Self-antifouling properties of magnetic Fe$_2$O$_3$/SiO$_2$-modified poly (piperazine amide) active layer for desalting of water: Characterization and performance

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**GRAPHICAL ABSTRACT**

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**ABSTRACT**

In this work, changes in structure and performance of poly (piperazine amide) thin layer membranes incorporated with Fe$_2$O$_3$/SiO$_2$ nanoparticles to fabricate new modified thin films were investigated. Thin films incorporated with Fe$_2$O$_3$/SiO$_2$ offered enhanced performance and antifouling properties compared with unmodified thin layers. AFM and SEM images clearly illustrated that the morphology and structure of the surface of thin layers varied in the presence of the nanoparticles. Moreover, the rejection capability of the thin films toward NaCl (from 13.2 to 30.1%), Na$_2$SO$_4$ (from 58.5 to 85.0%), Pb(NO$_3$)$_2$ (from 33.3 to 64.0%), and CuSO$_4$ (from 57.1 to 80.0%) showed favorable changes, leading to improved performance of the Fe$_2$O$_3$/SiO$_2$-modified poly (piperazine amide) thin film composite membranes. Increasing of the flux recovery ratio (FRR) to about 96% proved that the employed modification procedure was successful. It should be highlighted that a thinner poly (piperazine amide) layer containing more –COOH functional groups was obtained at a proper concentration of Fe$_2$O$_3$/SiO$_2$. On the contrary, higher concentrations of the nanoparticles led to undesired properties for the Fe$_2$O$_3$/SiO$_2$-modified thin films.
1. Introduction

In the 1970s, Cadotte et al. reported the formation of thin film composite (TFC) membranes by the interfacial polymerization (IP) technique in which polymerization took place at an interface between an organic solution consisting of a carboxyl chloride reagent and an aqueous solution containing a diamine [1]. Accordingly, an active layer of cross-linked polyamide was deposited as a thin film on the porous layer. TFC membranes include a dense and thin layer that controls the performance of the membranes (including permeability and selectivity), and a thicker porous moiety which provides mechanical properties to the thin layer. Hence, a thin layer with lower thickness and more hydrophilicity could result in valuable permeability and selectivity [2]. Overall, the performance of the top polyamide thin layer membrane can be significantly influenced by some physicochemical properties such as selectivity, permeability, surface roughness, charge and hydrophilicity.

Recently, many studies have been focused on the development and improvement of the thin layer properties to achieve the best performance conditions. These research activities include a wide range of changes such as alterations in monomer types, temperature, organic media, different additives (organic or inorganic), incorporated nanoparticles, etc. [3-14]. Several studies have reported the benefits of adding different inorganic nanoparticles to the polyamide thin layers to enhance their performance. A high flux reverse osmosis nanocomposite polyamide membrane was prepared by Cruz-Silva et al. by interfacial polymerization to incorporate multi-walled carbon nanotubes [15]. They reported increased performance and chlorine resistance for the membranes. In a different study, Ratto et al. [16] compared membranes fabricated with and without embedded carbon nanotubes. They argued that in the presence of carbon nanotubes, water flux was increased by two times. Hegab et al. also showed that the selectivity, mechanical strength, antifouling, water flux and thermal properties of the membranes fabricated were remarkably improved after the incorporation of graphene oxide [17]. Al-Hobaib et al. [6] added silver oxide nanoparticles into the polyamide thin film via interfacial polymerization process. As a result, 0.003 wt% Ag₂O nanoparticle-embedded membranes showed a significant change in the flux from 26 to 40 L/m²h and a desired alteration in salt rejection to about 99%. Mansourpanah et al. investigated modified polyamide thin layer in the presence of different salts (NaCl, Na₂SO₄, PbNO₃, and CuSO₄ salts) [23,24]. The salts were dissolved in deionized water under nitrogen atmosphere. After adequate time of stirring, ammonium solution was added to the mixture dropwise. Fe₃O₄ precipitate was separated by a magnet and was rinsed with deionized water. Silica coated iron oxide nanoparticles were prepared by the hydrolysis of TEOS. For this purpose, 2 mL distilled water, 0.8 mL ethanol, and 0.1 g iron oxide nanoparticles were sonicated for 1 h. The mixture solution was stirred slowly followed by dropwise addition of ammonium (0.5 mL) and tetra-ethylorthosilicate (TEOS, 0.2 mL) solutions. Fig. 1 schematically shows the structure of the silica-modified iron oxide.

