International Journal of Advanced and Applied Sciences, 5(2) 2018, Pages: 60-64

Contents lists available at Science-Gate

International Journal of Advanced and Applied Sciences

Journal homepage: http://www.science-gate.com/IJAAS.html

Membrane post-synthesis modifications and how it came about

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ARTICLE INFO

Article history:
Received 27 September 2017
Received in revised form
8 December 2017
Accepted 12 December 2017

Keywords:
Reverse osmosis (RO)
Membrane modification
Desalination
Water/wastewater treatment
Membrane fouling
Thin-film composite (TFC)

ABSTRACT

Nowadays, reverse osmosis (RO) is the most largely utilized desalination process at the World level. During the three last decades, amazing progress has been realized in the manufacturing of RO membranes using different materials. However, what is astonishing here is the fact that a new research field was open in a relatively short time with hundreds of scientific publications and patents which are made on membrane post-synthesis modifications in order to improve the structural properties and desalination performance opening a large debate about the membrane fabrication techniques and membranes capacities to deal with various water pollutants. This review aims to discuss this extra technological field dedicated to membranes modifications following their fabrication. As conclusions, membrane fabrication methods are a well-established and developed technology which however needs more technical improvements to overcome the needs of a post-synthesis industry and satisfy quantitatively and qualitatively the water guidelines. On the other hand, the large chemical products use in both membranes synthesis and post-synthesis should be avoided or at least reduced, since monomers, alcohols, acids and bases risk to be realized into drinking water. That is said because RO process has been presented hopefully as a promising powerful and green technology instead of chlorination and coagulation/flocculation which are proven highly polluting with their toxic metal salts injection and poisonous disinfection by-products formation.

1. Introduction

The shortage of access to drinking water and wastewater purification is a crucial origin of health problems and a barrier to potential development for a great portion of the worldwide inhabitance (Lee et al., 2011; Fry et al., 2008; Montgomery and Elimelech, 2007). Several growing states are undertaking fast manufacturing in the absence of convenient wastewater disposal frameworks, and are now knowing augmenting water pollution problems while yet fighting with bad water feeding and purification issues (WHO, 1997). Following the World Health Organization, there are more than 2.5 billion human beings (~40% of the World's inhabitance) that do not possess approach to sewer purification frameworks (UNICEF, 2008). Simultaneously, potential supply of proper water supplies is crucial to all states regardless of their dimension. The turn to biofuels will increase more important requests for water (Shannon et al., 2008). In several situations, born water provisions are reducing as a consequence of weather variation and unlimited usage, and resolutions such as water conservation and water transport, or construction of new dams, are not enough to satisfy the growing request. Consequently, the most demanding provocations nowadays comprise the recuperation of proper potable water from salty or seawater, by widely the most plentiful worldwide water resource, and the treatment and recycle of wastewater. Desalination, as an applied science that transforms saline water into clean water, gives one of the most vital resolutions to these issues (Gleick, 2009).

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https://doi.org/10.21833/ijaas.2018.02.010

Nowadays, reverse osmosis (RO) is the most largely utilized desalination process at the World level. During the three last decades, astonishing progress has been realized in the manufacturing of RO membranes using different materials.

However, what deserves to be noted here is the fact that a new extra research field was surprisingly open in a relatively short time after RO discovery and industrial applications with a huge number of scientific publications and patents which are made on membrane post-synthesis modifications aiming to improve the RO membranes' structural properties and desalination performance. The membrane post-synthesis modifications field development imposes an opening of a large debate about the membrane fabrication techniques and membranes capacities to deal with various water pollutants. This review aims to discuss this extra technological field dedicated to membranes modifications following their fabrication.

2. Actual up-to-the-minute RO applied science

RO is nowadays the most significant desalination applied science. It has surpassed classical thermal applied science such as multi-stage flash (El-Dessouky et al., 1995) and is predictable to preserve its control in the next decades, despite the fact that modern techniques such as membrane distillation (Hsu et al., 2002), electrodialysis (Sadrzadeh and Mohammadi, 2008), capacitive deionization (Porada et al., 2013) and forward osmosis (McGinnis and Elimelech, 2007) have been suggested.

Trade attention in RO technique is growing worldwide because of constant process enhancements, which successively conduct to important cost lowering. These improvements comprise growths in membrane materials and module conception, process conception, feed pre-treatment, and energy recuperation, or decrease in energy utilization. The improved mechanical, biological and chemical hardness of RO membranes, as well as the increased permeability, have decreased the membrane cost per unit volume of water treated by more than 10 times since 1978. The joined endeavor to reducing fouling and concentration polarization (Xie et al., 2014), and make as great as possible permeate flux and energy recuperation, has reduced the energy consumption from 12 kWh/m^3 in the 1970s to less than 2 kWh/m^3 in 2006 (Lee et al., 2011).

