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Understanding the dependence of contact angles of commercially RO membranes on external conditions and surface features

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HIGHLIGHTS

► We investigated the effects of external conditions on RO-membrane contact angles.
► The relationships between surface features and contact angles were analyzed.
► The action mechanisms on contact angles were systematically reported.
► The contact angles of three RO membranes were first comprehensively reported.

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ABSTRACT

The contact angles of three kinds of typically commercial reverse osmosis (RO) membranes (LP21, ULP21, and FR11) were firstly investigated. The relationships between the contact angles and external conditions were researched by well considering the effects of sample pretreatment, water-droplet volume, environmental humidity, water temperature and salinity. Furthermore, the surface features of these RO membranes, including functional groups, surface roughness, and zeta potentials, were also analyzed for exploring their influences on the contact-angle values, by using attenuate total reflectance infrared (ATR-IR) spectra, scanning electronic microscopy (SEM), and streaming potential instrument. The experimental results suggest that the sample pretreatment makes the hydrophilicity of RO membranes decrease, because of the part removal of physically coated hydrophilic aliphatic alcohols and protect agents introduced in the synthesis process. The water-droplet volumes have no obvious effect on the contact-angle measurement results. The contact-angle values can be gradually decreased with the enhancements of the environmental humidity, external temperature, and water salinity. Moreover, it was found that the enhancements on the density of modified hydrophilic functional groups, surface roughness and surface zeta potential are favorable for the decrease of contact angles.
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1. Introduction

The increasing human population combined with exploitation of water resources for domestic purposes, industry, and irrigation has resulted in a shortage of fresh water supply in many parts of the world [1–4]. To circumvent the crucial issue, various desalination technologies such as multi-effect distillation (MED), multi-stage flash (MSF), and electrodialysis (ED) [5,6] have been recently developed. Compared with other techniques, a powerful strategy, seawater and/or brackish water desalination using membrane-based reverse osmosis (RO) technology has attracted worldwide attention, due to its low energy consumption [7–9].

At present, aromatic polyamide composite RO membranes are extensively employed in most of the RO plants [10,11]. They are usually composed of separation layers, supporting layers, and non-woven fabrics, which can be prepared by interfacial polymerization (IP) using 1,3-benzenediamine (BDA) and trimesoyl chloride (TMC) as raw materials [4,12]. The hydrophilicity of RO membrane has an important influence on its performances, especially for the anti-fouling property and permeate flux [13–16]. Usually, the excellent hydrophilicity can make the RO membrane have good fouling resistance to foulants, such as organic substances, microbes, and charged inorganic particles [16]. It is because that the excellent RO-membrane hydrophilicity can decrease the interaction between the foulant and the membrane surface. On the other hand, the improvement on hydrophilicity can favor enhancing the permeate flux of RO membrane [14,17], because of the increasing interaction between membrane surface and water molecule via hydrogen bond and/or electrostatic attraction. Therefore, many researchers are trying to increase the

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hydrophilicities of RO membranes for improving their anti-fouling properties and permeate fluxes by adjusting synthesis conditions, surface modification, and exploring new raw materials [13,18,19].

As we all know, the common-evaluation approach for the hydrophilicity of RO membrane is based on the contact angle formed between the liquid–gas tangent and membrane–liquid boundary [15,20,21]. Regarding this, it is necessary to accurately measure the contact angle, and more importantly, to understand the impacts of external conditions (sample pretreatment, water-droplet volume, water temperature and salinity, and environmental humidity) on the RO-membrane contact angles. By this way, it is also favorable for accurately comparing the contact angles of different RO membranes. Furthermore, it provides effective evidences for investigating the interaction mechanisms between water molecules and RO membranes under different external conditions. In addition, it is also favorable for analyzing the variations of anti-fouling property and permeate flux with water salinities and temperatures, respectively. Although researchers are very familiar with the contact-angle measurement method, the effects of external conditions on the measurement results do not draw the attentions of researchers. Up to now, there have been only few reports [22] concerning relationships between the external conditions and hydrophilicity. Hurwitz et al. [22] found that the contact angles of commercial XLE RO membrane decrease from 68.9 to 56.5° with the increases of the NaCl concentrations from 0 to 1000 Mm, which implies that its hydrophilicity gradually increases. Meanwhile, it is notable that no systematical research on the relationships between the external conditions and RO-membrane hydrophilicity has been reported.

