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Fouling resistance and cleaning efficiency of stimuli-responsive reverse osmosis (RO) membranes

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ABSTRACT

A series of stimuli-responsive reverse (RO) membranes were prepared by tethering three stimuli-responsive polymers, poly (sulfobetaine methacrylate) (PSBMA), poly (4-(2-Sulfoethyl)-1-(4-vinylbenzyl) pyridinium betain) (PSVBP) and poly (N-isopropylacrylamide) (PNIPAM) onto the surface of a commercial thin-film (TFC) RO membrane via surface-initiated graft polymerization. The membrane surface was characterized by ATR-FTIR, XPS, zeta potential, water contact angle (WCA), FESEM and AFM. Membrane characterization indicates successful grafting of these polymers, with more negatively-charged, smoother and more hydrophilic surfaces as a result. Long-term fouling-rinsing cycled experiments were conducted to evaluate fouling resistance and cleaning efficiency. With $CaCO_3$ as the foulant, the modified membranes showed better fouling resistance in the whole testing as long as 320 h; with BSA as the foulant, they only showed better antifouling performance in short term. However, the modified membranes showed much higher cleaning efficiency in both cases, with the PA-g-PSVBP membrane as the best one.

1. Introduction

With the world-wide industrialization and population increasing, recent years have witnessed the aggravation of water scarcity [1]. Today, over one-third of the world's population suffers from water shortage. As estimated, this number can triple by 2050 [2]. Therefore, it is critical to develop cost-efficient desalination and waste water treatment methods to meet the increasing demand for clean water. At present, reverse osmosis (RO) has been regarded as the most economical solution for water scarcity. It has occupied 70% of the seawater desalination market and has also been widely used in wastewater reuse, seawater and brackish water desalination, pure water fabrication and so on [3–5]. As a major RO membrane material, the thin-film composite (TFC) membrane is prepared by interfacial polymerization of an aromatic polyamide with aromatic poly (acyl)-halides on a microporous polysulfone membrane from a non-solvent induced phase inversion technique. The TFC RO membrane has several advantages such as high water permeability and salt rejection, good resistance to pressure compaction, wide operation and pH ranges and so on. However, a major problem limiting application of RO membrane is membrane fouling, which usually leads to deterioration of membrane permeation and salt rejection performance [6]. To retrieve the membrane performance, routine membrane cleaning is required with acid and alkaline chemicals. The shortened membrane service life and disposal of toxic chemicals become inevitable with increased cost and second pollution as a result.

It is well known that membrane antifouling performance is strongly affected by membrane surface properties (e.g. chemical structure, hydrophilicity, roughness and charge properties) [7,8]. Therefore, a number of research articles have been devoted to membrane surface modification to improve membrane antifouling property, the membrane surface modification can not only alter the membrane surface properties, but also maintain the bulk characteristics of the membrane [9]. In spite of diverse surface modification methods, either physical or chemical, the most prevalent strategy for surface modification is to construct a membrane surface of high hydrophilicity and low roughness. However, as far as we know, there has not been a real non-fouling RO membrane reported up to now. That is, the flux decline is still inevitable for the modified membranes, although it can be significantly depressed [10]. In fact, it has been found that the modified membrane can lose its antifouling performance in a long-term fouling test, because the foulant–foulant interaction rather than membrane surface–foulant

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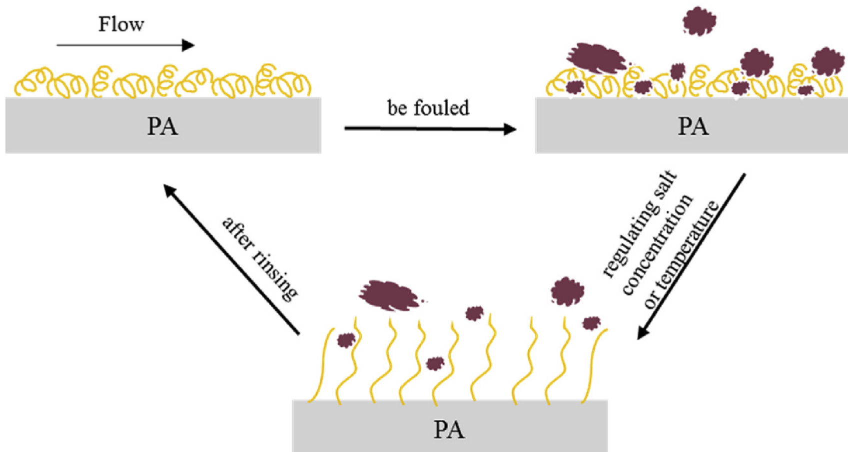

Fig. 1. Mechanism of stimuli-responsive polymer brushes improving membrane cleaning efficiency.

