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Preparation and characterization of polyvinyl chloride based nanocomposite nanofiltration-membrane modified by iron oxide nanoparticles for lead removal from water

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ABSTRACT

In this research (polyvinyl chloride-blend-cellulose acetate/iron oxide nanoparticles) nanocomposite membranes were prepared by casting technique to lead removal from wastewaters. The effect of blend ratio of polymer binder (PVC to CA) and Fe_3O_4 nanoparticles concentration on physico-chemical characteristics of membranes were studied. Water permeability and ionic rejection tests, water content and mechanical properties measurements and SEM analysis were carried out in membranes characterizations. Obviously, modified membrane containing 10 wt% CA and 0.1 wt% Fe_3O_4 nanoparticles showed better performance in lead removal compared to other modified membranes and also pristine ones.

1. Introduction

Wastewaters which contain heavy metals have attracted global attention because of their harmful effects on the environment and human health, certainly to be a risk for human beings [1]. Lead is one of the heavy metal that is non-essential and occurs naturally in the environment. But some physical and chemical properties of lead such as ductility, softness, malleability, poor conductivity and resistance to corrosion have led to wide use of this metal since ancient times in variety of applications. Today, the maximum concentrations found in environment are the result of human actions, while it is demonstrated that lead can cause dangerous health effects, even at trace level, such as nephrotoxicity, neurotoxicity and adverse effects on the hematological and cardiovascular systems [1,2]. So, it is very important to remove Lead from wastewaters effectively before their discharge into the environment. Several treatment techniques such as adsorption, electrochemical oxidation, coagulation-flocculation, and membrane filtration are used to eliminate pollutants from wastewater. Membrane process has verified to be very attractive and effective for the treatment of effluents. The main advantage of membrane-based technologies is that they do not need the addition of chemicals [3]. One of membrane techniques is Nano filtration (NF), that is becoming progressively universal in concentration and purification, pharmaceutical and chemical industries, water treatment and desalination [4,5]. NF has some good advantages, such as relatively low investment, low energy consumption, high permeation flux and singular separation capability for ions of different valences [6].

In NF membranes, two mechanisms affect the rejection behavior of solutes, surface charge and sieving, that are usually characterized using high rejection of bivalent ions, lower rejection of monovalent ions, and higher fluxes than reverse osmosis (RO) membranes [5,7,8]. NF membranes are increasingly known as one of the best procedures for water treatment and production of portable water [9].

Among the various polymeric materials which are used in preparation of membranes, polyvinyl chloride (PVC) is flexible and durable polymer with suitable biological and chemical resistance [10–12]. CA is also one of the most applicable polymers in fabrication of membranes due to its high hydrophilicity, good toughness, high biocompatibility, good desalting, high potential flux, good resistance to chlorine and solvent and it is cheap [13]. Use of these polymers (PVC/CA) and their blends as membrane binders can dedicate special selective characteristics into the prepared membranes and improve the separation properties of them [14].

One of the best modification techniques for enhancing membrane performance is blending with inorganic nanoparticles

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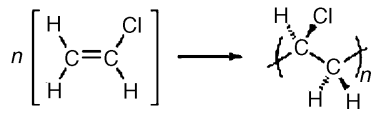
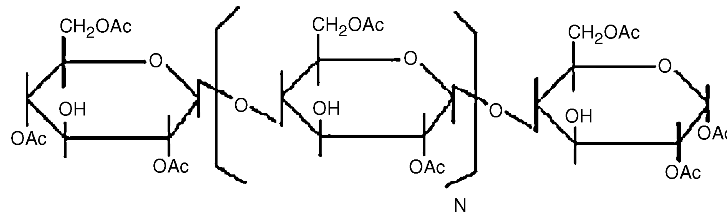
Table 1
Structure of used polymers.

