

Preparation of polyethersulfone membrane coated by a nanocomposite structure

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ABSTRACT

Nanocomposite membranes were prepared by coating a porous Polyethersulfone (PES) support containing 8-hydroxyquinoline (as complexing agent) with poly (vinyl alcohol) (PVA)/Fe₃O₄ nanocomposite solution. The prepared membranes were applied for removal of Zn(II) ions from water. The effect of membrane modification on the membranes performance for removal of metal ions was investigated. The results indicated that presence of ligand and Fe₃O₄ nanoparticles in the membrane structure enhanced the ions rejection. The prepared samples were characterized by scanning electron microscopy. SEM images indicated appropriate distribution of nanoparticles in the polymeric matrix.

Keywords: Colloidal synthesis; Ni-doped ZnSe NCs; Core/shell structures; Photoluminescence emission.

1. Introduction

Various techniques such as ion-exchange, evaporation, chemical precipitation, chemical oxidation or reduction, flocculation, electrochemical treatment, membrane filtration and

reverse osmosis have been used to remove heavy metal ions from industrial wastewater and urban water supplies [1-3].

Membrane adsorption is an applicable technique for removal of metal ions from aqueous solutions. Compared to the conventional methods for separation of metal ions e.g. ion exchange, chemical precipitation and adsorption columns, adsorptive membranes present several advantages such as higher flow rate, excellent removal efficiency, lower pressure drop, reusability, faster kinetic and facility of scale up [4-6]. A suitable adsorbent should offer a stable structure with abundant binding sites which is appropriate for adsorption of metal ions. The use of nanomaterials in the wastewater treatment has attracted significant attention due to their numerous active groups and large specific surface area. However, the instability in separation of nanomaterials from water and their regeneration limited their applications. Nanomaterials can be loaded on porous materials as supports to resolve mentioned problems. Also, these supports themselves might be employed as the additional adsorbents in enhancing the adsorption. Use of the nanostructure in membrane (as a porous medium) is alternative techniques to improve the removal efficiency of metal ions via polymeric membranes. However, metal oxides are classified as one of the desired agents for metal ions removal from aqueous systems due to their large surface area, suitable adsorption capacity and high activity.

Magnetite is a type of the most durable iron oxide under ambient conditions and can be prepared by a facile procedure and easy to be incorporated with other components because of its surface hydroxyl groups [7]. Moreover, magnetite has attracted great interest due to its unique adsorption, excellent reactivity, ion exchange capacity, environmental safety and low cost. However, recycling of magnetite nanoparticles is difficult after using. Therefore, improvement of recycle abilities and prevention from agglomeration are important for the use of magnetite nanoparticles. In order to overcome the problem and to modify adsorption

properties of the nanoparticles, they are typically dispersed on a high surface area carrier. In addition, introducing of additives such as ligands is an efficient method to provide high performance membranes. Polyethersulfone (PES) is a high-T_g polymer, which has suitable thermal, mechanical and chemical resistances. This is widely used in preparing asymmetric membranes with various pore sizes in the active layer.

In current work, PES/PVA/Fe₃O₄ nanocomposite membrane containing a chelating agent was prepared using magnetite nanoparticles to obtain a new mixed matrix membrane with the suitable affinity for Zn(II) ions. During this experiment, metal ions solutions were employed for membranes investigation.

2. Experimental

Materials and methods

Polyethersulfone (PES, Ultrason E 6020P, M_w= 58,000 g/mol and glass transition temperature T_g = 225 °C) and dimethylacetamide (DMAC) were obtained from BASF, Germany. The solvent (DMAC) was used without any purification. Polyvinylidene fluoride and polyvinylpyrrolidone (PVP) with 25,000 g/mol molecular weight as pore former were purchased from Alfa-Aesar and Merck, respectively. Poly(vinylalcohol) (PVA, M_w = 72000 g/mol), FeCl₂·4H₂O and NaOH were obtained from Merck Company. Distilled water was used throughout this study. Zn (NO₃)₂·6H₂O and 8-hydroxyquinoline were obtained from Sigma–Aldrich. PES flat membranes were prepared by phase inversion via immersion precipitation. Dope solution was prepared by dissolving PES polymer in DMAC and adding PVP as pore former at around 25 °C with mechanical stirring at 200 rpm for 4 h. The homogeneous polymer solution was kept to remove bubbles. The concentration of membrane matrix (PES) and pore former (PVP) were selected as 16 and 2wt. %, respectively. Then, a certain amount of the complexing agent (8-HQ) was added to the solution. The solution was cast using a home-made casting

knife with 150 μm thickness on glass plate substrate. This was immediately immersed in the non-solvent bath at room temperature without any evaporation. The fabricated PES membrane was then further treated with prepared nanocomposite solution of PVA/Fe₃O₄ nanoparticles.

3. Results and discussion

The performances of virgin and modified membranes were examined using a dead-end filtration cell under 3 bars at room temperature. Experimental setup composed of nitrogen gas cylinder, pressure regulator, membrane stirred cell and permeate tube. The detail of the experimental setup is shown in Fig. 1. Each membrane sample with an area of 12.56 cm² was located into the cell, and connected to a nitrogen tank via pressure tubing. The feed solution was stirred at 400 rpm using a magnetic stirrer to minimize concentration polarization. The permeated product was collected in a beaker and weighed using a balance. The rejections of the ions were evaluated by measuring the ions concentration in the feed and permeate using atomic absorption. Fig. 2 illustrates the SEM cross-sections of PES membranes after addition of PVP. As can be seen, after addition of PVP the formation of pores in the membrane's structure is clearly obvious. All the membranes showed a characteristic morphology of asymmetric membrane, consisting of a dense skin-layer and a porous sub-layer with finger-like structure. Fig. 3 shows the influence of the ligand addition and membrane coating with nanocomposite solutions on removal of Zn(II) ions from aqueous single metal solutions.

