Membrane Technology for Groundwater Purification: A review

Hassan A. Yasin¹,°, H.M. Mousa¹, M.S. Abd El-sadek²,° G. T. Abdel-Jaber¹,°

Abstract
Groundwater contains many impurities, salts, and mineral elements. Therefore, there is an essential demand to make water more purified from these impurities. There are many ways to purify water such as desalination and membranes technology.Polymeric, ceramic, and composite membranes are widely used in membranes manufacturing with a nanofiber/nanomaterial membrane for groundwater filtration. To enhance membrane water flux and fouling, inorganic materials are embedded to the membrane polymeric solution. In the present review, water challenges in Egypt and ground water distribution is the focus. In addition, membrane technology with focus in materials, techniques, fouling, modules, and filtration process will discuss.

Keywords: Water purification, electrospinning, membrane technology, membranes modules.

1. Introduction
Lack of water has become a serious threat in many areas around the world due to population growth and industrial growth. It is likely that in 2025 more than 1.8 billion people in the world will be exposed to water scarcity [1]. Freshwater only represents 2.5% of Earth's water the vast majority is saltwater (97%) in the ocean, and the small residual is brackish water (0.5%) found in surface estuaries and salty underground aquifers [2]. The decrease in water and increasing population have led to the reuse of drinking water in most countries in the world [3]. Water pollution is a major issue and threatens the society in which we live, so essential demand to find new technique such as wastewater reuse and desalination these methods are the best ways to solve this serious problem. Current days, water has been contaminated in large quantities because of the oil leakage and its mixing with water and rapid industrial development that casts a large amount of water contaminated with oil on the environment, such as petrochemicals, petroleum refining, food, and metal finishing [4]. However, such as most industrial activities, oil and gas production operations generating large quantities of effluents. Wastewater for oil fields or water contains various organic and inorganic ingredients. Water discharge contamination of surface water, groundwater, and soil [5]. Although, there are many desalination processes, researchers are focusing on membrane use at present because of low energy consumption. These days the membrane is widely used to produce drinking water from the sea [6]. Cleaning the industrial liquid waste, and restoring valuable components [7] and in the food industry, drugs, elimination of urea and toxins from the blood stream in an artificial kidney [8]. It is preferable to use the membrane in water purification because there are no chemical additives, however, there are many limitations such as; membrane fouling, low flux, and compromised rejection [9]. Microbial properties of poly (vinylidene fluoride) membranes was introduced by blending with lactate salts-based polyurea as surface modifiers in the reported work [10-12]. In this review, a focus on ground water in Egypt and membrane as green technology for water purifications will discussed and reviewed.

2. Ground water in Egypt

Groundwater is the second source of water after the Nile in Upper Egypt and the important source of water for different purposes in the desert areas, so checking groundwater quality is of a high advantage for insuring health [13]. These challenges increase the demand for the use of groundwater, and therefore purify and treat it for using in drinking and agriculture to face the risk of water poverty in the future [14]. Recently, major pollution and climate change have become a threat that leads to the decline of fresh water sources which uses in uses in domestic, irrigation and industrial purposes [15]. Groundwater contains large concentrations of salts, iron and manganese [16]. Fig.1 illustrate distribution of aquifers in Egypt.
3. Membrane technology

Membrane technology encompasses the related scientific and engineering approaches for the transport or rejection of components, species, or substances through or by the membranes [18]. Membrane has many advantages such as membrane properties can be adjusted, up scaling is easy, possibility of hybrid processing, and continues separation under mild conditions.

Membrane depends on the size of the pores in the different types of contaminants [19]. Fig. 2 shows a different pressure range in separation process. As shown in Fig. 2 filtration processes have been categorized according to the pressure required for the separation, the size of the pore, the molecular weight cutoff (MWCO), and the transport mechanism governing the separation [20].