Polyvinyl chloride (PVC)	
Cellulose acetate (CA)	

such as TiO_2 [5], Al_2O_3 [15,16], bentonite [17], and carbon nanotubes [3,5,6,10–31]. Inserting inorganic nanoparticles in the membrane matrix can improve the strength and stiffness, the hydrophilicity, the water permeability and rejection and the antifouling properties of polymer based Nano composite membranes [5,18–21]. Among these, nano-sized ferric oxides are used for the removal of heavy metals from aqueous systems [1]. This is because of some good features such as excellent thermal and chemical stability, magnetic performance and good biodegradation and biocompatibility. These features caused wide use of this particle in different separation techniques such as preparing magnetic targeting medicine and magnetic fluids, preparing magnetic microspheres for the quick separation of cellular, biomedical and bioengineering products [22].

The aim of this research is fabrication of novel nanofiltration membrane combined with absorbents particles by using nano-sized ferric oxides in membrane matrix to increase in lead removal efficiency from water. For the purpose, polyvinyl chloride-blend-cellulose membrane was prepared by solution casting technique. Nano-sized ferric oxide was also used as adsorbent in various concentrations to achieve nanocomposite nanofiltration membrane with high rejection and flux. The effect of blend ratio of polymer binder (PVC to CA) and Fe_3O_4 nanoparticles concentration on physico-chemical characteristics of membranes were studied.

2. Experimental

2.1. Materials

Polyvinyl chloride (PVC, Bandar Imam Petroleum Company, grade S-7054) and cellulose acetate (CA, Acros company, MW = 100,000 g/mol) as polymers – their structures presented in Table 1 – and tetrahydrofuran (THF, DAE Jung) as solvent and Fe_3O_4 nanoparticles (MW = 213.53 g/mol, APS = 60 nm, SSA > 55 m^2/g, purification = 99.2%) as a adsorbent and lead(II)nitrate ($(Pb(NO_3)_2$, Fulka company, MW = 331.2 g/mol, analysis number: 334371.1 41497) and distilled water from Alborz company were used throughout this study.

2.2. Membrane preparation

The asymmetric membranes were prepared by phase inversion method. The solution containing Polyvinyl Chloride (PVC) and Cellulose Acetate (CA) as polymer, Tetrahydrofuran (THF) as solvent and iron oxide nanoparticles was shaken for 24 h at 60 °C [22] (according to Table 2) and cast on a clean glass plate at ambient temperature by manual casting knife with 150 μm thickness. The membrane surface was exposed to air at ambient temperature (about 26 °C) for free-convective solvent evaporation. After a 60 s delay membranes were immersed into distillated water bath with the temperature about 26 °C. The polymeric skin layer was taken out after 15 min and then immersed in distillated water for 24 h to ensure complete elimination of residual solvent. The final membranes thickness was also measured by a digital caliper device (Electronic outside Micrometer, IP54 model OLR) between 135 and 150 μm.

To achieve final membrane two steps must be carried out: First, optimization on CA concentration to obtain membrane with maximum rejection and flux, and second step, investigation effect of various concentration of the nanoparticle adsorbent to improve rejection of lead. Two stages are presented by different colors in Table 2.

2.3. Membrane characterization

2.3.1. Permeability and rejection

For characterization permeability of the home-made nanofiltration membranes, a dead-end system was designed. This system consists a filtration cell with a stirrer in it and a nitrogen gas cylinder. Model of Filtration cell is 8200 Millipore Co. with inner diameter of 40 mm and volume capacity of 150 mL and effective area of the membrane was 12.566 cm^2. Fluid that reserved in cell was pressed by nitrogen gas. Fig. 1 shows symbolic view of apparatus.

The water flux (J_w) that resulted by this pressure was calculated by the following equation:

$$J_w = \frac{V}{A\Delta t} \quad (1)$$

V (L) is volume of permeated water from membrane that is collected in a graduated cylinder and A (m^2) is effective area of the membrane and t (h) is the time in which permeate is collected in the graduated cylinder.

Table 2
Composition of casting solution for the fabrication of homemade membranes.

Sample no.	Used polymer			Solvent (wt%) THF
	PVC (%w/w)	CA (%w/w)	Fe_3O_4 (%w/w)	
1	100	0	0	88
2	97.5	2.5	0	88
3	95	5	0	88
4	92.5	7.5	0	88
5	90	10	0	88
6	90	10	0.01	88
7	90	10	0.1	88
8	90	10	1	88