Unmodified PES/PVDF membrane offered negligible capacity for rejection of the ions. The ion rejection was enhanced by addition of 8-HQ to the casting solution. This is due to the improvement in the quantity of reactive sites for adsorption of metal ions.

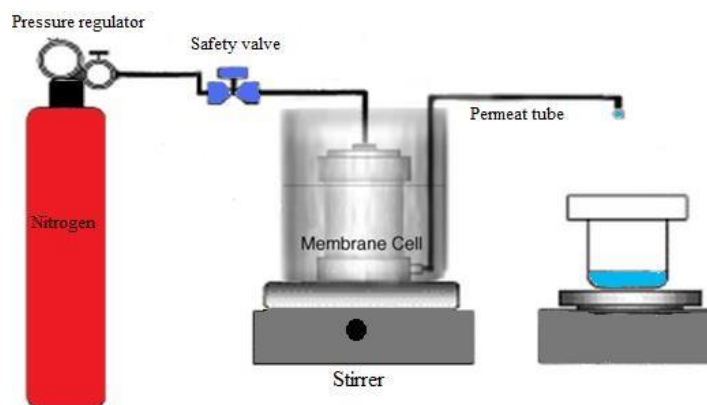


Fig. 1: Dead-end filtration system

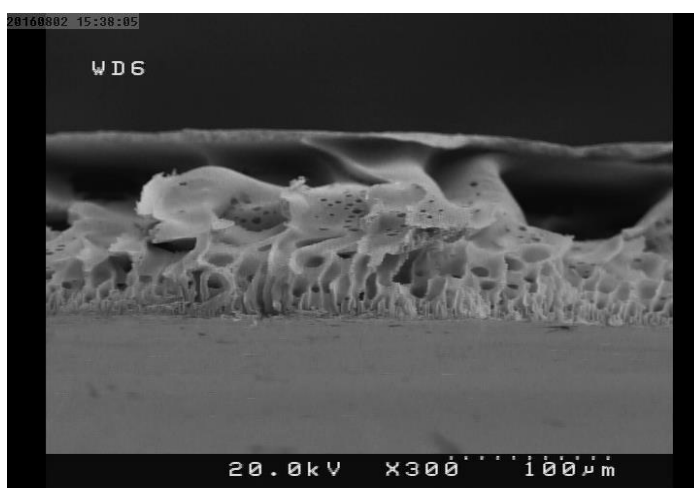


Fig.2: SEM cross-sections of PES/PVDF membranes

Results also show that coating of membranes with PVA containing Fe_3O_4 nanoparticles can affect the membrane performance. Whereas the membranes act as an adsorptive barrier, the increase of available active sites and higher surface area enhances the ions removal efficiency. In prepared nanocomposite membranes, higher amount of magnetite nanoparticles resulted in enhancement of ions rejection which supports this fact that unmodified membranes have weaker adsorption ability. Introduction of more reactive sites on the membrane surface (magnetite nanoparticles) increases the interactions between the ions and reactive sites leading to enhancement of adsorption and ions rejection.

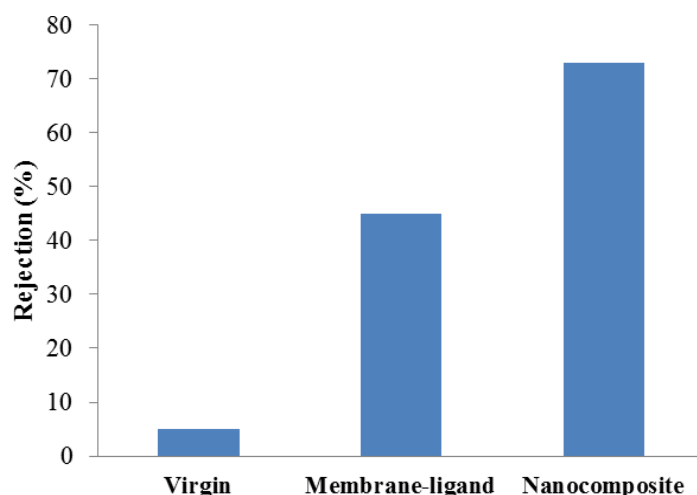


Fig. 3: The metal ions rejection of prepared membranes

4. Conclusions

A facile and one-pot method was suggested for preparation of the aqueous-based Ni:ZnSe/ZnS NCs with intense cyan emission and cubic zinc blend crystal structure. The coordinating interaction between cations and deprotonated thiol terminals of the NAC molecules was proved by elimination of the S-H related peak in FT-IR spectra. These phenomena in high temperature may lead to diffusion of the S^{2-} species to lattice structure of the ZnSe NCs and formation of the ZnSe(S) alloys which was indicated by blue-shift of the PLE and PL spectra after growth of the ZnS shell. The obtained optical results have also demonstrated that the Ni^{2+} ions show their own PL emission peak at around 476 nm which was further intensified by using of higher band gap ZnS shell. In addition, increasing of the refluxing time for shell overcoating was accompanied to further enhancement of the emission intensity which is attributed to better surface passivation of the doped NCs.

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