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Novel polyethersulfone nanocomposite membrane prepared by PANI/Fe_3O_4 nanoparticles with enhanced performance for Cu(II) removal from water

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ABSTRACT

A novel mixed matrix polymeric membrane was prepared from polyethersulfone (PES) and self-produced polyaniline/iron(II, III) oxide (PANI/Fe_3O_4) nanoparticles by phase inversion method. The core-shell structured PANI/Fe_3O_4 nanoparticles were verified and characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM) and fourier transform infrared spectroscopy (FTIR). Three different amounts of nanoparticles were introduced into the casting solutions to obtain the optimum value. According to the performance test, the membrane with 0.1 wt% nanoparticles indicated the highest Cu(II) ion removal but the lowest pure water flux. This is caused by nanoparticles located in the superficial pores of the membrane during preparation i.e., surface pore blockage. Morphological analysis including field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) as well as membrane performance tests revealed that adsorption is the most possible separation mechanism by the membranes. For better investigation of the adsorption mechanism, several isotherm models such as Langmuir, Freundlich and Redlich-Peterson were tested. Based on the isothermal results, the Redlich-Peterson model offered superior fitness indicating relatively complex adsorption mechanism. The reusability of the nanocomposite membrane was confirmed for several sequential adsorption-desorption processes using EDTA as regenerator.

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1. Introduction

Copper ion, as a toxic contaminant of potable water resources at unauthorized dosages (more than 2 mg/l), should be eliminated because of its dangerous risks for human being such as headache, depression and learning problems [1–5]. Heavy metals including copper are also toxic for plants and can affect the root growth [4].

There are several processes such as precipitation, coagulation, adsorption, ion exchange, electro-dialysis, electro-coagulation, and membrane separation processes for removing metal ions from effluents [3,6–8]. Membrane processes offer several advantages compared with other separation methods such as high removal efficiency, low energy consumption, high flow rate, small footprint and ease of scale up [9,10].

Elimination of copper ion by amphoteric polybenzimidazole nanofiltration hollow fiber membrane has been reported [6]. The removal of copper from effluents by Nanomax50 nanofiltration membrane resulted around 35%Cu(II) rejection at 4 bars [5]. Many studies describe preparation of adsorptive membranes by blending the polymers such as cellulose acetate, acrylonitrile butadiene styrene and polyvinyl alcohol with an adsorptive polymer like chitosan to enhance membrane performance for heavy metal elimination from water [11–14].

Adsorptive removal of copper ions is carried out not only by membrane separation processes but also with various granola adsorbents like silica gel and chitosan beads [15–17]. Guolin et al. used cross-linked magnetic chitosan beads prepared with a magnetic fluid containing iron salts [15]. Another study has reported the application of chitosan coated polyvinyl chloride beads to eliminate copper and nickel ions from water [16].

Utilizing the nanoparticles in membrane preparation is applied to improve process effectiveness. For example, metal oxide nanoparticles are widely used as an additive for optimizing ceramic membrane performance [18]. Hosseini et al. showed that addition of proper amount of magnetic iron- nickel oxide particles can improve performance of polyvinyl chloride based heterogeneous ion exchange membranes [19]. Influence of iron and aluminum oxide coating layer on ceramic membranes performance for the

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elimination of natural organic matter has been examined [20]. Application of iron oxide as filler in polyvinyl alcohol nanocomposite pervaporation membrane was developed for dehydration of organic solvents [21]. Compared with other metal oxides, conspicuous impact of iron oxide nanoparticles on membranes performance for arsenic removal is reported [22,23]. The observed effect is attributed to the great affinity of iron oxides toward heavy metals [22–24].

In addition to metal oxides, some polymeric materials such as polyaniline can remove toxic metal ions from water [17,25–27] due to the existence of nitrogen atom with a lone electron pair as a reactive adsorption site. It has been revealed that saw dust can efficiently adsorb cadmium ions when it is coated with polyaniline [25]. Belaib et al. modified silica gel and some natural solid materials by coating with polyaniline. They obtained significant enhancement in copper loading capacity as well as adsorption kinetics, using this adsorbent [17]. A polyaniline/inorganic cation-exchanger nanocomposite has been fabricated to obtain a high capacity ion-exchanger with increased ion exchange rate [26]. With regard to these studies, polyaniline can be applied as a modifier to achieve higher heavy metal uptake onto adsorptive nanoparticles. The properties of PANI blended membranes and PANI modified nanoparticles in nanocomposite membrane are crucial. These modified membranes represent significant properties. For example, a novel mixed matrix pervaporation membrane was successfully prepared by polyvinylalcohol and polyaniline treated TiO_2 nanoparticles [28]. This modification diminished the flux and improved the selectivity in separation of water-isopropanol mixture. Furthermore, polyaniline nanofibers were widely used as a pore former and additive in improving protein retention and antifouling properties of ultrafiltration membrane [29–32].