2. Experimental

2.1. Materials

FeCl₂·4H₂O, FeCl₃·6H₂O, ammonium, ethanol, and tetra-ethylorthosilicate (TEOS) were purchased from Merck (Germany) and were used for synthesizing Fe₂O₃/SiO₂ nanoparticles. Poly (ethersulfone) (PES Ultrason E6020P with M_w = 58,000 g/mol) was obtained from BASF Co. (Germany), and poly(vinylpyrrolidone) (PVP, 25,000 g/mol), acrylic acid (AA), dimethylformamide (DMF), and poly (ethyl- nylglycol) (PEG-600) (Merck, Germany) were used in this work. 1,3,5-benzenetricarboxyl chloride (TMC, 98%), n-hexane, piperazine (PIP) and triethylamine (TEA, 99.5%) (Merck, Germany) were employed to prepare poly (piperazine-amide) thin films. NaCl, Na₂SO₄, PbNO₃, and CuSO₄ salts (Merck, Germany) were utilized for the investigation of ion rejection capability. Bovine Serum Albumin powder (some properties are as follows: assay > 96%; mol wt., 66 kDa; solubility > 40 mg/mL in H₂O) were obtained from Sigma-Aldrich (Germany) and was used for the evaluation of antifouling properties of the membranes. Deionized water (DI) was used throughout the study.

2.2. Preparation of the polymeric substrate

PES, PVP, AA, and PEG-600 with 17, 2, 3, and 5 wt%, respectively, were dissolved in DMF. PVP, AA, and PEG-600 were added to the casting solution as pore formers [18]. To obtain a homogeneous solution, the polymeric solution was stirred in 300 rpm for 24 h at 50 °C. Then, to remove all air bubbles, the dope solution was kept at the ambient temperature for about 24 h. Afterwards, the homogeneous polymeric solution was cast on a glass plate at 200 μm thickness using a film applicator without evaporation at room temperature and in 30% humidity. Finally, the resulting film was subsequently and immediately immersed into a coagulation bath (distilled water) for at least 24 h to guarantee phase separation.

2.3. Preparation of magnetic Fe₂O₃/SiO₂ nanoparticles

Iron oxide nanoparticles were synthesized by co-precipitation of two salts of FeCl₃·6H₂O and FeCl₂·4H₂O at the molar ratio of (2:1) [23,24]. The salts were dissolved in deionized water under nitrogen atmosphere. After adequate time of stirring, ammonium solution was added to the mixture dropwise. Fe₃O₄ precipitate was separated by a magnet and was rinsed with deionized water. Silica coated iron oxide nanoparticles were prepared by the hydrolysis of TEOS. For this purpose, 2 mL distilled water, 0.8 mL ethanol, and 0.1 g iron oxide nanoparticles were sonicated for 1 h. The mixture solution was stirred slowly followed by dropwise addition of ammonium (0.5 mL) and tetra-ethylorthosilicate (TEOS, 0.2 mL) solutions. Fig. 1 schematically shows the structure of the silica-modified iron oxide.

2.4. Preparation of Fe₂O₃/SiO₂ nanoparticle-containing poly (piperazine-amide) thin films

Poly (piperazine-amide) thin layers were formed by interfacial polymerization process on a PES support. An appropriate flat sheet of the PES support was placed between two Teflon frames 0.7 cm in height with inner cavity of 7.5 cm × 20 cm and the poly (piperazine-amide) thin films were prepared using two aqueous and organic solutions as follows:

A 30 min sonicated (to avoid the aggregation of nanoparticles) aqueous phase containing PIP (0.15 wt%), TEA (0.4 wt%), and different concentrations of the magnetic nanoparticles (0.01 and 0.05 wt%) were added on the top of the support and were allowed to wet the surface. Then, the surface of the PES support was rolled by a soft rubber roller to eliminate any tiny bubbles formed. After 5 min, the excess of aqueous solution was discharged. Afterwards, the TMC-containing n-hexane