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Effect of iron oxide nanoparticles on the performance of polyamide membrane for ground water purification

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ABSTRACT

Maghemite iron oxide nanoparticles (γ-Fe_2O_3) with a size of about 10 nm have been successfully incorporated in mixed matrix reverse osmosis membranes based on interfacial polymerization (IP) of thin film nanocomposite (TFNC) on porous polysulfone supports. TFNC elaborated in this study comprise iron oxide nanoparticles (NPs), with different concentrations varying from 0.1 to 0.9 wt%, dispersed in polyamide host matrix. The performances of the obtained TFNC were evaluated based on the water permeability and salt rejection. Results indicated that the NPs improved membrane performance under optimal NP concentration. By changing the content of the filler, better hydrophilicity was obtained; the contact angle was decreased from 74° to 29°. Also, with initial NaCl concentration of 2000 ppm and under pressure of 225 psi, the permeate water flux increased from 26 to 44 L/m^2 h at NPs concentration of 0.3% with the maintaining of high salt rejection of 98%.

1. Introduction

Nanoparticles of iron oxides have attracted increasing attention due to their immense broad range of technological applications [1–4]. Among the magnetic nanoparticles, maghemite has attracted particular interest for several important applications such as drug delivery, cancer hyperthermia, magnetic resonance imaging (MRI) enhancement and water treatment [5–8]. For this kind of application, it was found that the particles size and the magnetic properties like saturation magnetization, remanence and coercivity of the nanoparticles are of great importance [7,8]. It is important to note that the properties of F_2O_3 nanoparticles are very sensitive and strongly depend on several factors including the preparation method, experimental conditions like the chemical routes, pH, type of precursors, solvent, temperature, gas atmosphere, post treatment, etc. [9]. For example, Iida et al. [10] synthesized Fe_3O_4 nanoparticles of 37 nm and 9 nm by hydrolysis in an aqueous solution containing ferrous and ferric salts. The authors showed that the magnetic properties of the obtained nanoparticles can be controlled by adjusting the molar ratio of ferrous (Fe^{2+}) to ferric (Fe^{3+}) ions as well as the particle size [10]. Compeán-Jasso et al. [11] prepared superparamagnetic nanoparticles of iron oxide with diameters of approximately 15 nm by the forced hydrolysis method. The authors claimed that the magnetic properties are affected by the nanoparticles size. Linh et al. [12] obtained iron oxide nanoparticles of 17 nm by co-precipitation with saturation magnetization of 65 emu/g. Shin et al. synthesized iron oxide nanoparticles of 9 nm by thermal decomposition methods [8]. Despite the preparation of maghemite nanoparticles with a small size and high crystallinity by several researchers, the variety of experimental parameters and the reaction mechanism make the synthesis complicated. A facile route to synthesize this kind of nanoparticles with a small particles size and magnetic properties that allowed their uses in technological applications needs to be developed. Recently, extensive efforts are being devoted to incorporate inorganic nanoparticles into polymeric membrane. It has been proved that inorganic materials could be incorporated, by using doping and coating technologies, into membranes [13,14].

The novelty of this paper is the synthesis and the incorporation of iron oxide (γ-Fe_2O_3) nanoparticles (NPs) aerogel synthesized by our co-authors protocol [15–19], in polyamide membranes in order to enhance the performances of the membrane in terms of permeation, rejection and fouling resistance. The membrane structure study was also investigated in this work.

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2. Experimental part

2.1. Preparation of the nanocomposite membranes

The polyamide TFC membrane was synthesized by immersing PS-20 (polysulfone supports) in an aqueous solution of 2% MPD (1,3-Phenylendiamine, $>99\%$) for 2 min (the excess MPD solution was removed by rubber roller) followed by immersing the membrane in 0.1% TMC (1,3,5-benzenetricarbonyl trichloride, $>98\%$)/hexane (99%) solution for 1 min, then rinsed with 0.2% Na_2CO_3 after that washed with deionized (DI) water, finally stored in refrigerator $\approx 4\,°C$ in DI water till use. The nanocomposite membranes were blended by maghemite aerogel nanoparticles, synthesized using El Mir et al. protocol [15–17], in a wide range of concentration (0.1–0.9 wt%) in the TMC/hexane solution. The dispersion was enhanced by sonication for 1 h.

