



Membrane fouling and modification using surface treatment and layer-by-layer assembly of polyelectrolytes: State-of-the-art review



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ARTICLE INFO

Article history:

Received 25 August 2015

Received in revised form 18 March 2016

Accepted 19 March 2016

Available online 4 April 2016

Keywords:

Fouling

Polyelectrolytes

Layer-by-layer assembly

Reverse osmosis

Membrane

ABSTRACT

Membrane technology has been recognized as one of the most important technologies in water desalination. However, this technology is challenged with the fouling phenomenon which causes higher operating pressure, flux decline, frequent replacement of membranes and eventually higher operating costs. Therefore, researchers have focused on developing methods to overcome this problem and to enhance the membrane resistance to fouling. In this paper, we reviewed the membrane fouling and control through surface modification techniques. Special attention was paid to the layer-by-layer assembly of polyelectrolytes (LbL) which has been widely used as a powerful technique for surface modification and multifunctional film preparation. Furthermore, detailed effects of LbL key-parameters on the membrane performance were revealed to help understanding the working mechanism of this method.

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Abbreviations: PDADMAC, poly(diallyldimethylammonium chloride); SPEEK, sulfonated poly(ether ketone); PAH, poly(allylamine hydrochloride); PET, poly(ethylene terephthalate); PEBAX, polyether-polyamide block co-polymer; BSA, bovine serum albumin; PSS, poly(styrene sulfonate); PEI, poly(ethylene imine); PVA, poly(vinyl amine); PVS, poly(vinyl sulfate); PAN, poly(acrylonitrile); PAA, poly(acrylic acid); PEG, poly(ethylene glycol); PEO, poly(ethylene oxide); PAA, poly(acrylic acid); SA, sodium alginate; CHI, chitosan.

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1. Introduction

Improving the access to clean drinking water is a serious concern around the globe [1]. According to WHO/UNICEF report of 2004, more than 1.1 billion people did not have access to better drinking water facilities and two third of this belongs to Asia [2]. Many countries in North Africa, South Asia, Middle East, part of Europe and western America is under high water stress index and this dispute is supposed to advance worse in the upcoming years [3].

Desalination is the technology that converts saline seawater (or brackish water) into clean drinkable-water. It can have a substantial effect on water shortage around the globe [4] and could be the best solution to overcome water scarcity [5].

The first major desalination plant based on distillation was built in Netherlands in 1928 with an operating capacity 60 m³/day. Then, Saudi Arabia built a desalination plant in 1938 [6]. Currently, more than 150 countries have desalination plants [7], of which 48% of global production is associated to the Middle East. In the Middle East, 61% of the desalination capacity belongs to six Gulf States in which the installed desalination capacity of Saudi Arabia alone is more than 5.25 million m³/day [8]. Fig. 1 represents the capacity of desalinated water of each region along with the type of source water [9]. The overall global capacity of desalinated water in 2008 was estimated as 61 million m³/d [10]. Nowadays, the total desalination capacity of the world has reached about 100 million m³/d [11].

The main technologies to accomplish desalination are split into two sets: thermal distillation and membrane separation. Thermal distillation technologies are energy intensive [12–14] and include Multi Effect Distillation (MED) and Multi Stage Flash (MSF) whereas membrane separation includes reverse osmosis (RO). RO is a rapidly developing approach to obtain pure water by removing salts from seawater or any other origin of saline water. Currently, the largest percentage of desalination plants is based on RO followed by MSF as shown in Fig. 2 [15].

The reason behind greater contribution of RO is its lower energy requirements of 4–7 kWh/m³ for seawater [16] compared to high energy demand of 15.5 kWh/m³ for MSF. The marketplace for RO equipment and membranes by the end of 2014 was around \$5.4 billion and it is expected to stretch to \$8.8 billion by 2019 with a compound annual growth rate of 10.5% [17].

The desalination technology is growing so fast that number of patents regarding desalination has been duplicated as it was in 2005. The reason behind this improvement is the development of high efficiency pumps, the evolution of energy recovery devices [18], and the development of new and efficient membranes. However, this technology is challenged with the fouling phenomenon which causes higher operating pressure, flux decline, frequent replacement of membranes and eventually higher operating costs. Therefore, researchers have focused on developing methods to overcome this problem and to enhance the membrane resistance to fouling.

2. RO membranes, fouling, and modification

In RO membranes, the separation of the dissolved salts is accomplished because of the hydraulic gradient that is created across the semi permeable membrane. The first commercialized RO membrane was developed by Loeb from Cellulose Acetate (CA) by using phase inversion method [19]. It showed better performance at that

time but CA membrane is easily compacted and hydrolyzed in the presence of water which leads to flux decline and eventually results in low efficiency of the system. The real boost in design of composite membrane was brought by Cadotte et al. [20] who introduced thin film composite membranes (TFC). He used interfacial polymerization in which very thin membrane of aromatic polyamide material is synthesized straight on the surface of polysulfone support [21]. The composite membrane consists of bilayers formed in two steps that are totally different from each other while the asymmetric CA membrane is homogenous in chemical composition and formed in one step. The structure of typical TFC membrane is shown in Fig. 3 [22].

A typical TFC RO membrane comprises of three layers that are polyester (130 nm thick), polysulfone (40 nm thick) and polyamide (0.3–3 nm thick). The non-porous polyamide layer is the active layer that is responsible for salt rejection. The advantage of TFC membrane over the asymmetric membrane is that each particular layer in a TFC membrane can be adjusted for its certain function. The thin barrier layer is adjusted to get a required consolidation of solvent flux and rejection of solute. The porous layer which acts as a support enhances the strength and provides compression resistance along with minimum flow resistance [22]. The detailed synthesis of polyamide membrane (PA) via interfacial polymerization using m-phenylene diamine (MPD) and trimesoyl chloride (TMC) is discussed by Chai and Krantz [23].

2.1. RO membrane fouling

Membranes effectively remove contaminants from drinking water while fouling increases operating expenses and decrease the applicability of membrane process. Membrane fouling can be defined as “A condition when membrane experiences blocking or coating by some component present in the processed stream, which eventually results in declining of flux” [24]. To some extent, fouling occurs in all RO systems. It is a leading restrictive feature in RO applications. Generally speaking, there are two fouling mechanisms that are commonly observed in membrane developments. These two mechanisms include fouling at the surface and in the pores. As far as RO membranes are concerned, they don't have distinct pores and are considered to be principally dense. Therefore, surface fouling is prominent in RO membranes [25].

Fouling of membranes can happen under various conditions which eventually require cleaning. The severity of the fouling decides the cleaning frequency, which depends on several variables such as recovery rate of the system, characteristics of feed water and pretreatment methods. Because all membrane systems are attacked by fouling, it is better to understand the basic types and their origin which will allow enhancing the valuable life of RO membrane element along with improved efficiency and economy of RO plant [26].

2.1.1. Types of fouling

RO membrane elements are attacked by different types of foulants that can be broadly categorized into four types: suspended particulate matter, dissolved organic substance, dissolved objects, and biological material [15,27–29]. Because of the repulsive potential by electrical double layer of charges, suspended solids preserve their suspended position and when the attraction forces (van der Waals forces) reduces the electrical repulsion, these stable suspended solids become unstable and form agglomerate. Eventually,

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