technology in the purification of ultra-pure and potable water by separating colloids, particulates, fat, and bacteria, while allowing low molecular weight molecules to pass through the membrane. Nanofiltration membranes are very economical compared to other types of filtration. Moreover, different salts, minerals, pathogens (fungus, molds, virus, and bacteria), monovalent and multivalent, cations, anions, and other suspended nanoparticles existing in surface and groundwater can be rapidly eliminated by NF membranes as well as total dissolved solids (TDS) (Agaie *et al.* 2018; Asif *et al.* 2018). The NF membrane has varied industrial and engineering applications such as in oil, textiles, beverages, food, chemicals, and many others. It is well known that the hole dimension of the nanofiltration membrane is commonly very low, around 1 nm, which helps in removing larger molecules from smaller molecules and also helps in removing bacteria (Khalid *et al.* 2018). Image processing software has been applied to assess contact angle through the tangent manner; moreover, the wettability can be performed as expressed by some researchers (Kruss EASY DROP, Hamburg, Germany). The contact angle is used to assess the membrane for modified cellulose and PH wettability through water and mineral oil. The entire membranes wetted by oil in air are in-air superoleophilic with oil CA values of approximately zero. Irregular wettability is one important method for suspension separation due to its directional liquid transport property. Chemical composition and the geometrical architecture affect surface energy and roughness, respectively, to control the wettability of

materials. Nanofiltration has very high effectiveness in removing protozoa (for example, *Cryptosporidium, Giardia*). Similarly, nanofiltration can remove bacteria (for example, *Campylobacter, Salmonella, Shigella*) effectively. Nanofiltration can also remove viruses (for example, enteric viruses, hepatitis A, norovirus, and rotavirus) effectively. However, nanofiltration has moderate effectiveness in removing chemicals. Membrane filtration has the potential to replace conventional filtration processes, since conventional filtration processes have limitations and are unable to remove several impurities consisting of activated carbon, sedimentation, flocculation, and coagulation (Alharbi *et al.* 2016). Several investigators have studied the application of nonreactive membranes from metal nanoparticles and nanostructured membranes from nanomaterials like nanoparticles, dendrimers, and carbon nanotubes (Kim & Van der Bruggen 2010). Absorption is an extensively performed technology due to its efficiency, usefulness, and relatively low process charges for water purification. Removal of diverse pollutants from contaminated water is achieved by operative absorbents such as activated carbon, modified clays, zeolites, silica, and layered double hydroxides. Nanotechnology offers a pioneering solution for sustainable water purification, distribution, and security. Membrane filtration produces high quality water. Actually, the enhancement of polymeric and ceramic membrane is well recognized and greatly influences the application of a membrane in water purification. Bae *et al.* (2016) fabricated PES membrane with NMP solvent for water treatment. It was found that low roughness and strengthened fibers have a great effect on electrospun nanofibrous membranes (ENMs) manufactured with NMP solvents, which will have flux recovery capability and high rejection compared to ENMs with DMF solvents. Furthermore, it is important to note that the flux performance was found to be eight times greater than commercial membranes. The only problem with membrane filtration is the fouling. With the development of membrane at nano or molecular scale, the fouling issue can be addressed, according to some studies (Asmatulu *et al.* 2013a, 2013b). Recently, the utilization of nanomembrane infiltration has been involved in numerous technical concerns, especially elimination of biological and organic toxins and impurities. Furthermore, some contaminants and toxins such as binding metal ions and 4-nitrophenol in

water solution can be decomposed by nanomembranes manufactured by nonreactive materials (Dolez *et al.* 2009). It has been noted that to reach higher operative and effective material to eliminate viruses, polysulfonate ultrafiltration membrane should be ingrained with silver nanoparticles (Asmatulu *et al.* 2013a, 2013b).

Electrospun nanofiber membrane

Membrane filtration is playing a vital role in water purification, since conventional water treatment processes such as flocculation, sedimentation, coagulation, and activated carbon are unable to remove organic pollutants to meet the necessary specifications (Taylor 1969). New progress and improvements in filtration expertise are based on electrospun nanoporous membranes. The polymers generally used for fabricating nanoporous membranes are cellulose nitrate, polyvinylchloride, polyacrylonitrile, cellulose acetate, aromatic polyamide, aliphatic polyamide, polysulfone, polycarbonate, polytetrafluoroethylene, polyvinylidene fluoride, polydimethylsiloxane, polypropylene, polyvinylidene difluoride, etc. The nanostructured provisions like electrospun nanoporous membranes are a possible explanation for delivery of portable water with minimum investment (Huang *et al.* 2003). Researchers have found a vital link between turbidity and human morbidity. High turbidity increases the chances of human diseases (Alarifi *et al.* 2016). Many studies have reported that electrospun nanofibers for water filtration help in reducing turbidity (Shin & Chase 2004; Wang *et al.* 2005). Electrospinning is a straightforward and novel process for fabricating nanofiber membranes, based on creating fibers from micro to nano size depending on electrostatic repulsive forces. This process is characterized by the lower cost of exploitation and small duration. Since the 1930s, the electrospinning technique has been identified and recognized, but lately this procedure has been given prodigious consideration since it has great potential to manufacture nanofibers with exceptional and specific characteristics, for example, higher permeability and surface with volume ratio and lesser diameter (Grafe & Graham 2003). Although there are a number of processes available for fabricating nanomembrane, electrospinning has a leading advantage over all of them, since electrospinning can easily control the morphology and orientation of fibers

due to its relatively low initial investment (Balamurugan *et al.* 2011). There are various other methods to fabricate nanofibers, including drawing, template synthesis, phase separation, and self-assembly. These processes are time-consuming and generally require large investment. Electrospinning is a straightforward, simple, and easy process with minimum investment. In electrospinning, the morphology of fibers can be controlled by process parameters. Electrospinning can generate fibers in a very short period of time. Polymeric nanofiber membranes fabricated via electrospinning are highly exploitable in water purification and have huge application potential in biotechnology, nanotechnology, and various other domains (Feng *et al.* 2013).