2.2. Characterization

The morphology and particle size of the used maghemite nanopowder was studied by transmission electron microscopy (TEM, JEM-200CX). The morphology and microstructure of the as-synthesized nanocomposite membrane was examined by means of scanning electron microscope (SEM, FEI Nova-Nano SEM-600, Netherlands). The quantitative analysis of the membranes was performed by the mean of energy-dispersive X-ray spectroscope (EDX). Contact angle analysis was performed using a Ramé-Hart Model 250 Standard Goniometer/Tensiometer with DROP image Advanced software (Ramé-Hart Instrument Co., Succasunna, NJ 07876, USA). A water droplet was placed on a dry flat homogeneous membrane surface and the contact angle between the water and membrane was measured until no further change was observed. The average contact angle for distilled water was determined in a series of 8 measurements for each of the different membrane surfaces. The performance of the prepared membranes was analyzed through a cross-flow system (CF042SS316 Cell, Sterlitech Corp.). The valid membrane area in this system was 42 cm^2. The feed temperature was 25 °C with pH adjusted between 6 and 7. The filtration was carried out at the pressure of 225 psi and the stirring speed of 2000 rpm. All measurements of the water flux and salt rejection were measured after 30 min of water filtration experiments to ensure that had reached stability. The flux was calculated with Eq. (1):

$$J = \frac{V_p}{A \times t} \tag{1}$$

where J is the water flux (L/m^2 h), V_p is the permeate volume (L), A is the membrane area (m^2) and t is the treatment time (h).

The salt rejection is measured by Eq. (2):

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

where R is the rejection ratio, C_p and C_f are the salt concentrations of permeate and feed, respectively.

3. Results and discussion

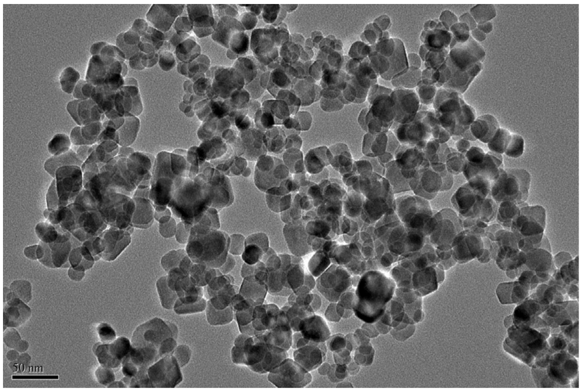

Fig. 1. TEM micrograph showing the shape and the size of used maghemite aerogel nanoparticles.

TEM image reported in Fig. 1 shows the shape and particle size distribution of the used maghemite powder. The sample shows broad range of particle dimensions and shapes; the majority of particles have a size of about 10 nm. Membrane surfaces synthesized were observed with scanning electron microscopy (SEM) coupled with EDX analysis. After the IP process, the TFC membranes layer coated on the PS support layer by the reaction between MPD and TMC has led to a leaf-like morphology (Fig. 2a). The impregnation of maghemite NPs does not have a great effect on the overall morphology of TFC in the tested concentration range, but partial aggregation of maghemite NPs was observed in samples (Fig. 2b). The difference between the images indicates clearly the presence of maghemite nanoparticles particularly on the surface. This was further confirmed by EDX quantitative analysis in Fig. 2b, and c which show clearly the presence of carbon and oxygen with iron peaks as component elements. Table 1 depicts the relative atomic proportions in the iron oxide phase which agree with Fe_2O_3 ones.

Our membranes were subjected to contact angle measurements. Standard deviations obtained on a single sample are of the order of a few degrees, which represent an acceptable reproducibility. Fig. 3 shows the measurements of the contact angle for the various weights of maghemite nanoparticles. The remarkable conclusion from Fig. 3 is that even at ultra-low concentration (0.3 wt%) of embedding iron oxide nanoparticles into TFC membrane, the contact angle drops significantly from 74° (control TFC membrane without iron oxide NP) to about 29°. However, the hydrophilicity remains almost constant when the content of maghemite nanoparticles achieved 0.5 wt%. In contrast, the contact angle increases slightly with that of the increasing maghemite nanoparticles content. It is known that there is a strong correlation between the orientation (geometry) of water at a solid–liquid interface and the hydrophilicity of the solid surface [20,21]. The restructuring of interfacial water molecules can explain the increase of the hydrophilicity. The increased ordering of the interfacial water molecules improves the water molecule's ability to form hydrogen bonds and, in turn, produces stronger interactions between water and the solid phase (TFC surface).

The decrease of the contact angles in the presence of the maghemite NPs could be caused by two reasons. First, the embedded spherical iron oxide NPs can be exposed on the membrane surface. Therefore, due to the hydrophilic properties of these NPs, the membrane surface hydrophilicity may increase. After embedding with maghemite NPs, the membrane surface could even become more hydrophilic due to the capability of the hydrophilic pores to imbibe water via capillary effects [22]. This result is in accordance with the work conducted by Jeong et al. [23], which has shown that the contact angle of the membrane surface decreased with increasing zeolite concentration and attributed this to the superhydrophilic property of zeolite. Second, the presence of the nanoparticles can improve the hydration and release of heat when contacting with MPD aqueous solution [24]. This process may affect the IP reaction between MPD and TMC, and subsequently the effect on the chemical structure of the PS support. In the case where more number of the acyl chloride groups in TMC remained

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