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Novel antifouling nano-enhanced thin-film composite membrane containing cross-linkable acrylate-alumoxane nanoparticles for water softening

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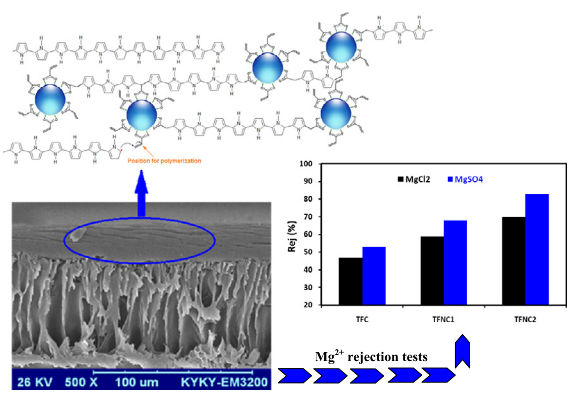
GRAPHICAL ABSTRACT



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ABSTRACT

A novel thin-film composite (TFC) nanofiltration membrane was prepared using polymerization of pyrrole monomers on the PES ultrafiltration membrane. To improve the characteristics of hydrophobic polypyrrole (PPy) thin-film layer, cross-linkable acrylate-functionalized alumoxane nanoparticles with different concentrations were embedded into the thin-film during polymerization process, and thin-film nanocomposite (TFNC) membranes were prepared. The characteristics and performance of TFC and TFNC membranes were assessed through the morphological analyses (SEM, AFM), measurement of hydrophilicity and solid–liquid interfacial free energy, water permeability and Mg^{2+} removal tests. Addition of proper amount of nanoparticles into the polymerization mixture led to the preparation of membranes with more hydrophilic, thinner and smoother active layer as well as higher water permeability compared to TFC control membrane. TFNC membrane prepared with 0.025 g of nanoparticles was the most efficient membrane since it exhibited the highest rejection of $MgCl_2$ and $MgSO_4$ salts. Antifouling capability of membranes, in terms of flux recovery and fouling parameters, demonstrated the high tolerance of TFNC against fouling.

1. Introduction

Hard water is undesirable in the domestic water supply and the industrial applications as a result of its high mineral content which

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Nomenclature

Symbols & abbreviations

A	active membrane surface area (m^2)
AFM	atomic force microscopy
C_F	Mg^{2+} concentration in the feed (mg/l)
C_P	Mg^{2+} concentration in the permeate sample (mg/l)
DMAc	*N,N*-dimethylacetamide
FR	flux recovery (%)
M	weight of permeated water through the membrane (kg)
NF	nanofiltration
PES	polyethersulfone
PPy	polypyrrole
PVP	polyvinylpyrrolidone
PWF	pure water flux (kg/m^2 h)
Rej	rejection (%)
R_{irf}	irreversible fouling ratio
R_{rf}	reversible fouling ratio
R_{tf}	total fouling ratio
RO	reverse osmosis
SEM	scanning electron microscopy
S_R	mean surface roughness (nm)
TFC	thin-film composite
TFNC	thin-film nanocomposite
$TFNC_1$	thin-film nanocomposite membrane prepared by 0.005 g of nanoparticles
$TFNC_2$	thin-film nanocomposite membrane prepared by 0.025 g of nanoparticles
$TFNC_3$	thin-film nanocomposite membrane prepared by 0.05 g of nanoparticles
WCA	water contact angle (°)
WF_i	initial pure water flux (kg/m^2 h)
WF_F	final pure water flux (kg/m^2 h)
WF_w	water flux during the filtration of whey solution (kg/m^2 h)
$-\Delta G_{SL}$	surface roughness corrected solid–liquid interfacial free energy (mJ/m^2)
Δt	sampling time (h)
Δ	relative surface area
γ_L	liquid surface tension (mJ/m^2)

reduces the household cleaning efficiency, makes scaling and corrosion problems, and causes serious difficulties in pipe lines of boilers, heat exchangers and electrical devices. To solve this issue, water softening processes are employed by which calcium and magnesium cations as well as other divalent or multivalent metal ions are eliminated from hard water. Compared with conventional water softening techniques including ion-exchange resins, zeolites or lime-soda ash treatment methods, water softening using membranes have received a specific place in this market due to higher efficiency, lower cost and less chemical and energy consumption [1,2]. Meanwhile reverse osmosis (RO) process as a high performance membrane filtration process serving for removal of solutes and minerals of hard water suffers the problems of high energy consumption and severe scaling and fouling [3,4].