Nanotechnology-based electrospun nanofiber membranes have shown great promise in laboratory tests, although their readiness for large-scale commercialization still varies widely. Some are already available on the market, while some are still under investigation and require research before they can be considered for large-scale production. Their commercialization and future development still faces some technical obstacles such as compatibility with the existing infrastructures, potential environmental and human risks, and operating cost. These technical obstacles are temporary and a concerted effort is needed between research institutions, government, industry, and stakeholders. By making unabated, concerted efforts and avoiding unintended consequences, nanotechnology will provide robust solutions to water/wastewater treatment.

Electrospinning

The electrospinning procedure of polymer nanofibers is shown in Figure 1. Applying a higher voltage to melt or to polymeric solution leads to the creation of a higher electrostatic field, which leads to creation of nanofibers. At the extremity of a capillary tube, the solution or the polymer melts arise under its superficial tension. Furthermore, the electric field can be attributed to a substantial charge into the liquid generated forces which are seen to be enhanced due to common charge repulsion owing to the reduction of tension in the surface. It is worthwhile noting that the summit of the capillary tube in the semicircular surface of the solution will be extended by applying an electric field
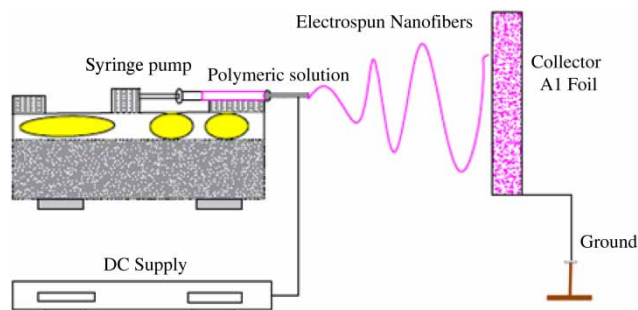
Figure 1 │ A schematic diagram of electrospinning of polymer nanofibers.

which, in turn, leads to the generation of a new structure identified as the Taylor cone (Taylor 1969).

It is well known that enhancing the electric field leads to increasing the repulsive electrostatic force which, in turn, exceeds the surface tension magnitude. The polymer solution/melt of the charged jet is evicted from the landfill of the Taylor cone. At the end, the polymer solution jet undergoes looping or pirouette movement because of the reciprocally repulsive forces of the electric charges of the jets, which is usually known as the winding variability of the electrified jet. The jet fluctuates between extended and tiny due to the bending variability. A charged polymer fiber is generated and assembled due to the evaporation of the solvent and bending instability. The charged polymer fiber is located at a close range to the capillary tube (Subramanian & Seeram 2013). The fibrous membrane thus fabricated via electrospinning possesses flexibility, and great superficial space alongside a permeable edifice, permitting maximum sites for filtration methods, which are generally referred to as electrospun nanofibrous membranes. Several studies have shown that electrospun membrane possesses high flux and low transmembrane pressure. The problem associated with ENMs is that the membrane possesses electrostatic charge since an electrostatic field has been used during electrospinning and the charge intensity intensifies as the thickness of membrane increases. Additionally, ENMs require additional support in order to provide strength. Therefore, these days, most of the applications of ENMs in membrane separation technology are generally based on a hybrid system. In these systems, nanofibers are generally placed on a support (substrate) or sandwiched between different layers or blended together with micro-sized fibers (Gopal et al. 2006a, 2006b).

In order to address the handling issue of electrospun nanofibers it is necessary to spin directly on a strong rigid support (collector screen). The electrospun nanofibers are generally heat treated to remove residual solvents and allow crystallinity. During an electrospinning process, the nanofibers are randomly oriented, giving rise to an open pore structure ideal for membranes. The subsequent heat treatment of ENM below the melting temperature of the constituent material, and the randomly oriented and overlapping fibers tend to fuse together, thereby improving the structural integrity of ENM and allowing easy handling. Additionally, heat treatment of ENM promotes crystallinity, which in turn improves mechanical strength (Kaur et al. 2007; Huang et al. 2013). ENMs with low density and an interconnecting open pore structure are ideal candidates for a wide variety of filtration applications. In membrane terminology, there are two factors that define the functionality of membrane: flux and selectivity. Selectivity is related to the surface properties of a membrane that distinguish the types of species that can pass through it. Selectivity in removing contaminants, mechanical strength, and porosity can be modified in ENMs to enhance their efficiency. Surface modification of ENMs enhances the efficiency of filtration. There are some surface modification techniques available, such as oxidation, plasma treatment, surface coating, and solvent vapor treatment. Flux refers to the rate at which the species are transferred across the membrane (Schiffman & Schauer 2007; Stephen et al. 2011). These two factors depend on parameters such as pore size, wettability, porosity, pressure drop across the membrane, and thickness of membrane (Haider & Park 2009).

The bubble-point method is used to determine the pore size of the ENM. The process involves the measurement of pressure needed to blow air through a liquid-filled membrane (Yoon et al. 2009a, 2009b). The membrane is placed in the supporting cell of distilled water and connected to a bubble-flow meter. Pressure is applied to the membrane base and at each pressure, the corresponding bubble flow rate is measured. The Young–Laplace equation, which relates pore size with the corresponding pressure, is used here:

$$R = \frac{2\gamma}{\Delta P} \cos\theta \qquad (1)$$

where R is the radius of the pore, Δp is the differential pressure, γ is the surface tension, and θ is the contact angle.