3.1. Microfiltration (MF)

Microfiltration is a physical process where the liquid is passed through a membrane to separate the exact and fine particles [21]. In membrane technology with a pore size range (100–1000 nm) used in filtration technologies made from ceramic or polymer materials. MF membranes remove hanging solids (more than 99% rejection) and provide log removal of protozoan cysts and coliform bacteria [22]. In addition, MF pore size range between 100 and 1000 nm and remove viruses. An example of MF membrane include remove heavy metal ions and oil/water separation [23, 24]. In addition, removing bacteria, algae, microorganisms larger than viruses and micro pollutants [19].

3.2. Ultrafiltration (UF)

Ultrafiltration is a pressurized membrane separation technology that makes the stray molecule dissolve and the solvent pass through a special film and stop the molecular solute from passing. Membrane has pore sizes ranging from 10 to 100 nm and used to remove viruses, color pigments, bacteria, and some natural organic colloids [25]. Dissolved components of salts and organic chemicals are not removed by MF and UF [26, 27]. There is a way to combine MF and UF named as membrane bioreactor. In the membrane bioreactor, membranes are immersed in a bioreactor under vacuum to permeate the treated water and the remaining solids are accumulated in the bioreactor. The main advantages of this process is that can save the consumed energy and decrease membrane fouling [28]. An example for UF membrane is removing a very fine endotoxin, plastics, proteins, silica, silt, smog, and viruses which is promising in the present pandemic COVID-19.

3.3. Nanofiltration (NF)

In this category of membranes, nanofiltration membrane remove impurities smaller than 10 nm [29]. Loose nanofiltration membranes with a remarkable water permeability are highly promising for the fractionation of dyes and salts in the treatment of textile wastewater [30]. These process undergoes a pressure driven process in the range of 5 to 20 bar [31]. Thus, this membrane is suitable in separation of polyvalent ions [32]. An example of NF membrane purification of pharmaceutical additives from genotoxic impurities and generation of pure water [33].

3.4. Reverse osmosis (RO)

Reverse Osmosis is universally accepted in both water treatment and desalination applications. RO is a water purification process in which membrane removes ions, impurities, and larger particles from drinking water. During RO process a pressure -driven with a semi- permeable membrane separates the impurities from the water as shown in Fig. 3. Reverse osmosis used for a variety of applications including food
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processing, semiconductors, pharmaceuticals, power generation, desalination, biotechnology, produce water from oil and gas production, mine and diary wastewater, tanneries, process and boiler water, and beverage industry [34]. RO represent 60% for desalination water in the world. There are different materials used in RO membrane like cellulose acetate and polyamide [35].

Fig. 3 Principle of osmosis, equilibrium and Reverse Osmosis (RO) process [36].

4. Membrane fabrication

There are many techniques are being used in polymeric membranes such as: phase inversion, melt extrusion, controlled stretching, electrospinning [37, 38], and track etching [39]. In the following part, description of membrane technology techniques will be described in detail.

4.1 Electrospinning technique

The first to invent electrospinning process was J. F. Gooley in 1900. Electrospinning consists of a DC power supply, plastic syringe, and a collector as shown in Fig. 4. The polymer solution which inside the syringe exposed to high voltage and then it will be polarized and the induced charges will distribute on the surface. Under the influence of the strong electric field, the charged polymer will be accelerated towards the collector [40]. Electrospinning is a technique that usually used for preparation of porous membranes structure with high surface to volume ratio and develop membrane with good hydrophobicity and excellent pore interconnectivity [41]. It has many applications in sensor materials, tissue engineering, lithium ion battery separators, piezoelectric nano-generators, and membrane applications [42]. There are various types of fibers produced from electrospinning process Fig. 5 [43]. During the electrospinning process, when high voltage is applied, the polymer solution droplet at the needle tip deforms into a cone shape called a Taylor cone under the electrostatic forces [44]. The distance between tip and collector has an effect on the jet path and the traveling time before resting on the collector [45]. When the voltage kept constant, the electric field strength will be inversely proportional to the distance between syringe and collector. The best and preferred distance in electrospinning usually range from 10 to 15 cm, which generally allows sufficient time for the solvent to evaporate such that a dry fiber strand is deposited. When the distance is long between tip and collector the resulted fiber has thinner diameter as there is a greater stretching distance [46].

