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Biofouling mitigation of TFC membrane by *in-situ* grafting of PANI/Cu couple nanoparticle

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ABSTRACT

This work deals with the simple and eco-friendly approach for the surface modification of thin film composite (TFC) membranes to have biofouling resistant effect for desalination of the water source. Coupled polyaniline/copper nanoparticle as an effective potential biocide was simultaneously grafted onto TFC Filmtec membrane. To confirm the presence of the novel couple nanoparticle over the thin polyamide layer without negative structural effect, the modified membranes were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), atomic-force microscopy (AFM), fourier transform infrared spectroscopy (FTIR) and zeta potential. The synergetic antibacterial effect of the couple nanoparticle was determined *via* SEM, colony forming unit (CFU) counting and bacterial inhibition zone by applying *Escherichia Coli* (E. coli) bacteria. The prepared membranes allowed nanoparticle reloading during desalination process with no need for disassembling and existence of any stabilizing agent. The Polyaniline/copper-thin film nanocomposite (PANI/Cu-TFN) membrane showed special anti-biofouling properties with water flux and NaCl rejection of 17.24 Kg/m^{2}h and 99.82%, respectively. The water flux recovery of the obtained membrane was 89.24% and water contact angle showed 37 ± 0.09 °

1. Introduction

Respect of sweet water demand worldwide, various technologies can be selected for water treatment or desalination [1]. Among these technologies, nanofiltration (NF) and reverse osmosis (RO) methods are considered as the most favorite processes due to their suitable and high performed salt rejection, reasonable permeability, definitely not harmful effects on the environment and low energy requirements [2–4].

One of the most problematic obstacles on the way of desalination process *via* thin film composite (TFC) membranes is fouling/biofouling [5,6]. In biofouling phenomenon, bacterial adhesion on the surface of the membrane occurs at first. After this attachment, bacteria start to reproduce and this reproduction causes a bacterial live film on the membrane surface. This can damage the membrane structure and also led to the lower performance of separation process [7]. To overcome this phenomenon, some strategies can be carried out, for instance, physical or chemical treatments and pretreatments (*i.e.* feed pretreatment, surface modification and cleaning in place or CIP) [8,9]. However, most of the pretreatments and anti-fouling methods are not efficient to prevent bio-fouling due to rapid reproduction and migration of live bacteria on the membrane surface [10]. On the other hand, using chemicals or biocides in the feed stream can potentially damage the membrane structure. It seems that employment of anti-biofouling agent directly on the surface of the membrane is the most plausible way to control biofouling.

For bacterial resistant surface modification of a membrane, various methods such as using hydrophilic or non-adhesive polymers on the surface of the membrane have been tested recent years [11]. Zhu et al. have been studied the effects of polyaniline (PANI) on the ultrafiltration (UF) membrane performance. The prepared UF membranes showed the admissible result with stable pure flux and also acceptable results as an anti-fouling agent. The increasing of the mean pore size with increasing of PANI contents in the substrate could be led to the higher water flux for the UF membrane [12]. This fact has been also investigated in another work which was prepared by Liu et al. To reduce hydrophobicity of polyvinylidene fluoride (PVDF) membranes for oil-in-water separation applications, PANI was decorated on the surface of these commercial membranes and the effectiveness of nanoscale PANI in the process and also effects on membrane pore size have been studied. The prepared membrane has shown better oil rejection, stable underwater properties in various harsh conditions and high/steady water flux in long-term experiments [13].

Carbon nanotube (CNT) thin film coated with PANI has been fabricated *via* an *in-situ* rapid method with interfacial

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polymerization by Ramana et al. [14]. In addition, PANI can be synthesized with other various procedures. However, *in-situ* fabrication method can be an effective strategy to control both quality and quantity of polymer on the structure of the membrane.

In another strategy, some anti-bacterial nanoparticles as the biocide sources can be grafted to the membrane surface to inhibit the bacterial activity [15]. The nanoparticles due to their size and characteristics can bind easily to the membrane surface. Dispersion of nanoparticles in the polymeric solution is a common way to fabricate an anti-bacterial membrane surface [16]. In an experiment which has been performed by Kim et al. Ag nanoparticles dispersed in aqueous solution while the thin layer was going to prepare. After the interfacial polymerization, thin film nanocomposite (TFN) membrane tested with *Pseudomonas aeruginosa* and the membrane showed a high decrease in bacteria attachment [17].

Ben-Sasson et al. suggested a loading procedure for nanoparticles on the RO membranes with much more advantages. In this method, Ag nanoparticles were synthesized on the polyamide layer. Hence, Ag nanoparticles were not wasted and also most of the prepared nanoparticles were embedded in the membrane surface with the size controlled. Furthermore, regenerating of membrane surface will be feasible after the membrane fabrication [18]. Regards to the one-step process of nanoparticles synthesis and graft on the membrane, lower cost of operation will be obtained. This fabrication procedure principally exposure as *in-situ* formation by Yang et al. [19].