Recently, a number of journal articles have been published dealing with applications of NF for water purification (Li *et al.* 2013). The recent guidelines for nanofibers in nanofiltration have been summarized by Feng *et al.* (2013) and Subramanian & Seeram (2013). ENMs have some exceptional properties, including great surface area to volume ratio, increased porosity, as well as remarkable water permeability, which plays a key role in the water purification process. These fibers are generally employed for nanofiltration, microfiltration, and ultrafiltration. In ENMs, small pore size, huge surface area, and flexibility in surface functionalities optimize their adsorptive nature and selectivity (Li *et al.* 2018). The possibility of incorporating a variety of polymers, biological agents, and particulate nanofibers during electrospinning leads to the development of nanocomposite/hybrid nanofibrous membranes with high efficiency and a much broader range of environmental applications.

SURFACE MODIFICATION OF ENMS

The ENMs produced by polymeric solution are an effective means of purifying water. However, they suffer from fouling during the filtration process. Surface modification is one way to alleviate membrane fouling, since it helps to maintain high levels of water productivity. Fouling is the unwanted accumulation of solutes on the membrane surface or within the pores, thereby increasing the resistance to mass-transfer and decreasing membrane productivity (Mei *et al.* 2012). The polymers that are suitable for membrane applications must be rather mechanically robust and chemically steady (Zhao *et al.* 2012). Generally, the polymers that provide the most convenient pore structure should be too hydrophilic to be used as a filter in aqueous media (Zhao *et al.* 2012). The polymers with active surfaces generally do not contain the desired mechanical stability, and therefore are not able to be a support or base membrane (Yoon *et al.* 2009a, 2009b). Thus, surface alteration is essential to achieve suitable surface chemistry and good mechanical constancy (Wu *et al.* 2013). Grafting, blending, surface coating, and interfacial polymerization are the

common approaches offered for surface alteration (Tadanaga *et al.* 2003). However, plasma-induced graft copolymerization is an excellent technique and effective method for forming a polymer layer on the surface of a hydrophobic membrane (Adamson & Gast 1997). The plasma-induced copolymerization results in the reduction of surface pores of ENM without any compromise on its bulk porosity. Kaur *et al.* (2007) applied plasma-induced grafting on ENM surface to lessen holes while maintaining the base structure. There are also other grafting techniques available for surface modification. PVDF and PSU electrospun membranes were exposed to plasma at diverse powder and exposure time in order to carry out polymerization in monomer solutions, such as methacrylic acid, to fabricate the high performance of UF membranes. Several studies revealed that the surface grafted membrane exhibits better flux throughput than untreated membrane. To further advance the role of ENMs in the filtration process, several other approaches, such as interfacial polymerization, are also used to apply a layer of polyamide on the surface of the membrane in order to enhance flux throughput. Electrospun nanomembranes possess several advantages, such as high flux, low operating pressure, low cost, good retention of multivalent anion salts, and low maintenance. Recently, Kaur *et al.* (2007) used interfacial polymerization to fabricate polyamide composite membrane to be used beyond the microfiltration range. Electrospun PVDF membrane was first heat treated at 60 °C for 1 hour to remove organic solvent (Asmatulu 2008), followed by another heat treatment at 157 °C for 3 hours to enhance physical and mechanical reliability of the membrane. Subsequently, by using trimesoyl chloride (TMC)/organic phase and interfacial polymerization reaction of the p-phenylenediamine (PPD)/aqueous phase a polyamide high film was made. PVDF polymer, in the case of the hydrophobicity of the membrane mixed with clay nanocomposites, is enhanced and the maximum static water contact angle reached (154°), the melting point of the PVDF–clay electrospun nanocomposite increases with the increase in clay concentration. The interfacial polymerization resulted in the rejection of 80% of $MgSO_4$ and 60% of NaCl (Yoshikawa *et al.* 2001). The surface alteration of electrospun PVDF membrane generates superhydrophobic features. The surface alteration comprises silver nanoparticle deposition,

hydrophobic treatment, and dopamine surface activation. A thin film nanofibrous membrane based on electrospun PAN nanofibers coupled with a thin layer of cross-linked PVA, exhibited a great flux up to 12 times greater than traditional PAN UF membrane with a rejection ratio of approximately 99.5% for separating oil/water mixture of up to 1,500 ppm in water. A PVA/PAN nanofibrous composite membrane was fabricated via an electrospinning process. The PVA layer was electrospun on PAN substrate. The PVA nanofibrous membrane was melted by water vapors in order to form a barrier film and cross-linked in glutaraldehyde water/acetone solution. A maximum fluidity of approximately 210 L/m^2 with the elimination rate of 99.5% for an operating pressure of 0.35 Mpa was achieved. Huang et al. (2013) used a post-treatment method to enhance the mechanical specification of PAN and PSU membrane. The mechanical properties of these polymers were improved by means of solvent-induced fusion at the inter-fiber connection point. The membrane displayed good improvement in the modulus of elasticity and tensile strength while maintaining high permeability and good absorbency. A PVDF membrane was surface adapted by attaching with acrylic acid and meth acrylic. High water fluidity of around 150 Kg/h-m^2 at a working pressure of 4 Psig, and a 79% elimination of polyethylene was achieved (Renu et al. 2017). Stephen et al. (2011) altered nanofibrous membrane with oxolane-2,5-dione, in order to increase the surface area of membrane and help detect heavy metals, such as lead and cadmium. Schiffman & Schauer (2007) modified chitosan by interconnection using glutaraldehyde and Schiff base. Similarly, Haider & Park (2009) demonstrated the solubility of chitosan nanofibers by treating them with trifluoroacetic acid. Yoon et al. (2009a, 2009b) demonstrated the modification of poly (ether sulfone) nanofibers by adding two solvents, such as n-methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF) in order to enhance the oxidation procedure and mechanical specifications. The surface property of membrane, such as hydrophilicity, was improved by treating it with 3% w/v of ammonium per sulfate. As far as the improvement in modulus and strength are concerned, a profound increase of 570% and 360%, respectively, was attained by accumulation of maximum boiling solvent, such as NMP and DMF. The static contact angle values of 120° and 28°