However, the most important performance advantages have emerged from the enhancement of the membranes. The structure, material, and morphology of RO membranes have been changed to ameliorate permeability, selectivity, and applicability (mechanical, chemical and biological stability). The actual RO membrane market is controlled by thin film composite (TFC) polyamide membranes composing of three films: A polyester grid working as structural support (120–150 µm thick), a microporous interfilm (about 40 µm), and an ultra-thin barrier film on the upper surface (0.2 µm) (Petersen and Cadotte, 1990). The polyester support grid has not the capacity to give direct support for the barrier film as it is too asymmetrical and porous. Consequently, enter the barrier film and the support film, a micro-porous interlayer of polysulfonic polymer is joined to allow the ultra-thin barrier film to resist elevated pressure compression. The thickness of the barrier film is decreased to diminish opposition to the permeate diffusion. Membrane pore size is usually less than 0.6 nm to obtain salt refusal systematically greater than 99%. The selective barrier film is most frequently produced of aromatic polyamide, for example via interfacial polymerization of 1,3-phenylenediamine (also known as 1,3-benzenediamine) and the tri-acid chloride of benzene (trimesoyl chloride) (Cadotte, 1977). With enhanced chemical resistance and structural robustness, it provides acceptable allowance to pollutions, improved durability and simple cleaning properties (Lee et al., 2011; Liu et al., 2014).

The spiral wound membrane module configuration is the most largely employed conception in RO desalination. This configuration provides elevated specific membrane surface area, easy scale up operation, inter-changeability, low replacement costs and, most importantly, it is the least expensive module configuration to manufacture from flat sheet TFC membrane (Pearce, 2007; Polasek et al., 2003). In spite of the fact that the spiral wound configuration was presented decades ago, enhancements in the dimensions of spacers, feed channels and vessels, as well as the materials of construction, have optimized the inter-connection enter module design and fluidic transport properties, that way reducing both fouling and pressure losses (Lee et al., 2011).

3. Membrane post-synthesis modifications

After the radical triumph of the submitting of crosslinked fully aromatic polyamide TFC RO membranes into the market, research and development across novel polymeric materials for RO membranes has reduced greatly. Actual products from important producers of RO desalination membranes are yet founded on the primary chemistry found through the 1980s, i.e. interfacial polymerization of monomeric aromatic amines. The gigantic producers of desalination membranes: DOWFILMTEC™ presently sells products founded on FT-30; membranes supplied by Toray are founded on UTC-70; Hydranautics membranes are founded on NCM1, which is identical to CPA2; and Trisep membranes are founded on X-20. But then, asymmetric membrane products are yet founded on the classical cellulose acetate materials; as an example, the Toyobo Hollosep™ interval of products is founded on cellulose triacetate and is the major asymmetric RO membrane (Lee et al., 2011; Saeki et al., 2014a;b; Dong et al., 2015).

Regardless of the fact that no novel polymeric membranes has been presented in the marked lately

(Lee et al., 2011), the efficiency of RO membranes has yet enhanced enormously, i.e. water permeability has been at least doubled, and the recuperation of fresh water may be more than 60%. These enhancements are the fruits of surface modification, and direct controlling of interfacial polymerization reaction parameters, as well as more efficient conception of the module composition (Uemura and Henmi, 2008; Antrim et al., 2005; Bartels et al., 2008; Zirehpour et al., 2017). Moreover, better comprehension of the membrane composition, connected with progress in membrane description methods, has certainly had a significant contribution (Matsuura, 2001). As an example, Atomic Force Microscopy has been a helpful instrument which has assured that surface roughness of a membrane may importantly ameliorate permeability, while at the identical moment fixing elevated salt refusal because of the augmentation in efficient membrane area (Hirose et al., 1996).

It has been hard to follow post-1990 evolution of commercially significant RO membranes because of importantly decreased patenting action by membrane producers (Lee et al., 2011). To show the chemical structure and post-treatment that has been realized on commercial RO membranes, scientists have been joining the utilization of different analytical methods. Rutherford back scattering spectrometry is a strong instrument for elemental structure analysis at various films and physicochemical identification (Mi et al., 2006; Zhang et al., 2007;2017; Coronell et al., 2008;2010). An integration of different analytical methods, XPS, ATR-FTIR, TEM, and streaming potential measurement has also been utilized to obtain a better comprehension of both physical and chemical structure of the membrane and how it links to the membrane efficiency (Tang et al., 2007;2009a;b). Cahill et al. (2008) have reviewed the usage of different analytical methods for membrane identification.

