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Anti-bacterial assay of doped membrane by zero valent Fe nanoparticle via in-situ and ex-situ aspect

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ABSTRACT

In this work, two categories of thin film nanocomposite (TFN) membranes have been synthesized via in-situ and ex-situ aspects for grafting biocide Fe^0 nanoparticles on the membrane surface. A comparison between ex-situ and in-situ routes also was comprehensively studied. The membrane morphology and surface properties were also studied using contact angle measurements, FT-IR, AFM and SEM, along with desalination performance in terms of water flux and salt rejection. The permeate flux of NaCl solution was 12.93 L/m^2 h for the neat TFC while it was 13.9 and 13.6 L/m^2 h for the TFN obtained in in-situ and ex-situ aspects, respectively. The river water flux recovery of TFN membranes was about 89% in the long term filtration experiments, while it was 71.29% for the neat TFC membrane. To study the anti-bacterial properties of doped membrane, a new method for evaluation the killing effects of iron nanoparticles on bacteria was differently suggested. The results showed good anti-adhesion effects of TFN membrane containing zero-valent Fe nanoparticles on river or seawater natural bacteria.

1. Introduction

On a global scale, desalting the huge sources of sour waters (i.e., seawater or river water), is the essential challenge due to the lack of pure and sweet water (Shehab et al., 2014). Revival of alternative sources of water by membrane filtration process was growing step by step worldwide due to the lower costs, higher performance and ease of operation than other traditional ways of pure water preparations (Han et al., 2013). Thin film composite (TFC) membrane as a promising nanofiltration (NF) membrane has been commonly used for water purification or wastewater treatments broadly (Khajouei et al., 2015). However, the substantial problem of groundwater or river water purification with TFC membranes, is the existence of many different viruses or bacteria in the feedstock which these lead to the membrane fouling or bio-fouling accurately (Ma et al., 2014).

Bio-fouling refers to the attachment of microorganisms on the surface of membrane (sometimes also growth of microorganisms) and blockage of membrane pores (Zhang et al., 2012a). This decreases the efficiency of nanofiltration through decreasing water flux permeation and increasing the waste of power and loose of energy (Diallo et al., 2015; Werner et al., 2013). Inconvenience of bio-fouling in comparison with the non-biological fouling is much more considerable due to the difficult cleaning and pretreatment limitations (Tang et al., 2015a; Yu et al., 2015).

The seawater or river water bacteria can live under the harsh situations, so that, utilizing some chemical pretreatments are sometimes useless (Prihasto et al., 2009). These microorganisms could stick and growth on the surface of membrane in any operational conditions. This adhesion makes a biofilm or a cake of live microorganisms on the surface of the membrane and increase the hydraulic resistance

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(Flemming et al., 1997; Zhang et al., 2012b). With respect to this undesirable character of microorganisms, the anti-biofouling characters of the TFC membrane should mainly consider in the desalination of seawater or ground water. One of the effective methods to overcome the biofouling challenge is modifying membrane surface with anti-bacterial agents (Vatanpour et al., 2015; Huang et al., 2014).

In recent years many researches have been done to show the effects of metal or metal oxide nanoparticles on the biological activities (Mahmoud et al., 2015; Goh et al., 2016; Park et al., 2016; Dong et al., 2015). For instance, in a work of Park et al. (2016) in recent year, the enhancement of silver nanoparticles on the bacteria in the TFN membrane has been studied. The resulting TFN membrane showed the strong and long-lasting antibacterial properties. The effect of silver nanoparticles in antifouling and bactericidal view has been also investigated in an experiment of Xia et al. (2015). That work presented the modified membranes exhibit inhibition and killing capability of membranes toward both *Staphylococcus aureus* and *Escherichia coli* bacteria.

Iron is not harmful for human body and the environment (non-toxic and biodegradable) (Mou et al., 2015). It also due to lower price and eases of synthesis in compare with other anti-bacterial metal nanoparticles can be a candidate for any anti-bacterial processes. Regarding the anti-bacterial aspects of Fe nanoparticle, grafting it on the surface layer of membrane could help the TFC membrane to overcome the bio-fouling phenomenon (Chen et al., 2015).

Surface modification of TFC membrane by nano-metals which is named thin film nanocomposite (TFN) membrane can be conducted through two strategies: (i) in the ex-situ route, metal nanoparticles graft directly on the membrane surface by dissolving them in the aqueous solution during interfacial polymerization. This method was followed in the work of Peyravi et al. (2014). Titanium dioxide nanoparticles have been functionalized and grafted on the TFN membrane surface via ex-situ procedure.