were observed before and after treatment, respectively. Silver ions are widely used as an antimicrobial agent. Silver ions are incorporated in polymeric solution to fabricate nanomembranes in order to eliminate pathogens and postponed particles from water. Some researchers demonstrated the formation of silver ions by immersing different polymeric membranes in AgNO$_3$ followed by NaBH$_4$ reduction. Li et al. (2013) produced microporous membrane via electrospinning and annealed it at 90–105 °C at different period ranges (30–120 min) to control the pore size and increase the tensile strength. These membranes were efficient at removing TiO$_2$ particles and subsequent hot pressing of these membranes enhanced their performance in particle rejection. Mei et al. (2012) transformed the nitrile group present in polyacrylonitrile (PAN) into the amino group and coupled hydrophilic supple spaces, shadowed by reaction through hexamethylene guanidine hydrochloride (PHGH). It is noted that guanidine hydrochloride replaced the role of an antibacterial agent and that the hydrophilicity of membrane was enhanced by spaced groups. It is perceived that the PHGH membrane proved to have a strong performance as an antibacterial; moreover, it showed significant potential after three series of antibacterial tests. Also assessed were the water flux of original and adapted electrospun nanomembranes and the results are shown in Table 1.

Zhao et al. (2012) used a coating of polymeric solution on ENMs to enhance the performance of membrane. The PVDF modified membrane exhibited high flux rate and good rejection efficiency. A literature survey revealed that the alteration of the hurdle stratum on the upper porous polymer membrane enhances the performance and rejection efficiency. Yoon et al. (2009a, 2009b) demonstrated the interfacial polymerization of PAN membrane at a diverse ratio of piperazine and bipiperidine in order to enhance the rejection rate of MgSO$_4$. The rejection rate was enhanced as soon as the concentration of piperazine was augmented. Wu et al. (2013) used trimesoyl chloride, triethanolamine, and B-cyclodextrin (CD) as additives with a concentration of 1.8% (w/v) of CD in aqueous phase during interfacial polymerization. Their results showed a two-fold rise water flux of TFNC compared to the usual polyester membranes.

Table 1 | Nanofiber surface modifications

Substantial	Adjustment	Active group	Objective metal	Exclusion
Chitosan	Nullification with K_2CO_3	-NH_2-Amine	Copper(II), Pb(II)	485.44 mg/g, 263.15 mg/g
Silica	Zonal dissolution of polyacrylonitrile	-SH-Thiol	Mercury(II)	57.49 mg/g
Acetate ester of cellulose	*In situ* polymerization	Fluorinated polybenzoxazine	Oil water	Maximum
Polysulfone	Graft copolymerization	Carboxyl group	Toluidine blue O.BSA	380 nmol of TBO/mg of TBO
Poly ether sulfone	1. Solvent induced fusion, 2. oxidation	Carbonyl	Waste water	1. flux: 2,626 L/m^{2}hpsi, 2. flux: 2,913 L/m^{2}hpsi
PETE, PCTE, PTFC, PA	$AgNO_3$ lessening	Silver	Pathogen, Waste water	Turbidity exclusion: 99.25%, COD: 94.73%, NH_4: 93.98%
Poly lactic acid	Annealing	-COOH-	TiO_2 removal	85% elimination
Polyacrylo nitrile	Hot press interfacial polymerization	-CN-	Salt rejection, $MgSO_4$	86.5%
Polyacrylo nitrile	Coupling	-NH_2-	Antibacterial	53.7–99.9%

WETTABILITY OF MEMBRANE

The wettability of solid surfaces plays an important role in our lives. The microstructure of a surface and its surface energy determine if a dewdrop of water will branch or expand out evenly or roll off a solid surface. Hydrophobicity is related to the physical characteristics of a solid surface in which hydrophobe molecules block water molecules, making a greater water connection angle (>90°). In other words, a hydrophobic surface is one on which water droplets do not spread (Schiffman & Schauer 2007). The water droplets stand up in the structure of droplets and a connection angle can be assessed according to the flat of the superficial. When the water contact angle exceeds 90°, the solid surface is conveniently called a hydrophobic surface. Hydrophobic molecules are non-polar natural and artificial materials, such as alkanes, greasy substances like fats and oils. When the water contact angle on the solid exceeds 150°, the surface is termed as superhydrophobic. Hydrophilicity is the opposite of hydrophobicity, in which hydrophilic surfaces interact with water molecules to form hydrogen bonds, thereby creating a minor connection angle (>90°) (Zhao *et al.* 2012).

Superhydrophobicity is a physical characteristic of a solid surface where water contact is higher than 150°. A droplet of water can easily bounce on such a surface and can roll off with a lower than 10° receding angle. Due to the surface chemistry and irregularity, hydrophobic surfaces have extremely high water-repelling characteristics, which make it very hard for the surface to get wet. Such surfaces are also called self-cleaning. Therefore, fungi, bacteria, algae, and other microorganisms are not able to develop on super-hydrophobic surfaces. Hydrophobic or water hating surfaces have very little or no tendency to absorb water, therefore water droplets tend to be ejected on such surfaces. When water is placed on such a surface, many beads form on the surface. Hydrophobic surfaces possess low surface tension and lack active groups in their surface to form 'hydrogen bonds' with water. On superhydrophilic surfaces, the water contact angle decreases to less than 5° in 0.5 seconds. Superhydrophilic surfaces possess numerous benefits, like antibacterial and antifogging. A contact angle below 90° designates a good wetting, while a contact angle above 90° designates poor wetting. Additionally, when the water contact angle is higher than 90°, water is not thermodynamically stable on the surface, and wetting is generally prohibited. Figure 2 shows schematic views of different superhydrophobic, hydrophobic, hydrophilic, and superhydrophilic surfaces (right to left, respectively). The contact angle on a superhydrophobic surface is larger than 150° and the contact angle on a superhydrophilic surface is less than 5°.
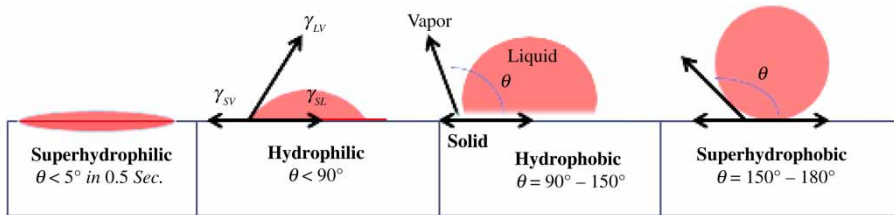
Figure 2 | Graphic views of different superhydrophilic, hydrophobic, hydrophilic, and superhydrophobic contact surfaces.