Fig. 4 Electrospinning process main component [40].

Table 1 summarize all the most effective parameters that affect on the nanofiber formation. These parameters affect the process of electrospinning including: (1) molecular weight, (2) needle size, (3) viscosity, (4) flow rate, (5) applied voltage, (6) humidity, and temperature. In addition, electrospinning is easy work and low cost, however, there are many processing parameters, which could highly influence fiber generation and nanostructure. The process parameters are necessary to help the stabilization of electrospun ultrathin fibers as shown in Fig. 6 [40].

Fig. 5 Examples of various nanofibers used for membrane technology adapted from [43].
**Table 1** Effect of different parameters in electrospinning technique [47].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>• Increasing concentration results in bigger fibers.</td>
</tr>
<tr>
<td></td>
<td>• Very low concentration can form beads on fibers.</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>• More bead formation at low molecular weight.</td>
</tr>
<tr>
<td></td>
<td>• Increasing molecular weight produces bigger and smoother fibers.</td>
</tr>
<tr>
<td>Viscosity</td>
<td>• Increasing fiber diameter with the increase of viscosity.</td>
</tr>
<tr>
<td>DC high applied</td>
<td>• Increasing voltage, fiber diameter becomes thinner.</td>
</tr>
<tr>
<td>voltage</td>
<td></td>
</tr>
<tr>
<td>Polymer feed rate</td>
<td>• Very high feed rate better than low feed because to avoid beads on fiber.</td>
</tr>
<tr>
<td>Temperature</td>
<td>• Increasing the temperature decrease the fiber diameter.</td>
</tr>
<tr>
<td>Humidity</td>
<td>• High humidity induces internal porous fiber.</td>
</tr>
<tr>
<td>Collector</td>
<td>• Various shapes are available for membranes such as flat and rounded drum.</td>
</tr>
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Fig. 6 Schematic diagram of a conventional electrospinning setup, as well as environment, solution, and electrospinning variables [44].

4.2 Phase inversion

Phase inversion is demixing process in which an initially homogeneous polymer solution is transformed in a controlled manner from a liquid to a solid state [48]. This transformation can be accomplished in several ways [49], namely: (a) immersion precipitation in which the polymer solution is immersed in a non-solvent coagulation bath (typically water). Mixing and precipitation occur due to the exchange of solvent (from polymer solution) and non-solvent (from coagulation bath). This solvent and non-solvent must be miscible. (b) a thermally induced phase separation, this method depends on the temperature as the quality of the solvent usually decreases when the temperature decreased. After demixing is produced, the solvent is removed by extraction, freeze drying or evaporation. (c) Evaporation-induced phase separation, in this process, polymer solution is made in a solvent or in a mixture of a volatile non-solvent, and the solvent can evaporate, leading to precipitation or demixing/precipitation. This technique is known as casting technique. In this process, the polymer is dissolved in an suitable solvent then the solution cast over a glass plate as shown in Fig. 7 [50]. (d) Vapor-induced phase separation method. In this process, polymer solution is exposed to an atmosphere containing a non-solvent (typically water); absorption of non-solvent causes demixing/precipitation. Overall, among these techniques, immersion precipitation and thermally induced phase separation are the most commonly used technique in the polymeric membranes fabrication with a various morphologies [51, 52].

Fig. 7 Schematic drawing of a non-solvent induced phase separation membrane fabrication (adapted from [50]).

