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Short Communication: Requiring Reverse Osmosis Membranes Modifications – An Overview

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Abstract: Do really reverse osmosis (RO) membranes need modification to cover their disadvantages or enhance their efficiency? Are there any defects in RO membranes manufacturing that require modification? These questions are discussed here in this short review. Through the world, there are thousands of patents, publications, and PhD theses dealing with surface modification and grafting of RO membranes. This growing phenomenon should attract the attention of the scientific community for technologic and economic reasons. Due to the increasing water pollution levels, which overpassed the RO membranes capacities, there is an urgent need to manufacture RO membranes, with multidisciplinary characteristics and high performance regarding both salts removal and fouling resistance, before sending them to the market and avoiding to think to their following modification.

Keywords: Reverse Osmosis (RO), Membrane Modification, Desalination, Water/Wastewater Treatment, Membrane Fouling

1. Introduction

Over the decades since the population and pollution are growing, it is going harder to satisfy humankind water supplies [1-4]. In many continents most of the fresh water flows into the sea with very little drinkable water remaining [5]. Transportation of water from one point to another is also not a very practical solution. Oceans constitute 97% of water on earth which is undrinkable [6]. The surface water and water melted from glaciers are the two main sources of potable water, which constitute less than 0.4% of total water [4, 7-10].

Several processes have been employed to increase the potable water supply [11-13]. Wastewater treatment has been accorded a good part of significance since it will not only help us enhance our water supply but also avoid more water contamination. Treated wastewater can be employed in irrigation, as a potable water source and in several industries for producing and other similar objectives. Brackish water which is not as contaminated as seawater can also be treated by this method. It is therefore vital to recycle undrinkable water (such as saline water and wastewater) to satisfy its increasing demand. Nowadays the techniques employed to reclaim wastewater are multistage flash distillation and reverse osmosis (RO) process. The distillation process is frequently used only in regions where energy production is available [4].

RO process has been largely used and continuous actions have been performed to regulate it to be very performant in producing convenient water without overconsuming energy [14-18]. To get familiarized with RO we have to know the basic of osmosis [19, 20]. By osmotic processes we are able to recuperate water from these polluted resources [21, 22]. Osmosis is a natural process which when regulated following its pressure difference characteristic can be employed in different applications [23]. These applications [24-26] comprise desalination, water and wastewater treatment, etc. The different configurations of osmosis are forward osmosis, RO and pressure retarded osmosis [4, 27-30].

Any osmosis process needs a membrane [31-34]. It is any support material capable of separating one substance from another: organic or inorganic, natural or synthetic [32, 35]. In osmosis technique different synthetic polymeric membranes have been examined to separate water from different aqueous solutions [4, 36-39].

This short review tries to show the increasing interest accorded to surface modification of RO membranes. A long list of pertinent and recent references is examined. A brief definition of RO is given.

2. RO

2.1. Definition

Osmosis is a natural process in which a solvent (water) travels through a semi-permeable material boundary, i.e. through a membrane from the side with lower solute (frequently salt) concentration to the higher solute concentration [40-42]. Water flows till there is an equilibrium state between the two media [43]. Equilibrium is a situation when the chemical potential, or the gravitational potential, on both media of the solution is identical [44]. The pressure difference between the two media of the membrane is equal to the natural osmotic pressure difference or osmotic gradient of the solution [45]. In desalination process, the salt concentration has to be removed, i.e. water must pass from a medium of high salt concentration to a low salt concentration [46, 47]. To attain this, pressure bigger than the osmotic pressure gradient between the two media is imposed to the salt water [48]. Therefore, water from the solution travels from high concentration of solute (salt) to a low concentration [49]. This process of imposing external hydraulic pressure is called *RO* and is widely employed in desalination, water treatment purposes, etc. [4, 50-53].

Unlike many conventional separation technologies such as distillation or ion exchange, RO set up is simple in design [54, 55]. RO can simultaneously manipulate separation of organic as well as inorganic substances. RO is a pressure-driven technique [3]. Therefore, there is no chemical change or any heat exchange, phase change process [4, 56].

A RO membrane performs as the semi-permeable boundary to flow of solute in the RO process [57, 58]. It permits selective travel of a particular species like water while partially or completely retaining other species (solutes) [59]. RO can separate solute particles as small as 0.1 to 1 nm [4, 60].