Hydrophilicity is a significant indicator as far as the wettability of filtration membrane and low-pressure filters are concerned. The minimum connection angle of hydrophilic membrane leads to a lowering of the capillary pressure of the filter media, as well as enhancing liquid flow rate and rejection rate. The hydrophobicity or wettability have a great effect on the efficiency of a membrane since a membrane with great wettability helps in getting the surface wet and then enhances the purification effectiveness.

UTILIZATION OF ELECTROSPUN NANOFIBROUS MEMBRANES FOR WATER PURIFICTION

Wastewater treatment

The presence of organic matter and traces of its accumulation in wastewater poses a major problem and the present-day technologies such as coagulation/flocculation and chlorine technology are unable to yield satisfying results. Additionally, these processes generate extra volumes of sludge, which need further treatment and disposal. Nanotechnology has great potential in filtration applications due to its capability to create precise structural controlled materials for such requirements. ENMs are an innovative membrane technology that offer substantial high flux and high rejection rate compared to conventional membrane. The electrospinning process fabricates electrospun nanofibrous membranes with manageable hole dimension in the scale of micro and nano, which may substitute for the classical membrane through lesser schemes that function at minimum pressure. ENMs present an innovation in water and wastewater purification by offering a lightweight, cost-effective, and less energy consuming process than conventional membranes. ENMs possess high porosity and high

surface area to volume ratio. Their porosity is generally around 80%, whereas conventional membranes have about 5–35%. The interconnecting structure and maximum permeability of ENMs permit permeabilities much higher than their conventional counterparts. The important features of ENMs, are pore size, porosity, and fiber diameter control flux, removal rate, and efficiency of ENMs. The porosity of ENMs are generally described as the proportion of the empty space in the membrane to the total volume of the membrane, such as (Schiffman & Schauer 2007):

$$Porosity =$$
$$\frac{Specific\ volume\ of\ membrane - Specific\ volume\ of\ polymer}{Specific\ volume\ of\ membrane}$$

It is well known that the specific volumes of polymer and membrane are the reverse of polymer and densities of membrane, correspondingly. The above equation can also be written in terms of densities as:

$$Porosity = \frac{\rho_p - \rho_m}{\rho_p}$$

where ρ_p and ρ_m are the densities of polymer and membrane, respectively.

Wastewater contains pathogens, such as bacteria, viruses, protozoa, molds, fungus, and helminthes and many chemical constituents.

Electrospun nanomembranes can swiftly and sensitively eliminate TDS from the water, pathogens, monovalent and multivalent anions and cations, salts, mineral and extra suspended nanomaterials (Yoshikawa *et al.* 2001). The electrospun nanomembranes have the potential to effectively remove protozoa. Likewise, nanofiltration is able to eliminate bacteria (for example, *Escherichia coli*, *Shigella*, *Salmonella*, and *Campylobacter*) efficiently. Moreover it is

able to eliminate viruses, for example, rotavirus, norovirus, enteric virus and hepatitis A (Li *et al.* 2013). The major problem with the reuse of municipal wastewater is the danger of infectious disease transmission. The presence of waterborne pathogens is very well known and they include *Escherichia coli*, coliform organisms, thermotolerant coliforms, *Enterococcus*, *Clostridium*, and bacteriophages. Electrospun membrane filtration is a novel process to inactive pathogenic microorganisms in water and wastewater and to preventing waterborne diseases throughout the world. Many researchers have demonstrated the applications of electrospun nanofibers for the removal of bacteria, particles, or dye from potable water or wastewater. Bacterial contamination of water is a concerning issue. At present, chemical disinfectants (chlorine or UV disinfectants) are used to mitigate microbial pathogens. Highly porous electrospun membranes possess great potential for removing bacteria from wastewater. Bacteria are generally in the range of microns, whereas viruses are in the scale of 10 nanometers. An ENM can remove bacteria easily. However, for virus removal, the size of the pore should be as small as possible. For efficient virus removal, the electrospun membrane can be fabricated with smaller pore size. By careful adjustment of process parameters, ENMs with smaller pore size can be fabricated to remove viruses. However, the reduced hole dimension diminishes water fluidity. Some researchers (Yoshikawa *et al.* 2001; Zhao *et al.* 2012) have fabricated an original membrane that has the capability to remove bacteria as well as viruses, thereby preserving water fluidity. In this compound membrane cellulose fine fibers were pervaded on a polyacrylonitrile ENM nonwoven substrate. To remove viruses effectively, they charge the membrane by incorporating cellulose fibers, and the positive cellulose fibers also attracted stick to the negatively charged viruses. They attained 99.99% efficiency in removing *E. coli*, which is in close agreement to the 2 cfu/mL set by the National Sanitation Foundation Standard. The bacteria are trapped in the membrane due to their large size. ENMs generally eliminate all bacteria such as *E. coli*, coliforms, *Salmonella*, *Cryptosporidium*, and *Giardia*. Silver nanoparticles (3–6 nm) were added in the PAN electrospun membrane and tested for Gram-negative *E. coli* microorganisms and Gram-positive *Bacillus cereus*. The fibers without silver nanoparticles did not show any antibacterial action compared to silver nanoparticle doped polyacrylonitrile nanofibers. A similar procedure was applied to PAN nanofibers by amidoxime functionalized polyacrylonitrile. Tests were conducted for finding microbes like *S. aureus* and *E. coli* for Ag+ and its reduction to Ag nanoparticles. The ASFPAN-3, amidoxime functionalized nanofibers have log 7 diminutions in the case of involvement for 20 min with NH_4OH. A similar trend was observed for $AgNO_3$ solution, in which PAN nanofibers were dipped in solution for 30 min and silver nanoparticles/polyacrylonitrile nanofibers, and displayed log 7 bacteria reduction. The results of some other studies using nanofibers for bacterial removal are given in Table 2 (Ahmadi *et al.* 2016).