4.3 Stretching

Microporous membranes usually used in MF, UF, and membrane distillation are fabricated by extrusion followed by stretching technique. Polymer membrane fabrication using stretching was invented in 1970’s and its proprietary was owned by the companies [53]. This is a solvent free technique and its featured that the polymer is heated above the melting point and extruded into thin sheet followed by stretching to make it porous [54, 55]. The stretching technique was developed mainly to fabricate chemical resistant semi-crystalline polymers such as polytetrafluoroethylene (PTFE), polyethylene, and
polypropylene. The generated pores are formed in the elevated temperature due to the stretching of the formed film in a perpendicular direction of its crystallite structure. Such polymer crystallites are oriented in the direction of extrusion as shown in Fig. 8. These membranes are extruded plastic rod rolled into a sheet with specific thickness and then stretched in uniaxial direction or biaxial direction [56].

Fig.8 Preparation of the PTFE membranes by uniaxial and biaxial stretching [50].

4.4 Track Etching

Track etching is undergoing in a high energy radiation or charged particle from a nuclear reactor to irradiate the films. The main concept is that particles passing through the film and damage the polymer chain and leave the damaged tracks [57]. The formed narrow path on the film due to a direct exposure of high energy radiation that named as tracks. Such tracks possess a higher chemical reaction than that of a non-radiated film that exposed to a well-chosen chemical reagent [58]. This selectivity of the polymer solution assist the formation of the microporous channel in the future [59].

4.5 Melt extrusion or casting methods

Extrusion technology is used broadly in thermoplastic membranes manufacturing. The molten polymer is forced by extruder screw through a mold or spinning die in the head of extrusion devices, and then cooled in air or cooling fluid whereby it solidifies to complete the continued tube, rod, plate, and fiber formation process [60]. The doctor blade casting is the alternative technique for the membrane manufacturing. With a gap size of usually around 150–200 µm the casting solution is flattened to a homogenous wet film. Further transportation gives the microphase separated or microphase separating BCP chains time to rearrange in the wet film and react to solvent evaporation induced gradients of concentration or temperature, before freezing the structure by a quick solvent non-solvent exchange, when it is immersed into a precipitation bath. Up to now the resulting block copolymer film thickness is limited to a minimum of ca. 11 µm using this method in our group [61].

5. Membrane modules

Membranes are designed and manufactured based on materials that fabricated and the module type which can packaged to perform water purification and filtration process. As a result, a wide range of membrane modules are suggested in industry and research area to meet the different applications. The polymeric membranes can be designed in in the form of flat sheet, hollow fiber, spiral wound, and tubular as shown in Fig. 9 [62, 63].

Fig.9 The most common membrane modules [19].

5.1 Plate and frame

This module used widely in laboratory experiments to test membrane properties and calculate efficiency of membrane distillation as shown in Fig.10 [64] [65]. In addition, flat membrane is used in a lower water purification that has a high viscosity of foulants. Recently, flat membranes are designed to overcomes and work under high pressure reach to 100 bar. These lead to water treatment of industrial textile wastewater in landfill and reuse of the treated water [66].

Fig.10 Plate and frame membrane module [67].

5.2 Hollow fiber

In this membrane module, thousands of hollow fibers are assembled and sealed into a housing [68]. Hollow fiber modules contain a small portion named as lumen with dimensions ranged from 0.5 to 1.5 mm with a thousand of hollow fiber as illustrated in Fig. 11. Hollow fiber membrane characterizes with high surface area/volume which is commonly preferred comparing to other large-scale membranes. Generally, such membrane category based on hollow fibers modules used as portable devices for further MF or UF applications. Recently, hollow fiber membranes are available for RO applications [69].

5.3 Spiral wound

NF/RO processes commonly uses spiral module membrane beside of its applications in MF/UF [62]. Spiral membranes characterize that it has a high packed density and easy to manufacture. Such kind of membranes are
6. Membrane Materials

There are many types of materials including polymeric, ceramic, metal, and carbon membranes. These membrane materials have advantages and limitations while used in membrane technology. The following section will focus on polymeric and ceramic membranes materials.

