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Enhancement of surface properties and performance of reverse osmosis membranes after surface modification: A review

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Fouling Water purification ABSTRACT

Reverse osmosis (RO) membrane process has become the most promising technology for desalination to produce purified water. Among numerous polymeric materials used to fabricate RO membranes, aromatic polyamide thin film composite (TFC) membranes are dominant in commercial RO membrane processes because of their high salt rejection and water permeability as well as their excellent chemical, thermal, and mechanical stability. However, the major hindrance to the effective application of polyamide TFC RO membranes is membrane fouling. Furthermore, polyamide TFC RO membranes have limited stability to chlorine, which is commonly used as disinfect to control membrane biofouling. These two factors deteriorate membrane performance and shorten membrane life span.

Membrane fouling depends strongly on membrane surface morphology and properties. Up to now, many physical or chemical surface modifications have been reported to alter the surface properties so as to improve the fouling resistance of the RO membranes. In this paper, different kinds of RO membranes fouling, chlorine effects, factors that influence RO membranes fouling, and the ways for reduction of fouling in RO membranes were discussed. Moreover, as a main part of this paper, all physical and chemical surface modification methods for fabricated polyamide TFC RO membranes were completely reviewed.

1. Introduction

Today water scarcity is one of the most serious global challenges and needs to be urgently solved, as it is exacerbated by population growth, industrialization, and climate change [\[1,2\]](#page--1-0). The fact that only around 0.8% of the total earth's water is fresh water conduct numerous researches in an effort to develop more sustainable technological solutions that would meet increasing water consumption [3–[6\].](#page--1-1)

Desalination is the process of removing salts or other minerals and contaminants from seawater, brackish water, and wastewater effluent and it is an increasingly common solution to obtain fresh water for human consumption and for domestic/industrial utilization. Desalination technologies can be classified by their separation mechanism into thermal and membrane based processes. Thermal desalination separates salt from water by evaporation and condensation and includes multistage flash (MSF), multiple effect distillation (MED), and vapor compression (VC). In membrane desalination, water diffuses through a membrane, while salts are almost completely retained and includes reverse osmosis (RO) and electrodialysis (ED) [7–[13\].](#page--1-2)

While thermal desalination has remained the primary technology of choice in the Middle East due to easily accessible fossil fuel resources and the poor water quality of the local feed water, RO membrane processes have rapidly developed and now surpass thermal processes in new plant installations [\[3,14](#page--1-1)–16]. [Fig. 1](#page-1-0) shows the global desalination capacity by process, highlighting the high capacities shares of RO and MSF [\[17\]](#page--1-3).

There are many significant advantages of using membranes for industrial processes which make membranes as a popular technology in various fields such as water treatment. Membrane technology are modular which is easy to scale up, simple in operation, relatively low energy consumption, no chemical additives, etc. [18–[21\]](#page--1-4). Separation with membranes occurs because of the existence of a gradient across the membrane, and membrane processes may be divided into groups based on the specific type of gradient. The most common way of categorizing membranes is to divide them into two groups: non-pressure driven and pressure driven. In non-pressure driven membrane processes, the driving forces are concentration gradient (such as gas separation and pervaporation), temperature gradient (membrane distillation), and electrical potential gradient (electrodialysis). The pressure driven process includes four main groups depending on the size of particle they retain: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) [\(Fig. 2](#page-1-1)) [22–[27\].](#page--1-5)

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Fig. 1. Global desalination capacity by process [\[17\]](#page--1-3).

Fig. 2. Particle size retention for pressure driven membranes [\[26\].](#page--1-15)

Polyamide TFC RO membranes are the dominant technology for fresh water supply, but the major obstacles for application of these membranes is membranes fouling. Also, those RO membranes are vulnerable to chlorine. These two factors cause a decrease of membranes permeability, deterioration of permeate quality, increases in energy consumption, and shortening membranes life. In this paper, the basic principles of polymeric RO membranes and their drawbacks are completely reviewed. Also, the surface properties of RO membranes are explained. In addition, the methods for reduction of RO membranes fouling are introduced. Moreover, as a main part of this article surface modification of polyamide TFC RO membranes for improving the membrane surface properties and performance of those RO membranes are thoroughly reviewed.

