Preparation and characterization of UZM-5/polyamide thin film nanocomposite membrane for dewaxing solvent recovery

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ABSTRACT

Thin-film nanocomposite (TFN) membrane containing amino-functionalized UZM-5 nanoparticles was synthesized by interfacial polymerization on polyetherimide (PEI)/modified SiO_2 asymmetric substrate tailored for organic solvent nanofiltration OSN process. m-Phenylenediamine (MPD) with trimesoyl chloride (TMC) was polymerized to prepare polyamide layer. UZM-5 nanoparticles ($\sim$73 nm) were synthesized and then functionalized by aminopropylediethoxymethylsilane (APDEMS) and finally incorporated into polyamide (PA) selective layer at concentrations ranging from 0 to 0.2 w/v%. The as-prepared TFN membranes were characterized by scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), attenuated total reflection Fourier transform infrared (ATR–FTIR) spectroscopy and contact angle measurements. The performances of membranes were also evaluated through dewaxing solvents (MEK and toluene) recovery from lube oil. FESEM and SEM images clearly confirmed that the polyamide/UZM-5 nanocomposite top layer was formed on the support surface and its morphology was significantly affected by UZM-5 loading. Interaction between functional groups of modified UZM-5 nanoparticles and polyamide matrix was established by ATR–FTIR. AFM results revealed that in the range of 0–0.1 w/v% zeolite loading, the surface roughness of TFN membranes decreased due to the change of polyamide structure while at 0.2 w/v% of zeolite loading, an increase in surface roughness was observed. It also resulted in enhanced hydrophilicity of TFN membranes in the range of 0–0.1 w/v% UZM-5 loading, proved by a decreased water contact angle. The permeation test results indicated that the existence of UZM-5 in the polyamide selective layer improved both oil rejection and permeate flux under optimal concentration (0.02% w/v of UZM-5).

1. Introduction

Organic solvent nanofiltration as a promising separation technique is of interest to the petrochemical industry including solvent recovery in lube oil dewaxing, desulfurization of gasoline, deacidification of crude oil, aromatic separation in petrochemical or refinery streams, etc. [1,2]. The introduction of OSN in petrochemical processes leads to saving energy and the reduction of organic solvent wastes. In the case of solvent recovery in lube oil dewaxing, several attempts have been made to introduce OSN membranes as a new alternative to traditional separation equipments. The ExxonMobil refinery in Beaumont (Texas) is the largest plant to utilize spiral wound OSN membranes in industrial scale [2,3]. Up to now, both types of asymmetric [4–7] and composite OSN membranes [8–10] have been prepared and used in dewaxing

solvent recovery. Although these OSN membranes showed appropriate oil rejection and solvent flux during the separation process, comparison of resultant data is not possible due to different operating conditions and the lack of information about the properties of lube oil in some cases.

Chemical stability of polymeric OSN membranes is the key part of OSN membranes preparation and has been improved via the synthesis of highly stable polymers. Polyimides (PIs) are the most popular polymers used as OSN membranes material due to their excellent chemical stability in several organic solvents [11]. In addition to chemical stability, the OSN membrane should possess high solvent permeability and solute rejection. In this case, thin film composite (TFC) membranes have been developed for OSN processes. TFC membrane comprises an ultra-thin dense layer (generally PA layer) on the UF support membrane in which the characteristic of each layer can be optimized by controlling the preparation conditions of the layer. The use of the TFC membrane for OSN application has been previously reported by some researchers [10,12–15].

One approach to improving the performance of TFC membrane is the application of nanotechnology enhanced membrane materials [16]. Nanotechnology has introduced TFN membrane by the incorporation of nanomaterials (i.e. filler) into a thin film layer of composite membrane. It is expected that the TFN membrane shows enhancement of membrane properties such as separation performances and permeate flux [17]. There are several studies which utilized nonporous [18–23] or porous [17,24–28] nanoparticles to prepare TFN membranes for separation in an aqueous system. Among the various particles which can be applied as filler, zeolites have gained more attention due to their ability to increase permeability without significant loss of rejection, and also they can be easily functionalized by chemical agents. Type, size, pore diameter and surface properties are important factors in the selection of zeolite nanoparticles as filler. Lind et al. [26] reported that zeolite crystal size plays an important role in water permeability and solute rejection enhancement. They claimed that when the upper layer of TFN membranes is embedded with zeolite, internal porosity and hydrophilicity of zeolite crystals create a preferential flow path for solvent molecules (water) through nanocomposite thin films [26].

The use of nanomaterials to enhance the performance of OSN composite membranes was first proposed by Gevers et al. [29]. They added different inorganic fillers in the polydimethylsiloxane (PDMS) dense layer of composite membrane to reduce the swelling of the PDMS network. According to their results, incorporation of ZSM-5 in the PDMS layer improved the performance of PDMS coated on polyacronitrile (PAN) membrane for separation of non-polar solvents. Basu et al. [30] also prepared nanocomposite PDMS/PI by introducing metal organic frameworks (MOFs) in the PDMS matrix. Their prepared nanocomposite membranes showed that permeability increased, but solute rejection decreased compared with the unfilled PDMS/PI membrane. Although the above-mentioned information about OSN membranes is available, so far no study has been conducted on polyamide thin film nanocomposite membranes for the OSN process.