On the other hand, RO-membrane contact angle has close relations with its surface features, including surface functional groups, zeta potential, and surface roughness [16,23,24]. By investigating the relationship between of them, the synthesis procedures can be effectively improved, for improving the hydrophilicity. At present, many lab-scale synthesized RO membranes were reported and their relationships between the contact angles and surface features were investigated [13,18,20]. It was demonstrated that the increase on the surface hydrophilic-group density, such as −OH, and $-NH_2$ groups, is favorable for improving the hydrophilicity [13,19]. Coarse membrane surface is advantageous for decreasing RO-membrane contact angle [4,14,15]. However, the proprietary of the manufacturers on the production techniques makes the membrane end-users and researchers can not comprehensively understand the hydrophilicities of commercial RO membranes. Sometimes, the related informations provided by membrane manufacturers can be misleading [14,15]. Until now, only few literatures [15] have reported the relationships of surface features and hydrophilicity for commercial RO membranes. The related action mechanisms have also not been systematically investigated. Tang et al. [15] reported that the contact angles of polyvinyl alcohol (PVA) coated commercialized LFC1 and LFC3 membranes are smaller than those of uncoated XLE and SWC4 commercial RO membranes, due to the presence of abundant −OH groups of PVA macromolecules. In addition, as excellent-performance RO membranes, ULP21, LP21 and FR11 membranes have been extensively employed for saline-water desalination. However, the dependences of the contact angles on their surface features has not been investigated until now.

Herein, the contact angles of three commercial RO membranes (ULP21, LP21 and FR11) have been firstly investigated. The effects of external conditions on their contact angles are detailedly analyzed including sample pretreatment, water-droplet volume, external temperature, environmental humidity, and water salinity. Furthermore, for exploring the dependence of their contact angles on surface features, the surface features have been characterized by using streaming potential instrument, SEM, AFM, and ATR-IR. The results show that the contact angle is obviously affected by sample pretreatment, water temperature, surrounding humidity, and water salinity. However, it cannot be impacted by water-droplet volumes in the measurement process. In addition, it was found that abundant hydrophilic functional groups, high zeta potentials and rough surfaces of RO membranes are favorable for the decrease of their contact angles.

2. Experimental

2.1. Chemicals and materials

KCl and NaCl (A. R.) were purchased from Tianjin Guangfu technology Co., Ltd. Purified water was supplied in-house from a MilliQ Advantage A10 Water purification system (Millipore, USA) with a resistivity of 18.2 Mohm-cm.

Three kinds of commercial polyamide RO membranes (ULP21, LP21, and FR11) were provided by Vontron Technology Co., Ltd. (China). Under the optimal operation condition provided by the manufacturer, the salt rejection and permeate flux of ULP21 membrane (1500 ppm of NaCl feed water, 150 psi working pressure, 25 °C) are 99.5% and 27 gal per square feet per day (GFD). For LP21 and FR11 membranes (2000 ppm of NaCl feed water, 225 psi working pressure, 25 °C), they exhibit the same salt rejections (99.7%), and the permeate fluxes for LP21 and FR11 membranes are 25 and 20 GFD, respectively.

2.2. Contact angle measurements

The contact angles of the commercial RO membranes were measured on KRÜSS DSA100 contact angle instrument (Germany) in sessile drop mode. Briefly, before the measurement, the parameters of the contact angle instrument were set as 60 V of voltage, 5000 μs of period, 100 μs of pulse, and 100 of drop count. Therein, "voltage" indicates the power of a single impulse. "Period" indicates the time for a single pulse. "Pulse" indicates the length of a single pulse, and "drop count" indicates how often the pulse sequence is repeated to form multiple drops. In this case, the droplet volume was about 0.05 μL. Then, a droplet of liquid (purified water and/or NaCl saline water) was delivered onto a RO membrane, and a static image of the droplet in equilibration with the membrane surface was taken. Image analysis and contact angle computation were performed using the drop shape analysis software assuming a circular profile of the droplet. For ensuring the accuracy, the measurements were performed at 10 different locations, and then the average value was regard as the final contact-angle result.

2.3. RO-membrane pretreatment

For investigating the influence of sample pretreatment on the hydrophilicity, the contact angles of the fresh commercial RO membranes were firstly measured using the above method, and the used liquid droplet was purified water. Then, the three freshly commercial RO membranes were pretreated using the following approach: a small piece of membrane coupon was immersed in 300 mL of purified water for 24 h at room temperature. Then, it was rinsed with 100 mL of purified water for 3 times and dried in vacuum oven for 24 h at 60 °C. After this, their contact angles were determined again. In addition, the environmental temperature and relative humidity were fixed at 25 °C and 30%, respectively.

2.4. ATR-IR spectroscopy characterizations

For analyzing the relationships between the hydrophilicities and surface functional groups of commercial fresh and pre-treated RO membranes, their ATR-IR spectra in the range of 4000–400 cm^{-1} were collected on a VERTEX 70 IR spectrometer (Bruker, Germany) in the ATR mode, respectively. The ATR accessory contained a ZnSe crystal at a nominal incident angle of 45°, yielding a single reflection on the membrane surface. In addition, the IR spectra of the pretreated RO membranes heated in different temperatures (40–90 °C) were

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