6.1 Polymeric membrane

Polymeric membranes are the most widely used in water filtration and purification these days due to their low cost and fabrication. There are many polymers used in membrane fabrication such as Polysulfone (PSF), Polyethersulfone (PES), Polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), and cellulose acetate (CA). Polymeric membranes remove impurities, small particles, and dispersed oil. However, it can't separate volatile compounds and has limitation of quick fouling which decrease flux and rejection, especially for treating oily wastewater.

6.2 Ceramic membrane

Ceramic membranes are widely used as portable device and considered as promising membrane materials. However, polymeric membranes have been the primary component in drinking water purification. Ceramic membranes are lower in cost and have larger pores and lower permeability. In addition, ceramic membranes can be reused by cleaning with harsh chemicals which are not suited to polymeric membranes. As a result, ceramic membranes are promising and great potential in water treatment for high fouling feeds, filter backwash is a good example of that category of ceramic membranes.

7. Classes of membranes

Membrane is a thin physical layer that moderates certain species to pass through depending on their physical and/or chemical properties. Generally, there are two classes of membranes: isotropic and anisotropic membranes as shown in Fig. 13. Isotropic membranes are chemically homogenous in composition. Examples include microporous membranes, nonporous dense films, and electrically charged membranes. In contrast, there are two main types of anisotropic membranes: phase-separation membranes (Loeb-Sourirajan membranes) and composite membranes such as thin-film, coated films, and self-assembled structures.

8. Membrane fouling

Membrane fouling refers to molecules collection in the membrane pores or/and surface of the membrane as shown in Fig. 14. Membrane fouling is a result of different processes such as Gel layer, pore blocking, and adsorption. These lead to membrane fouling and hence decrease permeate flux, productivity and the lifespan of the membrane. Fouling can be classified into two
types: biofouling, colloidal fouling, inorganic scaling, and organic fouling. Fig. 15 shows scanning electron microscope (SEM) images of four fouling types on membrane surfaces. More specifically, Fig.15A shows the surface of a RO membrane contaminated by bacteria while Fig.15B displays the RO membrane surface that is fully covered by an organic foulant, sodium alginate. Fig.15C clearly demonstrates calcium sulfate (CaSO$_4$) scaling on a RO membrane surface and Fig. 15D reveals a RO membrane surface fouled by a common colloidal foulant, silica [83].

9. Wettability

The surface hydrophilicity of membrane is an important factor to membrane water flux enhancement. Water contact angle (WCA) is a powerful tool to assess membrane hydrophilicity using angle goniometer via distilled water at room temperature [84]. Membranes surfaces characterized by the contact angle of water smaller than 90° are usually termed hydrophilic. Where, WCA: $\theta > 90^\circ$ called hydrophobic. Surfaces on which the water contact angle is above 140° are termed superhydrophobic as shown in Fig.16 [85].

Fig.16 WCA measurements and their corresponding wettability [85].

10. Membrane Porosity

Membrane porosity is another essential factor i.e (membrane characteristics) that effect on water flux. The term porosity is the ratio between the existing size of membrane pores and the total membrane size [86]. Porosity of membrane can be calculated by the following equation:

$$\varepsilon = \left[ \frac{m_1 - m_2}{\rho_1} \right] / \left[ \left( \frac{m_1 - m_2}{\rho_1} \right) + \left( \frac{m_2}{\rho_2} \right) \right]$$

Where: $m_1$ is the weight of wet membrane by water, $m_2$ is the weight of dry membrane, $\rho_1$ is the density of water and $\rho_2$ is the density of membrane materials.

11. Modification in polymeric nanofibers

There are still many challenges that need to avoid such as low water flux. These limitations can be avoided using membrane surface modifications. As shown in Fig.17, there are three ways to enhance nanofiber membrane water flux according to [87]: (a) Modification of nanofibers, (b) Functionalization on outer surface of membranes nanofibers, and (c) Coating the surface of membrane. In addition, composite membrane i.e (polymeric and ceramic nanoparticles) is another technique that can enhance membrane characteristics and improve its applications.
Fig. 17 Nanofiber membrane surface modifications. (A) nanofiber structure design; (B) nanofiber functionalize with target molecules; (C) membrane surface coating with interfacial polymerization (adapted from [87]).

