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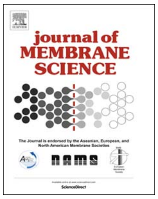

Preparation of high water flux and antifouling RO membranes using a novel diacyl chloride monomer with a phosphonate group

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ABSTRACT

A novel diacyl chloride monomer dimethyl (3,5-bis(chlorocarbonyl)phenyl)phosphonate (compound(I)) with a phosphonate group (–PO(OCH_3)$_2$) was successfully synthesized and then blended with 2,2′,4,4′-biphenyl tetraacyl chloride (BTEC) as organic phase monomers to prepare RO membranes for brackish water desalination. BM-X was utilized to represent RO membranes prepared by compound (I). X represented the concentration percent of compound (I) (%) in Isopar G solutions , which was the ratio of the concentration of compound (I) to the concentrations of compound (I) and BTEC. When X increased from 0% to 50%, the water flux of BM-X improved from 35 L/m^{2}h to 79 L/m^{2}h while holding high salt rejections (99.1–99.5%). The enhancement of membrane hydrophilicity was certified by the contact angle decreasing from 83° to 38° with compound (I) content increasing from 0% to 50%. Because the improvement of membrane hydrophilicity made for the enhancement of membrane antifouling, BM-50 exhibited a lower water flux decline and irreversible fouling degree compared with a commercial RO membrane (BW30FR, Dow Filmtec). The irreversible fouling degree reached 6.8% after 1500 min three cycles fouling which was lower than 14.1% of BW30FR. Finally, BM-50 showed a very good and stable desalination performance for 30 days measured in a pH = 6.0 and 2000 ppm NaCl solution.

1. Introduction

Desalination is the process of removing dissolved salts and other minerals from seawater and brackish water (e.g. river water) to obtain water that is suitable for human and animal consumption, irrigation and other industrial uses [1]. Membrane processes and thermal desalination are two most conventional desalination technologies [2,3]. In those technologies, reverse osmosis (RO) membrane technology is the most efficient and widely used in the world [4,5]. Currently, polyamide(PA) thin film composite(TFC) reverse osmosis membranes consisting of a dense polyamide active skin layer deposited through interfacial polymerization, a polysulfone support layer, and a polyester non-woven fabric have been the main stream in RO membranes because of their outstanding water flux, salt rejection, and wide operating temperature range and pH range [6,7]. Despite PA TFC membranes having many advantages, membrane fouling is still a major problem for large-scale application of RO technology, which results in reduced water flux and increased operation costs [8,9]. Therefore, how to enhance membrane antifouling is a problem that needs to be solved.

It is widely accepted that the resistance of PA TFC membranes to fouling has a closed relationship with the surface morphologies, hydrophilicity and charge [10]. Many researchers have shown that increasing membrane hydrophilicity can alleviate fouling problem and simultaneously increase the water flux of PA TFC membranes [11,12], because a pure water layer is produced on the hydrophilic active layer to hinder contaminant (many foulants such as protein are hydrophobic in nature) absorption and deposition on the membrane surface. On the other hand, the pure water layer will become denser with the increase of membrane hydrophilicity. Hence, most of strategies for enhancing membrane antifouling are to deposit a new hydrophilic layer upon the PA active layer through a coating method or a grafting method. For example, a membrane surface with excellent hydrophilicity was obtained by using poly (vinyl alcohol) (PVA) as a coating material and glutaraldehyde as a cross-linking agent which remarkably enhanced membrane antifouling property [13,14]. Meng et al. [15] prepared a novel salt-responsive TFC membrane by tethering a zwitterionic polymer, poly(4-(2-sulfoethyl) − 1-(4-vinylbenzyl)pyridiniumbetaine)(PSVBP), onto a commercial RO membrane. The membrane surface hydrophilicity was significantly improved and the water flux was 90% restored after 100 h of pollution. The salt-responsive

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Nomenclature

A	effective membrane area (m^2)
AFM	atomic force microscopy
ATR-IR	attenuated total reflectance infrared
BSA	bovine serum albumin
BTEC	2,2′,4,4′-biphenyl tetraacyl chloride
C_p	concentration of the permeation(mg ml^{-1})
C_f	concentration of the feed (mg ml^{-1})
CA	contact angle
DSC	differential scanning calorimeter
EA-PE	ethyl acetate- petroleum ether
F	water flux (L /m^2 h)
H_f	the heat of fusion of pure ice
IPDC	isophthaloyl dichloride
J_0	initial water flux
J_f	instantaneous water flux
J_{wf}	water flux fouled
L	liter
MPD	*m*-phenyleneamine
PA	polyamide
R_{ir}	irreversible fouling degree
$R_{(j)}$	salt rejection (%)
RO	reverse osmosis
SEM	time(h)
t	time(h)
TEA	triethyl amine
THF	tetrahydrofuran
TMC	trimesoyl chloride
TFC	thin film composite
V	volume of permeate water (L)
X_{fw}	amount of samples free water
XPS	X-ray photoelectron spectroscopy