In the case of organic solvent permeation, in addition to the molecular-sieving effect of porous filler such as zeolite, affinity between filler and organic solvents can help solvent molecule transportation through the upper thin layer of TFN. Several researches have investigated the adsorption capacity and affinity between various zeolites and organic solvents such as toluene and MEK [31–33]. However, each type of zeolite possesses specific Si/Al ratios, cation types, pore structures, and acidities which affect its adsorption capacity [34].

In this study, zeolite-based TFN membranes comprising a thin film layer containing UZM-5 and PEI containing SiO_2 were prepared, characterized and used in dewaxing solvent recovery. UZM-5 were synthesized and then modified by APDEMS to assist in the proper dispersion of nanozeolites in the polyamide matrix. XRD, particle size analysis, N_2 adsorption and FTIR were performed to characterize assynthesized UZM-5. The modified UZM-5 and SiO_2 nanoparticles were used as filler in the PA top layer and the PEI support layer, respectively. The prepared TFN membranes were characterized using AFM, SEM, FESEM, ATR-FTIR and contact angle tests. The oil rejection, permeate flux and MEK to toluene mass ratio of TFN membranes were investigated using a cross-flow OSN experimental setup.

2. Experimental

2.1. Chemicals

Hydrophilic fumed silica nanoparticles (Aerosil 380) were provided by Degussa. 3-Aminopropyldiethoxymethylsilane (Sigma-Aldrich) was used to functionalize silica and UZM-5 nanoparticles. N-Methyl-2-pyrrolidone (NMP), methanol and n-hexane with analytical grade, 1,3-phenylenediamine (MPD), aluminum sec-butoxide (95+%) and

tetramethylammonium chloride (TMACl, 97%) were supplied by Merck. Polyetherimid (PEI), 1,3,5-benzenetricarbonyl trichloride (TMC), tetraethylammonium hydroxide (TEAOH, 35%) and colloidal silica (Ludox AS-40, 40% SiO_2) were purchased from Sigma-Aldrich corporation. Lube oil (VI: 83), methyl ethyl ketone (MEK) and toluene were kindly supplied by Pars Oil Company (Iran).

2.2. UZM-5 synthesis and functionalization

The UZM-5 nanoparticles were synthesized by hydrothermal reaction following previously published procedures [35]. In the first step, aluminum sec-butoxide (2.8 g) was added to TEAOH (40 g) and stirred for 2 h. Then colloidal silica (13.86 g)+distilled water (0.47 g) were added and vigorously stirred to achieve a homogenous mixture. For hydrothermal reaction, the final mixture was moved to a Teflon lined stainless steel autoclave and heated in oven at 95 °C for 18 h. In the second step, 35% TMACl in deionized water solution was added to the reacted mixture with vigorous stirring for 1 h and then transferred to a Teflon-lined autoclave and heated in an oven set at 150 °C for 96 h. Finally, solid particles were separated from the obtained suspension by filtration, washed with excess deionized water and dried at 95 °C. The as-synthesized zeolite nanoparticles were calcined at 540 °C for 12 h to obtain pore-opened UZM-5 zeolites by removing the template inside the pores.

APDEMS was used to functionalize UZM-5 nanoparticles according to a previously reported procedure for nanosilica functionalization [10]. UZM-5 nanoparticles (1.5 g) were added to the mixture of APDEMS (12.5 mL)+toluene (250 mL) and stirred for 24 h at room temperature. The functionalized zeolite nanoparticles were separated from the mixture by filtration. The unreacted APDEMS were removed from modified UZM-5 nanoparticles through Soxhlet extraction apparatus using 250 mL of toluene for 12 h followed by Soxhlet extraction in 250 mL methanol for 12 h. Finally, the modified UZM-5 was dried for 1 h at 80 °C. Fig. 1 presents the schematic of the procedure which leads to functionalization of UZM-5 by aminosilane coupling agent.

2.3. TFN membrane preparation

PEI/modified SiO_2 nanocomposite membranes have been used as support for both TFC and TFN membranes. Preparation of nanocomposite support has been thoroughly explained in our previous study in which optimal physical–chemical stability and membrane performance were achieved at 5.0 wt% of modified nanosilica in the polymer matrix [10]. Therefore, modified nanosilica at loading of 5 wt% was added to NMP and stirred for 2 h, followed by sonication for 60 min. 20 wt% PEI was gradually added to the mixtures and stirred for 24 h. The homogeneous solution was cast on (i) a glass plate for characterization and (ii) non-woven polyester for permeation test, using an adjustable casting bar (Neurtek2281205) with a thickness of 250 μm. The casted film was immersed in a water coagulation bath to form a membrane with asymmetric structure and then air-dried overnight to remove residual solvent and water.
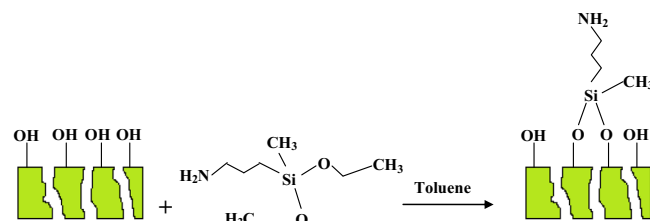

Fig. 1. Schematic of amino-functionalization of UZM-5 by APDEMS.