(ii) As an in-situ aspect, metal nanoparticles prepared via different methods (i.e., reduction hydrothermal, sol–gel and etc.) which can be size controlled and grafted upon active layer of TFC membrane, simultaneously. Tang et al. (2015b) prepared a membrane via reduction method for grafting silver nanoparticles for biofouling mitigation. The membrane showed better hydrophilic surface and strong antimicrobial properties. The metal ions released were 2–3 orders lower than the traditional metal grafting procedure. The sol–gel preparation method is also reported in a paper of Zhang et al. (2013) for fabrication of PAA-g-PVDF/TiO_2 nanocomposite hollow fiber membranes.

In the presented work, a polyamide TFN membrane was fabricated via in-situ modification route to graft iron nanoparticles from the $FeCl_3$ metal salt with the reducing agent of $NaBH_4$. In this method, with the help of reducing agent, two stages of nanoparticle fabrication and binding of synthesized nanoparticles to the membrane surface were merged into one step. Further, a summarized comparison between in-situ and ex-situ reduction methods has been studied for river water. To the best of our knowledge, no feasibility study has been accomplished on the anti-bacterial capability of iron induced TFN membrane through colony forming unit counting, quantitative and qualitative analyses of surface imaging. Moreover, in an individual study, the killing effects of iron nanoparticles on bacteria was investigated differently. The natural mixed culture of bacteria from river water for anti-bacterial studies and the 2000 ppm NaCl solution for the desalination simulation studies have been employed.

2. Experimental

2.1. Materials

Iron metal salt >98% $FeCl_3$, >96% *N*-hexane, 99% methanol, 99% $NaBH_4$, 1,3-phenylenediamine (MPD), and *N*,*N*-dimethylformamide (DMF) were purchased from Merck chemicals (Germany). As the base polymer of the support layer, polysulfone (PSF) p-3500 was employed from Udel (Germany). The extra pure NaCl was bought from Dr. Mojallali Company (Iran). Polyvinylpyrrolidone (PVP) as a pore former and NaOH for setting the pH in ex-situ aspect of nanoparticle synthesis were purchased from Scharlau (Spain). For preparation of solid media, type one agar and Luria-Bertani (LB) broth was obtained from HiMedia (India) and Merck (Germany), respectively. The 98% 1,3,5-benzenetricarbonyl trichloride (TMC) was prepared from Sigma–Aldrich (USA). The non-woven polyester backing material was supplied from Viledon novatexx Co. (Germany). Deionized water (DI) was used throughout this study.

2.2. Methods

2.2.1. Preparation of Fe^0 nanoparticles via reduction

For synthesize of iron zero-valent nanoparticles, 1% wt. of $FeCl_3$ and 0.8% wt. of $NaBH_4$ were solved and stirred 5 min into 150 mL DI water separately. After preparation of solutions, $FeCl_3$ solution was reduced with drop-wise addition of $NaBH_4$ solution and the rate of about 2 drops per seconds (Lee et al., 2008). In this step, pH was controlled around 8 with addition of NaOH into the solution.

After the reducing agent solution was finished, the initial solution was recolored from brown to black due the fabrication of iron nanoparticles and their sedimentation in the container (Crane and Scott, 2012). The produced nanoparticles were centrifuged (Froilabo-SW14, France) for 10 min in 4000 rpm, then the nanoparticles were collected and washed several times and after all, the obtained powder was dried in the vacuum oven of 60 °C (Chou et al., 2005).

2.2.2. Ultrafiltration PSf support layer

To prepare asymmetric PSf ultrafiltration (UF) membrane, phase inversion method was employed with 16% wt. of PSf alongside of 2% wt. PVP was dissolved in DMF as the solvent, and then the mixture was stirred at 200 rpm in the room temperature for 12 h till the homogenous solution was obtained. For bubble removal, the solution was left about 3–4 h at room temperature (Mollahosseini et al., 2012).

During the casting step, the solution was loaded on the non-woven polyesters and casted in the humidity of around 30% with the casting knife applicator and the thickness of 75 μm. It was then immediately immersed in the DI water bath at 25 °C to precipitate. The fabricated sheet of membrane was washed two times to clean it from residual solvents or polymers. Then the prepared support was soaked in the pure water for 12 h (Rahimpour et al., 2007). Ultimately, the membrane was left to dry in the room temperature for 24 h. In our another work, the more complete procedure and preparation methods of UF membranes was discussed (Rahimpour et al., 2008).

2.2.3. Thin film composite (TFC) membrane

For fabricating TFC membrane, following two stages were accomplished. In the first step, the MPD solution was allowed to penetrate into the support layer and after that, it was reacted with TMC solution within the pores wall of support to achieve the TFC membrane. The detailed procedure is as followed (Peyravi et al., 2012a).

The support layer was divided into small pieces and attached on the clean glass plate. This was soaked in the aqueous solution containing 0.5% wt. of MPD for 30 s and then excess solution was removed from the surface in one direction with the soft sponge. The membrane was aged vertically for 120 s to remove and the possible bubbles. That saturated sup-