Among various nanoparticles with anti-bacterial effect, the silver nanoparticle is known as a powerful source of highly-effective biocide [7,20,21]. However, its high price and damaging consequence on the human body have the researchers to quest alternative anti-bacterial sources. Copper nanoparticles due to acceptable anti-bacterial and non-toxic characters can be effective replacements for silver nanoparticle [22,23]. Grafting TFC membrane with Cu nanoparticles in the aspect of *in-situ* method can control the bio-fouling without any significant effects on the process performance [24]. Anti-bacterial properties of zero-valent Cu (nano-Cu^0) nanoparticles have been investigated in Raffi et al. results showed the reduction in adhesion, growth, and reaction of *E. coli* bacteria alongside nano-Cu^0 nanoparticles [25]. Many researches have been accomplished about the coating of copper nanoparticles on a variety of membranes surfaces in recent years. In another study of Ma et al., biocide effects of Cu nanoparticles have been investigated on the TFC membrane surface. In that work, two bridging agents of cysteamine (Cys) and graphene oxide (GO) were employed. As a result, the antibacterial effects of Cu nanoparticles have been proved beside the increase in performance of finalized membranes [26].

In the current work, the commercial TFC membranes have been developed *via* PANI/Cu couple grafted on the surface of the membrane. PANI was polymerized in an acidic aqueous solution initiated by aniline oligomers and grafted upon membrane surface simultaneously as a novel procedure to provide appropriate surface functional groups for coupling nanoparticles [27]. To collect and stack up all benefits of copper in the membrane surface, nano-Cu^0 was synthesized and grafted on the polyamide layer *via* one step *in-situ* method. Anti-bacterial characters of Cu in a presence of PANI were assessed by scanning electron microscopy (SEM) and colony forming unit (CFU) counting. Furthermore, the connection of PANI with nano-Cu^0 can prevent the release of nanoparticles from the membrane due to the attachment and trapped of nanoparticles in the PANI chains. For this reason, ICP tests were selected to investigate the stability of nano-Cu^0 on the membranes surfaces. The physiochemical properties of PANI-Cu coupled TFN membranes were investigated *via* FT-IR, scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray analysis (XRD), colony forming unit (CFU) and some other significant analyzing methods and instruments.

2. Material and methods

2.1. Chemicals

Copper metal salt >98% copper sulfate ($CuSO_4 \bullet 5H_2O$), 99% methanol, sulfuric acid and 99% sodium borohydride ($NaBH_4$) as a reducing agent were purchased from Merck Chemicals (Germany). In order to membrane development, dried sheets of RO DOW FILMTEC^{TM} TW30-1812 membranes were employed. The extra pure NaCl was bought from Dr. Mojallali Company (Iran). Aniline monomers as a pore former and ammonium per-sulfate (APS) as the catalyst were purchased from Sigma-Aldrich (USA). For the preparation of solid media, type one agar and Luria-Bertani (LB) broth were obtained from HiMedia (India) and Merck (Germany), respectively. Deionized water (DI) and *E. coli* bacteria were used throughout this study.

2.2. Model bacteria strains

Kanamycin resistant *Escherichia coli* (*E. coli*) BW26437 was employed. The *E. coli* culture was maintained on LB agar plates and grown in LB media 25 mg/L included kanamycin sulfate prior to any experiments. The bacterial culture for all steps of this study was prepared in OD600 of around 0.15 ± 0.5.

2.3. Loading optimization of $CuSO_4 \bullet 5H_2O$

Different concentrations of $CuSO_4 \bullet 5H_2O$ ranging from 0.01 M to 0.05 M were added to 10 antiseptic vials that contain the same amount of LB, DI water, and 0.3 ml prepared *E. coli* bacteria solution to study the concentration needed for off-use antibacterial effect of copper and then, all vials were incubated in 37 °C for 24 h. After incubation, the concentration of bacteria was measured using UV spectrophotometer (Jenway-6305, England) device at the wavelength of 580 nm. A vial contained same amounts of LB, DI water and 0.3 ml bacterial solution was selected as a blank sample. As a results, vials contain 0.03 M $CuSO_4 \bullet 5H_2O$ and more, have no bacterial activity. Thus, 0.04 M $CuSO_4 \bullet 5H_2O$ was employed as an insure concentration for this solution to have an efficient antibacterial effect on the membrane.

2.4. In-situ *preparation of Cu/TFN membrane*

Dried sheets of RO membranes were washed through immersion in a solution contained 20% methanol and 80% DI water for 15 min, then washed three times with DI water and left to dry. For *in-situ* formation of nano-Cu^0 on the surface of the membrane, coupons of membranes were attached to the clean glass plates to hold them in a solution and prepared the active layer for the reaction. The membranes soaked in 150 ml of 0.04 M $CuSO_4 \bullet 5H_2O$ solution for 10 min to complete the reaction of Cu ions with the active layer (the concentration has been obtained from the previous section). Subsequently, membrane surface was allowed to react with $NaBH_4$ for 10 min in 150 ml of 0.8 wt.% reducing agent solution. After passing the time, the surface color was changed to black due to the formation of the copper nanoparticle. The prepared *in-situ* nano-Cu^0 modified membrane was rinsed for approximately 10 s with DI water. All steps of the experiment were carried out at the ambient room temperature.

2.5. In-situ *surface modification of PANI-TFC membrane*

To *in-situ* synthesis of PANI, aniline monomers were distilled twice with a Raymand distillation setup (C-496, Iran) and stored at low temperature about 5 °C protected from light. Polyaniline

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