2.2. RO Membrane Materials

Materials employed to produce RO membranes are function of the type of application for which it will be employed [61]. Both physical and chemical types of the polymer impose the membrane manufacturing [62]. An acceptable RO membrane has to be resistant against chemicals and microbes [63]. It has to be mechanically and structurally stable over a long time [64]. It has to possess a great selectivity for certain solutes. These membranes are usually hollow fiber or flat [65]. They are arranged in modules to provide maximum surface area per unit volume of the membrane [66]. The hollow membranes are frequently furnished in bundles and then utilized in the RO technique [4, 67-70].

The most frequently employed RO membrane materials are cellulose acetate, polyamide, any heterocyclic polymer, crosslinked water soluble polymers and polymerizable monomer (formed by crosslinking), polybenzimidazole, polyacrilonitrile, poly-piperazinamides, etc [71-75]. However, they are broadly classified into two groups: asymmetric membranes containing one polymer, and thin-film, composite membranes consisting of two or more polymer layers [4, 76-82].

Cellulose acetate membrane is the most well-known asymmetric or anisotropic membrane structure discovered by Loeb and Sourirajan in 1960. It has a very thin solute rejecting layer on a coarse supporting layer [83]. The supporting layer is also frequently produced of the same material as that of the selective layer but the thickness of the selective dense layer imposes fluxes and rejection and the global efficiency of the membrane [84]. The supporting layer just provides mechanical strength to the membrane. These membranes are usually made using non-solvent-induced phase inversion or polymer precipitation method. Loeb and Sourirajan made the first asymmetric cellulose acetate membranes for RO. An issue with asymmetric membranes is that they are very thin, of ~ 0.1 to 1 μm; consequently, they give largely great fluxes without performant rejection [4].

After cellulose acetate, it was the period of linear aromatic polyamide membrane [85]. It avoided a part of the disadvantages of cellulose acetate membranes [86]. At the first line with cellulose acetate membranes, linear aromatic polyamide membranes became popular. Polyamide is one of the most performant selective layer know until now. They possess a great rejection performance which can be employed for single state seawater desalination. However, still these membranes were as thin as cellulose acetate membranes (0.1 to 1 μm) thick and great fluxes issue continued [4].

The thin film composite membranes were invented by Cadotte and his coworkers in 1970s (Figure 1) [4]. It is composed of a dense active layer of ~ 200 nm upon a porous polymer support. A non-woven fabric is fixed to provide a support (Figure 1). The porous support layer is usually 50 μm of thickness. The support layer regulates all the water flux, salt flux and therefore the water and salt molecules diffusion processes. The non-woven support fabric is ~ 120 μm thick and is responsible for handling the great hydraulic pressures during RO process (Figure 1). Consequently, the mechanical strength of the support fabric has to be elevated. Polysulfone, polycarbonate and poly (phenylene oxide) are the three well-known polymeric substrates available in RO industry. Polysulfone has the best efficiency and is largely employed commercially [4].

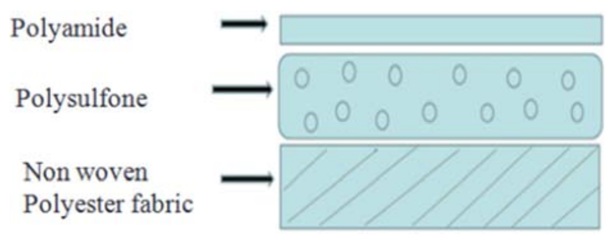

Figure 1. *Structure of a thin film composite membrane [4].*

These membranes are produced by interfacial polymerization, i.e., polymerization at the interface of two immiscible liquids. The polymeric substrate is immersed in an aqueous solution of amine monomer. Then, it is immersed in acyl chloride monomer for the interfacial polymerization to happen. This conducts to the formation of very thin highly selective polyamide rejection layer on the polymeric substrate [4].

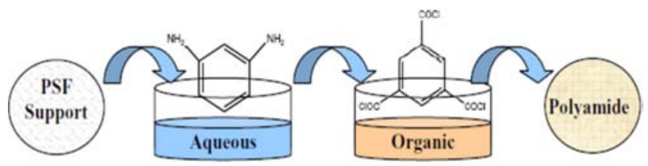

Figure 2. *Formation of a thin film composite membrane [4].*

The thin film composite membranes provide high water molecule diffusion velocity, very performant mechanical properties and stable over a large pH interval [4]. They have very elevated rejection. However, the fouling of thin film composite membranes is a very hard issue in the industrial applications [3, 86-91]. Different manners have been employed to well calculate the thin selective layer to decrease fouling [92-96]. Until now, there are different other issues attached to RO applications [4, 97-101].