In this work, iron oxide/polyaniline nanoparticles (NPs) as a core-shell structured adsorbent was prepared and utilized in PES matrix to obtain a new nanocomposite membrane with enhanced affinity for copper ions. The performance of the prepared membranes was tested for removing low concentrations of Cu(II) ions from water. The mechanism of copper ion elimination by the membranes was investigated by application of adsorption isotherms. The reusability of the membranes was examined using EDTA as eluting agent. FESEM, AFM, TEM, XRD and FTIR were applied for characterization of the prepared membranes and nanoparticles.

2. Experimental

2.1. Materials

The chemicals used in the current study are presented in Table 1. All reagents were used without further purification except for aniline which was double-distilled to obtain pure aniline monomers.

Table 1
Used chemicals identification.

Chemical	Supplier	Purification
$FeCl_3 \cdot 6H_2O$	Merck, Germany	–
$FeCl2 \cdot 4H_2O$	Merck, Germany	–
NH_4OH	Merck, Germany	–
Aniline	Merck, Germany	Twice distillation
HCl	Merck, Germany	–
$(NH_4)_2S_2O_8$	Merck, Germany	–
DMAc	Merck, Germany	–
PES, Ultrason E6020P, MW=58000 g/mol	BASF, Germany	–
PVP, MW=25,000 g/mol	Merck, Germany	–
EDTA	BDH Chemicals Ltd., England	–
NaOH	Merck, Germany	–

2.2. Preparation and characterization of PANI/Fe_3O_4 nanoparticles

Briefly, $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ were dissolved in deionized water with 3:1 M ratio and stirred. The dissolved oxygen in the solution was removed by means of a vacuum pump. Then, the ammonium hydroxide solution was added to the orange-colored solution to adjust the pH value at 10 under vigorous stirring. The solution immediately became black due to formation of Fe_3O_4 precipitates. After that, the product (Fe_3O_4 nanoparticles) was thoroughly washed with deionized water and subsequently with ethanol for several times and dried at room temperature. The obtained product was used for coating with polyaniline.

Table 2
Prepared membranes composition (values in wt%).

Name	PES	PVP	DMAc	PANI/Fe_3O_4
Pristine PES	18	1	81.00	–
FA0.01	18	1	80.99	0.01
FA0.1	18	1	80.90	0.1
FA1	18	1	80.00	1

The PANI/Fe_3O_4 core-sell nanostructure was prepared by in situ chemical oxidative polymerization of aniline in the presence of Fe_3O_4 particles. In this method, certain amount of Fe_3O_4 nanoparticles (mass ratio of Fe_3O_4 to aniline monomer was 1:2) were added to 50 ml of 0.1 M HCl solution containing 3 ml of distilled aniline monomer and ultrasonicated for 15 min. The mixture was mechanically stirred for efficient dispersion. The reaction initiator, ammonium persulfate (APS), (6 g of APS in 50 ml of 0.1 M HCl solution) was slowly added to the suspension to initiate the polymerization of aniline under constant stirring in an ice bath. After 60 min, the polymerization was completed and the suspension color turned to dark green. The product was obtained by filtering the solution. Afterward, it was washed with deionized water, and dried in a vacuum oven for 48 h at 40 °C.

X-ray diffraction spectra (X'Pert PRO MPD apparatus with $Cu_{(\alpha)}$ radiation) was used for investigation of iron oxide type and grain size. The structure and particle size of produced PANI/Fe_3O_4 was monitored using transmission electron microscopy (TEM), Philips CH 200, LaB6–Cathode 160 kv. Finally, FTIR (ABB Bomem, MB–104, Canada) spectroscopy was applied for verification of PANI formation on the iron oxide nanoparticles.

2.3. Preparation of PANI/Fe_3O_4/PES mixed matrix membrane

The conventional phase inversion method was used for fabrication of PES nanocomposite membrane. Three mixed matrix and one pristine PES membranes were prepared. The composition of casting solutions is detailed in Table 2. Distinct amount of PES and polyvinylpyrrolidone (PVP), as pore former was dissolved in *N*,*N*-dimethylacetamide (DMAc) under stirring at 400 rpm for 24 h. In the case of nanoparticles addition, it was impossible to use magnetic stirrer because of magnetic properties of PANI/Fe_3O_4 particles. Hence, nanoparticles firstly dispersed in 1 to 2 g of total required DMAc with the aid of ultrasonication for 30 min and then added to PES solution in DMAc. This mixture was located on a magnet until noticeable diffusion of NPs suspension to PES solution was observed. Afterward, the mixture was ultrasonicated for 45 min. The obtained homogeneous solution was

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