3.1. Surface modification

An important field of membrane post-treatment research implicates hydrophilization, which may produce an augmentation in permeability and chlorine durability (Low et al., 2011; Vercellino et al., 2013; Emadzadeh et al., 2015). In spite of the fact that there has been several successes in producing membranes utilizing monomer chemical products with combined hydrophilic groups (such as carboxylate) and removed amidic hydrogen, the monomer chemical products utilized are not easily obtainable and the synthesis technique is complicated (Kim et al., 2000; Li et al., 2008; Roh et al., 1998; Moon et al., 2004). Consequently, post-remediation to change in a chemical manner the membrane surface characteristics is promoted, and different chemical and physical procedures have been conceived (Zhao et al., 2014). Different water soluble solvents, like acids and alcohols, have been employed to remedy the membrane area. Combinations of alcohol (ethanol and iso-propanol) and acid (hydrofluoric and hydrochloric acid) in water have also been utilized to ameliorate flux and refusal because of the fractional hydrolysis and skin change started by the alcohol and acid (Mukherjee et al., 1996; Anis et al., 2014). The existence of hydrogen bonding is pretended to promote influence among the acid and water, which gives more surface charge and finally ameliorates the hydrophilicity and water flux astonishingly. Mickols (1998) presented a patent about post-remediation of a membrane area with ammonia or alkyl compounds, especially ethylenediamene and ethanolamine, which obtained both improved flux and salt refusal (Lee et al., 2011; Kang and Cao, 2012).

3.2. Optimization of polymerization reactions

An additional domain of dense investigation is the optimization of interfacial polymerization reaction mechanisms, comprising kinetics, reactant diffusion coefficients, reaction time, solvent solubility, solution composition, nucleation rate, curing time, polymer molecular weight range, and properties of the micro-porous support (Song et al., 2005; Karode et al., 1998; Dhumal et al., 2008; Ghosh et al., 2008; Ghosh and Hoek, 2009). The premature triumph of Tomaschke (1990) and Chau et al. (1991) in utilizing added ingredients in the casting solution (amine reactants) has conducted to strong study in utilizing various types of added ingredients (Lee et al., 2011). The utilization of amine salts, like the triethylamine salt of camphorsulfonic acid, as an added ingredient in the aqueous amine reaction solution authorized post-reaction drying at temperatures bigger than 100°C. Consequently, a more cross-linked membrane was produced with an enhancement of the salt refusal without affecting the flux. Chau et al. (1991) combined polar aprotic solvents, particularly N,N-dimethylformamide, into the casting solutions which finally produced higher residues of carboxylate content and thus augmented the water permeability (Saeki et al., 2014 a;b; Dong et al., 2015)

The embodiment of additives into the casting solution has a fundamental contribution in modification of monomer solubility, diffusivity, hydrolysis, protonation, and they can also take action to scavenge inhibitory reaction by-products (Ghosh et al., 2008). Many patents divulge that the introduction of alcohols, ethers, sulphur-containing compounds, water soluble polymers, or polyhydric alcohol to the amine solution may ameliorate membrane permeability without important variation in salt refusal (Koo and Kim, 2000; Hirose and Ikeda, 1996; Koo and Yoon, 2000; Kwak et al., 2001). As an illustration, the miscibility of water and hexane has been enhanced by the introduction of dimethyl sulfoxide into the casting solution. Diffusion of the monomer amine reactants has been improved leading to the apparition of a thinner barrier film and ameliorated water flux (Kim et al., 2005; Ghernaout and El-Wakil, 2017).

4. Conclusion

The RO membrane post-synthesis modifications field is widely expanded. This amazing phenomenon needs to open a large discussion in terms of both scientific and technological aspects about the membrane fabrication techniques and membranes capacities to deal with increasing quantitatively and qualitatively water pollutants. This review aimed to treat this extra technological field dedicated to membranes modifications following their fabrication. Whereas nanotechnology is conducting the road in the expansion of new RO membranes for desalination, there are several basic scientific and technical aspects that have to be classified before the likely interests can be achieved. An example objective is the production of single-pass RO utilizing multifunctional membranes, avoiding the demand for pre-treatment. At this level, these new techniques are yet too expensive for practical application, and therefore the development of new RO membranes with enhanced salt refusal and permeability at an acceptable cost is yet the major attention of RO desalination applied science. Post-synthesis membranes modification should be avoided once synthesis techniques will be well designed and optimized to satisfy the required potable water qualities.

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