2. Reverse osmosis membranes

Today reverse osmosis membrane is the most widely used desalination process. Over the past few decades remarkable advances have been made in the preparation of RO membranes from different materials. Commercial interest in RO technology is increasing globally due to improvement in RO technology in terms of membrane material and energy consumption, which has enabled a reduction in cost of pure water production [28–[30\]](#page--1-6).

There are two parameters used to indicate RO membrane performance: water flux and salt rejection. Water flux, J_w , is the superficial velocity of water through the membrane, and is defined as the amount of water transported across membrane per unit time per unit area. The water flux is described by:

$$
J_w = A(\Delta P - \Delta \pi) \tag{1}
$$

where, J_w is water flux (g/(cm² s)) (which can be converted to (L/ $(m² h))$), A is the intrinsic water permeability coefficient of the membrane ($g/(cm^2 s bar)$), ΔP is the transmembrane pressure difference (bar) and $\Delta \pi$ is the difference in osmotic pressure between the feed and permeate (bar).

In many cases it is more appropriate to refer to salt rejection, R, which is a measure of the ability of the membrane to separate solute from the feed solution. The definition of salt rejection is either the observed rejection (R_o) or real rejection (R_r) . Observed rejection is calculated from bulk (feed) and the permeate concentrations according to:

$$
R_o = 1 - \frac{C_P}{C_b} \tag{2}
$$

While the real rejection is calculated from membrane surface and the permeate concentrations as:

$$
R_r = 1 - \frac{C_p}{C_m} \tag{3}
$$

Here, the difference between C_m and C_b is due to rejected solute concentration polarization ([Section 5\)](#page--1-7) [\[31](#page--1-8)–35].

Polymeric RO membranes have dominated commercial applications. Due to their technological maturity they offer low-cost fabrication, ease of handling and improved performance in selectivity and permeability [\[29\].](#page--1-9) Aromatic polyamides and cellulose acetate (CA) are two of the main polymeric materials used in the fabrication of commercially available RO membranes [\[36\]](#page--1-10).

Cellulosic derivatives and their fabricated membranes have shown a number of good properties, including hydrophilicity, mechanical strength, wide availability, chlorine tolerance, fouling resistance, and low cost. However, CA membranes have some drawbacks [\[37,38\]](#page--1-11). These membranes are known to undergo hydrolysis in both alkaline and acidic conditions. The operational pH range for these membranes is hence very narrow (pH 4–6). Slow hydrolysis increased the flux, but reduced the rejection drastically [\[28\]](#page--1-6). The rate of hydrolysis also increases with temperature, and therefore CA is limited to an operating temperature below 30 °C. Furthermore, CA membranes are compacted under high operating pressures causing a period of flux decline [\[39\].](#page--1-12)

Since the concept of interfacial polymerization (IP) of creating polyamide thin film composite membrane was introduced by Cadotte [\[40\]](#page--1-13), the polyamide TFC membranes form the most important and widely used class of RO membranes [\[23,28\]](#page--1-14).

Polyamide TFC RO membranes are composed of three layers: an ultra-thin skin polyamide polymer barrier layer on the upper surface, a microporous interlayer support, and a non-woven polyester fabric base acting as structural support as shown in [Fig. 3](#page-1-2). The polyester support layer cannot provide direct support for the barrier layer because it is too irregular and porous. Therefore, between the barrier layer and the support layer, a microporous interlayer is added to enable the ultra-thin barrier layer to withstand high pressure compression [\[29\].](#page--1-9)

Polymer barrier layer:

· Ultrathin, < 200 nm.

Fig. 3. Schematic illustration of a polyamide TFC RO membrane [\[41\].](#page--1-16)

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