11.1 Nanoparticles within polymer matrix.

Carbon Nanotubes (CNTs): Carbon nanotubes have many advantages appropriate for enhancing water flux of polymeric membranes such as narrow size distribution, atomic scale smoothness, uniformity of the tubes, outstanding biofouling resistance, and chemically inert interior walls [88]. CNTs among polymer matrix provide a porous network through their hollow nanotubes, this creates external nanotubes within the membrane and helps to improve membrane permeability [89, 90]. Moreover, CNTs can disrupt bacteria, viruses, and remove the microbial contaminants from drinking water [91, 92].

Titanium dioxide (TiO2): There are several advantages of TiO2 NPs that make it more suitable in membrane technology applications such as easily tunable morphology, chemical resistance, and catalytic functionality, as well as antifouling properties [93-97]. The photocatalytic property of the TiO2 NPs facilitate the decomposition of organic compounds [98, 99]. Beside of that, TiO2 NPs used for filtration purposes due to its resistance of fouling by degrading the organic foulants which resulted in the nanocomposite membrane [100].

Zinc oxide (ZnO): Zinc oxide nanoparticles (ZnO NPs) are widely used in membrane technology. As an example of that, ZnO NPs was used with PVC polymer to modify membrane morphology and enhance its performance. Addition of ZnO NPs, increase water flux and improve water flux recovery ratio [101]. Addition of ZnO NPs within polymer matrix increased water flux of the membranes from 213 kg/m².h for the bare PVC membrane to 402 kg/m².h for 3 wt.% ZnO/PVC membrane. This was mainly due to the resulted higher surface hydrophilicity of the modified membranes and sufficient porous structure. However, increasing of ZnO NPs water permeation could be decreased, this is due to the nanoparticles’ agglomeration and dense morphology at ZnO concentration. Previous studies showed that ZnO NPs improve water flux ratio and composite membranes showed much higher antifouling properties compared to bare membrane [101].

Silica (SiO2) NPs: Silica is the second most prominent element in the earth crust after oxygen [102]. Silica released in soil by means of biological or chemical processes [103-106]. In addition, silica is an important inorganic material with extensively wide application such as molecular sieves, catalysts, biomedical, and electrical applications [107-113]. Among metal oxide nanoparticles, SiO2 NPs is widely used to improve membrane properties such as stability, mild reactivity, excellent resistance towards chemicals and solvents as well as easy synthesis [114]. The use of silica nanoparticles at different concentrations has reported to improve mechanical strength [115-118] and thermal stability of membrane [119].

11.2 Graphene oxide (GO): Recently GO is widely used in several application, especially water distillation applications. GO’s abundant functional groups, include epoxide, carboxyl and hydroxyl, provide functional reactive sites, and hydrophilic properties. Its amazing resulted membrane with a thin thickness and nanocomposite content has been applied in pressurised filtration. Its consider as an ideal candidate for the of water desalination application [120]. This is due to multilayer GO laminate have a unique architecture and superior performance that push industry ad research to design a novel desalination membrane technology. Furthermore, GO have many advantages including good mechanical properties, easily fabricated, and ability manufactured in industrial scaled in the near future. Beside of improving of membrane pore size and subsequently increase water flux [121].

Conclusion

Water purification and filtration are essentially in daily life and there are may wastewater are generated. As a result, membrane tecnology considered as an important for water purification and living organism disinfection as well as sepration. Still there are many challenges during membrane sepration and purification such as low flux, antifouling. These challenges are avoided through membrane fabrication by using polymeric membrane with a nanoparticles to increase water flux and creat a smart membrane with self cleaning and antibacterial effect as well as increasing water flux. In addation, avoiding pores blocking and thus eliminate antifouling and increase of membrane durability. This review foucs in ground water distribution in en and different types of membrane materials and modules and membrane surface modification techniques.
References