The primary stage of a wastewater controlling system is wastewater generation. Usually, sewage is categorized into three classes: first, black water (water containing feces); second, yellow water (water containing urine); and third, grey water (sink water, water from baths, laundry apparatuses, etc.). All these three components are different in concentration and composition. Black water contains pharmaceutical residuals and pathogens and therefore it is detrimental to human health. Yellow water contains phosphorus and nitrogen N and is used as manure. The sanitization of grey water makes it usable for washing and irrigation. The World Health Organization standards were established to specify the quality of water for which sewage purification procedures are considered to attain these values. The presence of organic matter and traces of organic accumulation in wastewater pose a major problem, and current technologies such as coagulation/flocculation and chlorine technology are unable to yield satisfying results. Membrane filtration has the potential to replace conventional filtration processes, since conventional filtration processes have particular limitations and are unable to remove several impurities as they consist of activated carbon, sedimentation, flocculation, and coagulation. Coagulation improves natural organic matter removal rate and reduces membrane fouling.

Wastewater is commonly soiled by biological pollutants, microorganisms, solid wastes, and industrial and commercial sewage. There are two kinds of wastewater, industrial and municipal. The latter has a better quality. Wastewater flows are not steady and their composition varies widely depending

Table 2 │ Nanofibers for bacterial elimination

Polymer	Membrane thickness (nm)	Characteristics				Antibacterial action
Polyacrylonitrile	100	Average hole dimension: 0.22 ± 0.01 μm, Flux: 1.5 L/m^2 h				E. coli
Polyacrylonitrile	50	Average hole dimension: 0.4 μm				S. aureus, E. coli
Nylon – 6	650	OD culture at 600 nm				
		E. coli		pristine – 3.4, Mat 1 – 1.57, Mat 2 – 1.75		S. aureus
		S. aureus		pristine – 2055, Mat 1 – 1.68, Mat 2 – 1.88		E. coli
Polyacrylonitrile (PAN)	200	Area reticence (mm)				
		Microorganism	NaBh$_4$ reduction	Heated @160 °C	Heated @80 °C	
		B. subtlilis	7.5	6	10	B. subtlilis
		S. aureus	9	10	10	S. aureus
		E. coli	–	6	9	E. coli

on several conditions such as groundwater stages, land uses, and especially the degree of separation between sanitary and storm water flows. The most important varieties of organic composites include oil, saccharides, amino acids, fatty acids and hydroxyacids, as well as aromatic compounds, steroids and emerging pollutants.

Wastewater includes colony making units of virus particles, protozoan cysts, fecal streptococci, and coliform organisms. Every characteristic associated with water contamination must be taken into account during municipal wastewater treatment since purified water has to be free of toxic chemicals, effectively disinfected, reliable and fit for human consumption and the environment. Water treatment is based on the composition of wastewater. Figure 3 presents the wastewater treatment procedures.

Conventional wastewater treatment is based on the following steps:

1. The preliminary treatment: eliminating inorganic materials and large particles whose size is greater than 0.2 mm.
2. Primary treatment: removing both organic and inorganic particles with sizes varying from 0.1 nm to 35 μms.
3. Biological treatment: breakdown of the biodegradable organic materials and nutrients.
4. Tertiary treatment: getting rid of a part of the entire residual organic and inorganic particles and germs via filtration.

Manufacturing wastewater is generated by industrial processes like farming, nutrition, and mining. The structure and concentration of wastewater are altered from one kind of activity to another. Consequently, the filtration process is the best choice in order to be able to produce high quality filtered water with minimum investment. Nanofiltration can effectively remove manufacturing pollutants, for example pharmaceuticals, bisphenol-A, phthalates and alkylphenols. Nanofiltration is able to be incorporated into industrial waste treatment plants to generate effluent with a slight concentration of manufacturing impurities. Nanotechnology has been recognized as a technology that can contribute to a higher standard of water quality, viability, and accessibility through the application of nanofiltration which leads to recovery and purification.

Wastewater purification from Tabuk Sewage Treatment Plant

There are hundreds of small villages and towns in Saudi Arabia and for centuries the inhabitants of these communities have been using groundwater resources to fulfill their needs. Anthropogenic impacts such as contamination and over-pumping have resulted in unhygienic groundwater. Due to the low population density and barren nature of the climate, there are quite meager options available to supply water to maintain these
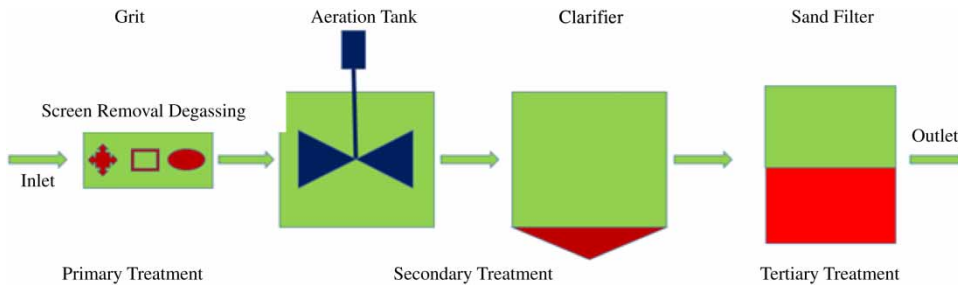
Figure 3 | Processes in wastewater treatment.