Greek letters

Δ	the relative surface area
ΔH	the melt endotherm of water
$-\Delta G_{SL}$	solid-liquid interfacial free energy
γ_L	water surface tension

property of the PSVBP brush was believed to provide a driving force for the release of protein foulants. Ni et al. [16] synthesized a novel random terpolymer via free radical polymerization and used it as a coating material to meliorate membrane antifouling. The coated membrane can retain its water flux very well during protein filtration. As mentioned above, grafting and coating methods can enhance the antifouling property of membranes. However, it should be noted that the coating and grafting materials will increase the thickness of the permeation layer and then increase the permeation resistance which results in a decrease in the water flux of membrane [9]. On the other hand, coating materials are combined with the membrane surface only through Van Der Waals attractions, hydrogen bonding or electrostatic interaction, which leads to the gradual loss of the coating layer during long-term operation and deterioration of the antifouling property of modified. Moreover, the grafting method requires a membrane surface own special functional groups which can further react with other monomer to produce grafting layer, limiting its practical application.

Based on the above discussion, enhancing the active layer hydrophilicity without an extra coating or grafting layer is a feasible method that is simple and worth studying. Besides, enhancement of membrane water flux can be achieved when membrane hydrophilicity increases. One method to improve the membrane hydrophilicity is to introduce a new monomer containing hydrophilic functional groups into active layer. Zhou et al. [17] used *m*-phenylenediamine-5-sulfonic acid (SMPD) as a novel aqueous monomer to prepare RO membrane. The water absorption of polyamides increased with the increase of SMPD content, which demonstrated the enhancement of membrane hydrophilicity. Nevertheless, compared with *m*-phenylenediamine (MPD), SMPD with a hydrophilic and withdrawing electron group had a lower reactive activity and diffusion rate into the organic phase, which led to a deteriorated salt rejection of membrane prepared by SMPD. Besides SMPD, sulfonated poly(arylene ether sulfone) (SDADPS) [18] and disulfonated bis[4-(3-aminophenoxy)phenyl]sulfone(*s*-BAPS) [19], which contained sulfonic acid and amino groups, were also confronted with the same difficulty although these novel monomers can enhance membrane hydrophilicity. Zhao et al. [20] used a novel hydrophilic additive, o-aminobenzoic acid-triethylamine(o-ABA-TEA), and incorporated it into the PA TFC membrane. After incorporation, a decrease in the contact angle from 74° to 58° was observed, indicating enhanced surface hydrophilicity. The fouling tests illustrated the membrane prepared by o-ABA-TEA and MPD owned excellent antifouling compared with the membrane prepared by MPD.

Poly(alkylphosphonate)s have been shown to be as hydrophilic as polyvinyl alcohol (PVA) because they are similar to biomacromolecules, such as nucleic acids which have forceful hydrogen bonding with water [21,22]. In this paper, a phosphonate group was introduced to the side chain of polyamide to produce a similarly structure as that of poly(alkylphosphonate)s. Therefore, a novel organic phase monomer with hydrophilic $–PO(OCH_3)_2$ group was synthesized through a Phosphorus-Carbon coupling reaction and then was used to blend with 2,2′,4,4′-biphenyl tetraacyl chloride(BTEC) as organic phase monomers to prepare TFC RO membranes as shown in Fig. 1. The hydrophilic functional group $–PO(OCH_3)_2$ was introduced to an acyl chloride monomer not to amine monomer which decreased the influence of the monomer reaction activity and diffusion rate on the permeability of membranes and maintained a high salt rejection. In addition, combined with earlier research of the diacyl chloride effect on the membrane property from our group, the monomer with the $–PO(OCH_3)_2$ group has the ability to enhance the water flux of membrane due to its chain structure and hydrophilicity [23]. Finally, bovine serum albumin (BSA) was utilized as the model foulant to characterize the antifouling property of the self-prepared membranes and commercial membrane (BW30FR).

2. Experimental

2.1. Synthesis of monomers

2.1.1. Materials

The dimethyl isophthalate (purity > 98%), I_2, concentrated H_2SO_4, $NaIO_4$, Na_2SO_3, NaOH, $SOCl_2$ and KOAc were purchased from Beijing chemical works. $Pd(OAc)_2$(analytical grade), triphenylphosphine(PPh_3) (analytical grade) were bought from Aladdin.

2.1.2. Synthesis of dimethyl 5-iodoisophthalate

Dimethyl 5-iodoisophthalate was prepared from dimethyl isophthalate referring to the literature [24]. Yield: 85%. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.56(s, 1H), 8.47(s, 2H), 3.88(s, 6H).

2.1.3. Synthesis of dimethyl 5-(dimethoxyphosphoryl)isophthalate

The synthesis of dimethyl 5-(dimethoxyphosphoryl)isophthalate accorded to the literature [25,26]. In brief, a 500 ml three-necked flask was equipped with magnetic stirring and then pumped and filled in with nitrogen three times. $Pd(OAc)_2$ (0.80 g, 3.56 mmol), KOAc(1.40 g, 14 mmol), and PPh_3(2.80 g,10.7 mmol) were added to the three-necked round-bottomed flask. Subsequently, 100 ml of tetrahydrofuran (THF)