Table 1
The rinsing procedure for the fouled membranes.

	Step 1	Step 2	Step 3	Step 4	Step 5
Temperature (°C)	25	15	35	15	35
NaCl concentration (g L^{-1})	0	2.0	2.0	2.0	2.0
Time (h)	0.5	1	1	1	1

Table 2
The composition of the feed solution for inorganic fouling experiments.

Ion	Ion concentration (mg L^{-1})
Ca^{2+}	208.9
Mg^{2+}	9.5
Na^{+}	925.2
HCO_3^-	296.6
SO_4^{2-}	380.8
Cl^-	1584.6
NO_3^-	72.8

interaction predominates when the fouling sustains [11].

Stimuli-responsive polymers have attracted increasing attention in recent years because of its distinctive properties that the polymer changes its conformation from a coiled state to a globular one in the presence of a stimulus [12]. The stimulus can be chemical stimuli, such as instant acid–base reactions, complexation, bonding breaking or making, redox and electrochemical reactions etc, or physical ones such as changes of the pH, temperature, ionic strength, pressure, light, electric and magnetic field etc [13].

The intensive interest in functional materials with stimuli-responsive properties has led to significant work on development of stimuli-responsive membranes. Stimuli-responsive membranes have strong potential for future applications in tissue-engineering, bioseparation, drug delivery etc [14]. Other than that, the reversible switching of the polymer from a coiled state to a globular one also provides a new way of fabricating antifouling membrane having self-cleaning abilities, thanks to the foulant-releasing property of stimuli-responsive polymer brushes. The mechanism of stimuli-responsive polymer is shown in Fig. 1. Temperature-responsive polymers, with poly (N-isopropylacrylamide) (PNIPAM) as the typical one, have attracted the most attention as candidates to be incorporated onto membrane surface to endow the membrane high cleaning efficiency [15,16]. Yu and coworkers modified TFC polyamide membranes by grafting PNIPAM onto the membrane surface [13,17]. It was found that the grafted membranes had good anti-fouling performance and easy-cleaning property, which was demonstrated by slow foulant accumulation and easy rinsing-off by just changing the feed solution temperature. Recently, zwitterionic polymers, with poly (sulfobetaine methacrylate) (PSBMA) as a typical one, have been intensively used as membrane modifiers, due to their strong hydration capacity aroused by the hydrogen bonding and electrostatic interaction between zwitterions and water molecules [18]. In fact, besides their strong hydration capacity, the ion-specific conformation behavior of zwitterionic polymer brushes also renders them salt-responsive foulant release ability. Very recently, Laschewsky et al. have reported a novel zwitterionic monomer 4-(2-Sulfoethyl)-1-(4-vinyl-benzyl) pyridinium betain (SVBP), whose polymer shows a prominent salt-responsive property than traditional ones [19]. Inspired by this, we have developed a novel salt-responsive RO membrane by grafting PSVBP onto the polyamide RO membrane surface [20]. In this case, the membrane shows good fouling resistance and can be cleaned by tuning the salt concentration in the feed solution. We believe that salt-regulated rinsing is more energy-efficient than temperature-regulated rinsing one since the concentrated can be used directly for the former while tons of water need to be heated up in the latter process.

Obviously, the stimuli-responsive membrane is becoming a new type of antifouling membrane with the fouling problem addressed

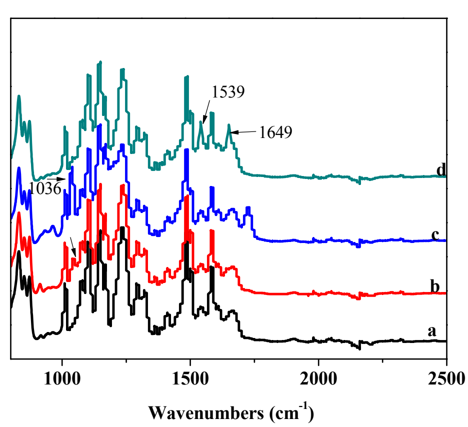

Fig. 2. ATR–FTIR spectra of (a) XLE, (b) PA-g-PSBMA, (c) PA-g-PSVBP and (d) PA-g-PNIPAM membranes.