populations. Therefore, treatment of wastewater has become an urgent demand for these populations. Alharbi et al. (2016) fabricated a composite membrane consisting of PAN and PVP membranes containing gentamicin sulfate in order to perform chemical and physical analysis of wastewater. A sewage model was extracted from the Tabuk (Kingdom of Saudi Arabia) wastewater treatment plant. This wastewater treatment plant consists of three major stages, i.e., primary treatment, secondary treatment, and tertiary treatment. ENMs are used between secondary and tertiary treatment and they are tabulated in Table 3. According to the results, the mean pH for the wastewater after purification was determined as 7.70. The mean turbidity was determined as 14.22 NTU and TDS was found to be 1,589 mg/L. The electrical conductivity was found to be 3,219 μS/cm. Normally, the important parameters that should be taken into account for assessing the quality of purified wastewater are turbidity, TSS (total suspended solids), COD (chemical oxygen demand), and BOD (biochemical oxygen demand). Results from Asmatulu et al. (2013a, 2013b) revealed that BOD, COD, TSS, and turbidity were reduced by 67.6%, 28%, 83%, and 78.57%, respectively. ENMs have the potential to contribute towards long-term water quality, availability, and viability.

Alharbi et al. (2016) also performed bacterial analysis of filtered wastewater from Tabuk STP. Their results are given in Table 4. They demonstrate that PAN sample with 10 wt. % PVP containing 5 wt. % gentamicin reduced both the E. coli concentration to 1,119.9 MPN/100 mL and coliform concentration to 980.4 MPN/100 mL.

Gopal et al. (2006a, 2006b) fabricated electrospun polysulfone membrane with a hole dimension ranging from 1.2 to 1.6 μm for filtration. The removal efficiency was found to be 99% for particles greater than 7 μm

which were deprived of any enduring fouling. For smaller particles of 0.1–0.5 μm, the membrane achieved a deepness filter medium with elimination efficiency of around 89%. Another examination utilized electrospun polysulfone fiber membranes to eliminate subdivisions from secondary bio-treated wastewater. They achieved a removal efficiency of 86.7%, 71.2%, and 91.7% for solid, COD, and ammonia, respectively.

Wastewater contains heavy metals, which are able to cause considerable damage to nature and human beings. ENMs play an important role in removing heavy metals from wastewater. Chromium (Cr) is determined as a noxious contaminant in wastewater. Hexavalent chromium is a severe threat to human health since it has been found to cause cancer. ENMs exhibit a significant performance with regard to chromium removal. An investigation demonstrated the synthesis of amine functionalized cellulose acetate/silica composite membrane for the removal of Cr(VI) with a removal rate up to 19.45 mg/g. The same group used PVA polymer matrix for removing Cr(II) up to 97 mg/g. Composite membrane of $PAN/FeCl_3$ displays approximately 110 mg/Cr g removal and converts Cr(IV) to Cr(III), which is less destructive. Lead and copper can be removed by chitosan nanofiber membrane. Some studies have reported the elimination of other metal ions like cadmium, copper, and nickel achieved by means of ENMs.

Membrane fouling

Municipal wastewater is generally the most abundant source of water for purification since its volume remains the same almost throughout the year. The reuse of such water requires treatment to an acceptable quality level that satisfies

Table 3 │ Models' investigation of purified sewage

Nanofibers	pH	Turbidity (NTU)	TDS (mg/L)	Cond. (μS/cm)	TSS (mg/L)	COD (mg/L)	BOD$_5$ (mg/L)	Phosphate PO$_4^{3-}$ (mg/L)	Ammonia NH$_3$-N (mg/L)	Oil/Grease (mg/L)	DO (mg/L)
Raw water before separation	7.45	42	1,658	3,356	36	55	21	35.3	19	2	6.2
PAN + 0 wt% PVP +0 wt% Gent.	7.52	18	1,599	3,238	14	33	10.1	35.1	18	0	5.52
PAN + 0 wt% PVP +2.5 wt% Gent.	7.71	17	1,597	3,229	12	27	9.2	34.2	17	0	5.48
PAN + 0 wt% PVP +5 wt% Gent.	7.77	15	1,604	3,247	11	22	8.5	34.6	17	0	5.61
PAN + 5 wt% PVP +0 wt% Gent.	7.55	18	1,587	3,217	9	36.9	9.4	34.9	17	0	5.78
PAN + 5 wt% PVP +2.5 wt% Gent.	7.78	15	1,607	3,253	8	38.3	9	33.5	16	0	6.05
PAN + 5 wt% PVP +5 wt% Gent.	7.76	11	1,591	3,221	8	39.4	8.1	35	17	0	5.43
PAN + 10 wt% PVP +0 wt% Gent.	7.80	14	1,601	3,245	8	40.87	9.6	33.8	18	0	5.66
PAN + 10 wt% PVP +2.5 wt % Gent.	7.68	11	1,570	3,179	8	40.3	7.3	34.1	16	0	5.92
PAN + 10 wt% PVP +5 wt% Gent.	7.72	9	1,553	3,148	6	39.36	6.8	34.7	16	0	5.83
Average	7.70	14.22	1,589.89	3,219.67	9.33	35.24	8.67	34.43	16.89	0	5.70
Removal %	+3.62	78.57	6.33	6.20	83.33	28.44	67.62	1.70	15.79	100	5.97