In order to understand the issues in RO plant, we have to get familiarized with the working of a typical RO plant. First, the saline feed water is pumped to a pre-treatment stage. In this step, all large particles are removed which may clog the membrane and decrease its performance. The saline water is then sent at an elevated pressure using hydraulics to the membrane assembly where salt and other minerals are removed by the RO technique. After the membranes have finished their task, the water is separated in two streams: the feed water, and the brine water which is frequently discharged. A post-treatment is performed to stabilize the feed water [4].

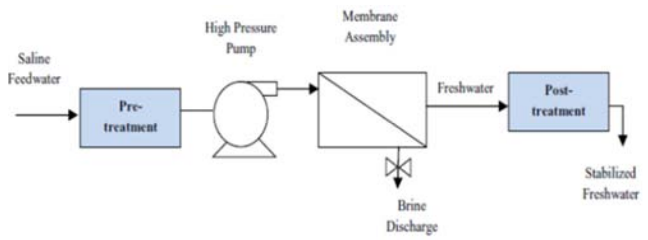

Figure 3. *Working of RO plant [4].*

2.3. Problems Arising in RO Process

Despite the thin film composite membranes have fixed a new level in RO process, they suffer from compaction effects under pressure [102-104]. If the applied hydraulic, or consequently the water pressure, is elevated, the polymers will be reoriented in a various direction that conducts to a lower porosity and finally influencing the membrane efficiency [4].

Surface or internal fouling of membranes is a very frequent issue [105-108]. Fouling is the precipitation of foulants on the membrane surface [109,110]. Foulant is any specie (solutes) which enters in interaction physically or chemically with the membrane [109]. They can be organic, inorganic, bio-compatible or colloidal [109, 111-113]. They strongly interfere with the travel of water through the membrane [114]. They degrade membrane efficiency and decrease its life span [115]. Consequently, membranes require to be changed usually conducting to elevated operating costs [116]. The great reason of fouling is the elevated pressures implicated in RO [4, 117-119]. RO is always opposite in direction to the natural water flow gradient [120]. Naturally, water flows from an area of low solute concentration to elevated solute concentration [121]. In RO, we push water out of an area of elevated solute concentration [122]. For this reason, a pressure, significantly bigger than the osmotic gradient of water, is needed [123]. Great hydraulic power is needed for the same cause [124]. This further elevates operating costs [125]. Feed water recovery is also restricted in RO which makes the brine discharge greatly concentrated [126]. This can have huge ecological effects on usage in coastal areas [4, 127-130].

2.4. Concentration Polarization as an Important Factor Affecting Performance of Membranes in RO Process

In RO process, the effects of concentration polarization are taken into account only on the feed side of the membrane [131, 132]. This is attributed to the fact that we take in consideration the mass transfer on the feed side of membrane which is pressurized [133]. Convective forces push the solute to pass from the bulk solution to the surface of the selective rejecting layer. Water permeates through but the solute remains on the surface at high concentrations. The water flux or the pressure with which water travels through the membrane has to be greater than the pressure produced because of this salt layer concentration. This deposition of salt on the surface which influences the water flux through the membrane is mentioned as *concentration polarization* rather *external concentration polarization*. This is also one of the reasons why higher external pressures are needed in RO [4, 134-137].

3. Conclusions

This short review tried to answer to some questions such as: Does RO membranes manufacture need a fundamental reformulation to meet the treated water qualities requirements?

RO is nowadays the number one desalination industry and it knows huge increase in the world market. Until now, polymeric membranes have overpassed the RO desalination technology. Until the 1980s the research focused on the optimum polymeric membrane materials. In following decades the efficiency of RO membranes has been elevated via control of membrane manufacture mechanisms. On the other hand, the increasing registered water pollution levels qualitatively and quantitatively have overpassed the RO membranes capacities.

The appearance of nano-technology in membrane materials industry could present an interesting solution to polymeric materials. It is suggested that RO desalination efficiency will be more increased in the next few years; however, some challenges have to be resolved.

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