Nanofiltration (NF) membranes have a looser structure rather than RO membranes. Hence, a lower applied pressure is required for NF to achieve an acceptable salt removal and water permeation even higher compared to RO membranes [5–7]. In water softening process for household consumption, it is not needed to completely remove the water hardness, so NF membranes might be a beneficial alternative to RO membranes. Among the currently available NF membranes, thin-film composite (TFC) membranes are particularly applied in water softening processes. These membranes enhance both selectivity and permeability with less energy consumption compared to the typical asymmetric membranes [3,8]. They are usually composed of an ultra-thin active layer responsible for separation and a porous substrate layer providing mechanical resistance. Polyethersulfone (PES) is frequently used for fabrication of substrate in TFC membranes due to the excellent chemical, thermal and mechanical resistance as well as almost a low price. On the other hand, thin-film in the most of TFC membranes is prepared using interfacial polymerization of hydrophilic polymers such as polyamide and polyvinyl alcohol on the substrate. Despite many advantages of a hydrophilic thin-film especially in view of increasing the water permeability, high hydrophilicity is not necessarily the only criterion to choose the material for thin layer. Adhesion between substrate and top layer is really important in the preparation of TFC membranes. It was proved that the adhesion of a hydrophilic layer on a hydrophobic substrate is weaker in comparison with that in the case of a hydrophobic thin-film [3]. Despite the particular characteristics of polypyrrole (PPy) (good thermal and environmental stability as well as ease of preparation [9]), no study has been conducted in which the thin-layer is composed of the hydrophobic PPy. Hence, PPy would be an appropriate choice for fabrication of thin-film on PES substrate; however, it should be noticed that low water permeation and high fouling of TFC membrane with hydrophobic thin-layer cause crucial problems in practice.

The key merit for composite membranes is that the characteristics of thin layer and porous substrate layer can be independently optimized to achieve better performance [10]. In this regard, thin-film nanocomposite (TFNC) membranes were developed [3] in which some nanoparticles such as TiO_2 [11–16], clay [17], graphene oxide [18–20], iron oxide [21], zeolite [22,23], SiO_2 [24,25], and carbon nanotubes [26,27] were embedded within the thin dense layer of TFC membrane mostly with the aim of increasing the hydrophilicity without sacrificing the separation efficiency of membrane [17–19,21]. Boehmite (γ-AlOOH) as the other applicable nanoparticles were also employed in the fabrication of nanocomposite membranes due to their specific characteristics particularly high hydrophilicity [28]. Reviewing the literature revealed that addition of boehmite nanoparticles into the membrane matrix resulted in improving the hydrophilicity due to the extra hydroxyl groups of nanoboehmites [29,30]. Moreover, nanoboehmite can be modified using acrylic acid due to the ability of carboxyl groups to be coordinated with aluminum as unidentate and bidentate ligands [28,31,32]. This process leads to the production of acrylate-alumoxane nanoparticles containing C=C bonds with capability of participating in the polymerization reaction [28].

The current study aims to prepare TFNC membrane with improved efficiency in water softening. PES was applied for fabrication of ultrafiltration substrate, and the thin-film was developed through aqueous polymerization of pyrrole on the surface of the substrate. Acrylate-alumoxane nanoparticles were employed as additive for raising the hydrophilicity and improving the quality of PPy thin-film layer. Hence, different concentrations of nanoparticles were introduced as filler into the thin-layer during polymerization reaction. To probe the effects of the employed method on the characteristics and performance of membranes, morphological analyses (scanning electron microscopy (SEM), atomic force