Table 4 │ Bacterial examination of purified sewage

Nanofibers	E. Coli (MPN/100 mL)	Total coliforms (MPN/100 mL)
Raw water before purification	>2,420	>2,420
PAN + 0 wt% PVP +0 wt% Gent.	>2,420	>2,420
PAN + 0 wt% PVP +2.5 wt% Gent.	>2,420	>2,420
PAN + 0 wt% PVP +5 wt% Gent.	1,732.9	1,986.3
PAN + 5 wt% PVP +0 wt% Gent.	>2,420	>2,420
PAN + 5 wt% PVP +2.5 wt% Gent.	>2,420	1,732.9
PAN + 5 wt% PVP +5 wt% Gent.	1,553.1	1,203.3
PAN + 10 wt% PVP +0 wt% Gent.	>2,420	>2,420
PAN + 10 wt% PVP +2.5 wt % Gent.	1,986.3	1,413.6
PAN + 10 wt% PVP +5 wt% Gent.	1,119.9	980.4

regulatory guidelines. One study demonstrated that hydrophilic membranes possess the lowest susceptibility to fouling by organic colloids. This work was further supported by another study which demonstrated that membranes with a higher negative surface charge and higher hydrophilicity are less susceptible to fouling due to fewer interactions between the chemical groups in the organic solute and the polar groups on the membrane surface. The fouling process is a complex phenomenon in which the physico-chemical properties of the membrane, the quality of water, the type

of solute atoms, and the type of cell all play an important role. Generally, the fouling surface cannot be cleaned to its original state. To address this issue, the plant must be operated below the critical flux and feed water must be pre-treated. Some works (Yoshikawa et al. 2001; Zhao et al. 2012) demonstrated that colloid stability, particle size and concentration play an important role in RO and UF membrane fouling. Stable colloidal suspensions cause less fouling. The use of acid, which is commonly used to avoid scaling, usually promotes colloidal fouling. Some works (Yoshikawa et al. 2001; Zhao et al. 2012) identified two different fractions of wastewater effluent organic matter, which exhibited different characteristics in fouling of NF and UF membranes. For instance, the colloidal fraction showed high flux decline due to blockage in pores and hydrophobic membrane surface. The polysaccharides and amino sugars were found to promote fouling. Studies have shown that natural organic matter is the major ultrafiltration membrane foulant and different ingredients of natural organic matter cause different types of fouling. According to one study, the organic colloidal fraction causes considerable fouling. A typical flux-time curve for ultrafiltration is depicted in Figure 4. Stage I shows a rapid initial drop of the permeate flux, followed by a gradual decline in flux (stage II), and stage III shows a steady-state flux. Flux decline in filtration is due to the resistance by membrane pore blockage and
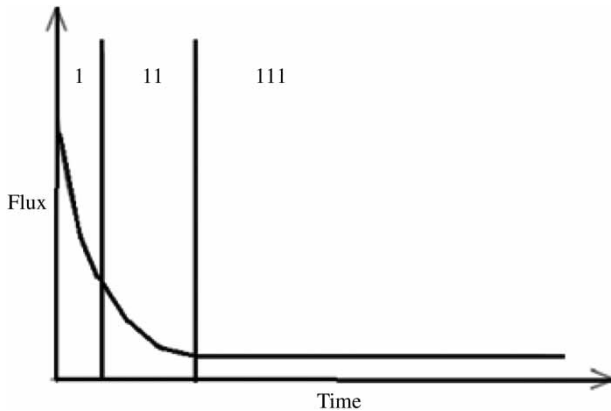
Figure 4 | Diagram showing phases of flux failure in UF.

formation of a layer on the membrane surface. Pore blockage and the formation of a layer on the membrane surface are considered two essential mechanisms for membrane fouling.

Electrospun nanofibrous membranes produced by polymeric solution are an effective means of purifying wastewater. However, they suffer from fouling during the filtration process. Fouling is more severe in NF due to the small size of pore and pore distribution. Surface modification is a way to alleviate membrane fouling, since it helps to maintain high levels of water productivity. Surface modification is essential to combine the attributes of a suitable surface chemistry and good mechanical stability. Microfiltration membranes are fouled by colloidal matter and natural organic matter, as well. The pretreatment of wastewater reduces fouling to a significant extent. Natural organic matter plays a vital role in microfiltration. The contribution of natural organic matter to membrane fouling depends on many factors, such as membrane material, type of pretreatment, and type of natural organic matter. Coagulation improves natural organic matter removal rate and reduces membrane fouling.

CONCLUSIONS

The application of nanotechnology for water/wastewater treatment is gaining tremendous momentum all over the world. The exotic properties of nanomaterials and their incorporation with current technologies have the potential to revolutionize water/wastewater treatment. Electrospun nanofibrous membranes have shown promising results in the laboratory testing stage; however, their readiness for large-scale commercialization still faces some technical challenges, such as compatibility with the existing infrastructures, environmental and health risks, potential degradation of polymer with time and cost. These challenges seem to be temporary and through coordination of research institutions, government, and industries, these challenges will be overcome with time. Blending surface modifying macromolecules drastically changes the ENMs, surface properties. This can be further investigated to fabricate membranes with extremely hydrophobic or hydrophilic features. The application of hollow ENMs in filtration still needs to be tested as well as their performance. Grafting of ENMs with other polymers with desirable properties is worth investigating. There is the potential for the development of temperature and pH sensitive smart membranes and membranes for vapor separation with small swelling of the polymer matrix.

This review outlines the importance of ENMs regarding water filtration. Different surface modification techniques have been developed for addressing the fouling issue associated with ENMs. Gentamicin was used in some studies to remove bacteria and microorganisms and reduce fouling, as well. Due to the nanosized structure, the nanoporous membranes practically diminish bacteria, for example, total coliform bacteria and *E. coli*, to a considerable extent. Additionally, the greatest influential aspects that should be considered before determining the quality of water are biochemical oxygen demand, total suspended solids, turbidity, and chemical oxygen demand. Finally, the nanoporous membranes lessened all these issues to a substantial extent.

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