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Fabrication of polycarbonate mixed matrix membranes containing hydrous manganese oxide and alumina nanoparticles for heavy metal decontamination: Characterization and comparative study

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ABSTRACT

In this study, novel ultrafiltration polycarbonate (PC) mixed matrix membranes (MMMs) containing hydrous manganese oxide (HMO) and alumina nanoparticles were fabricated for the removal of Cd^{2+} and Cu^{2+}. The weight percent of HMO and alumina nanoparticles in the polycarbonate mixed matrix membrane was changed from 0 to 15. The synthesized MMMs were characterized in terms of structural morphology and hydrophilicity using FESEM, water contact angle and FTIR analysis. The effects of HMO and alumina loadings on the pure water flux, mean pore size, porosity and water contact angle of the membranes and removal of Cd^{2+} and Cu^{2+} were further studied. By increasing the loading of HMO and alumina nanoparticles in the casting solution, the mean pore size of membrane increases while the membrane porosity decreases. The increase in HMO and alumina loadings resulted in an increase in water flux of the membrane. It can be attributed to the enhancement in mean pore size and decrease in contact angle (more hydrophilicity of membrane). Furthermore, the UF experiments showed that the MMM prepared by the highest HMO nanoparticles loading had very fast kinetics and demonstrated the highest Cd^{2+} and Cu^{2+} removal efficiency (e.g. 98% and 97%, respectively). Furthermore, these data were higher than the removal efficiency of MMM prepared by alumina nanoparticles (about 91% and 81% for Cd^{2+} and Cu^{2+}, respectively) due to the higher adsorption capacity of HMO nanoparticles compared to alumina. The generic results revealed that HMO nanoparticles can be a good candidate for MMMs preparation and can be conveniently used in the Cd^{2+} and Cu^{2+} removal from polluted water resources.

1. Introduction

Nowadays, many researches have been focused on heavy metals removal, as the major contaminants in water resources. These pollutants are not biodegradable and tend to accumulate in the living organisms, causing various diseases and disorders. Therefore, because of environmental, health and safety aspects, it is necessary to remove dangerous species from water (Jamil et al., 2010; Yin et al., 2014). Hence, in recent years, drinking water regulations reduced the allowable maximum contaminant level (MCL) for heavy metals.

According to United Stated Environmental Protection Agency (USEPA) and World Health Organization (WHO) regulations, the typical

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heavy metals such as Cd^{2+} and Cu^{2+}, in aqueous solutions are more toxic even at trace levels and have caused adverse health impacts on human beings. Owing to the stringent environmental regulations, great demands exist to improve the efficiency of the techniques for heavy metal removal from contaminated water resources (United States Environmental Protection Agency, 2012).

A wide range of processes has been applied for treatment of heavy metals ions from aqueous solutions including chemical precipitation, ion exchange and biological treatment (Fu and Wang, 2011a; O'Connell et al., 2008) which suffer from some drawbacks such as low metal removal efficiency, high loss of reagents, uneconomical energy consumption and imposed post-treatment operations due to the secondary waste production. Application of membrane-based filtration is another technique for removal of heavy metals ions. Even though nanofiltration (NF) and reverse osmosis (RO) membranes have been proposed for this purpose, the high operating pressure limits the commercial utilization of these two types of membranes (Chan and Dudeney, 2008; Oh et al., 2004; Qdais and Moussa, 2004). On the other hand, microfiltration (MF) and ultrafiltration (UF) membranes, which operate at lower pressures, are not effective processes for the removal of heavy metals ions due to their intrinsic porous structure and larger pore size (Fatin-Rouge et al., 2006; Fu and Wang, 2011b).

Adsorption, one of the most widely used processes, is another technique to decontaminate toxic heavy metals ions from polluted water, as it has been found to be very effective, economical, versatile and simple (Abbas et al., 2014; Koduru et al., 2014; Roh et al., 2015). Traditional adsorbents for the removal of toxic metals include activated carbon, zeolites, ion exchange resins, as well as many low cost materials such as agricultural wastes, natural zeolite and fly ash. Unfortunately, these adsorbents can not remove the toxic substances to meet the new stringent regulations. Thus, it necessitates the development of new specific adsorbents for efficient removal of toxic heavy metals from aqueous solution. Among the available adsorbents, metal oxides nanoparticles show a remarkable potential for cleaning the environmental contaminants due to their high surface area and unique structural characteristics (Hua et al., 2012). The nanostructured metal oxides such as ferric oxide and aluminum oxide were reported as efficient materials to remove various toxic heavy metal ions from wastewater (Feng et al., 2012; Hakami et al., 2012; Srivastava et al., 2011; Wang et al., 2012; Zhang et al., 2008). Furthermore, hydrous metal oxides such as hydrous ferric oxide, aluminum oxide and manganese oxide have received a great deal of attention in sorption applications because of their large surface areas and porous structure (Afkhami et al., 2010; Taffarel and Rubio, 2010; Trivedi and Axe, 1999; Trivedi et al., 2003; Wang et al., 2007). Specially, hydrous manganese oxide (HMO) nanoparticle is the most favorable adsorbent for decontamination of toxic heavy metal among various types of hydrous metal oxides due to its high adsorption capacity (Fan et al., 2005). There are limited researches about the application of hydrous manganese oxide for water purification, especially heavy metal separation which most of them focused on fluoride, lead, arsenic and cesium decontamination (Fu and Wang, 2011b; Teng et al., 2009) and few studies have been devoted to other spices, such as copper and cadmium (Hua et al., 2012).

Even though metal oxide nanoparticles are known as strong materials for the adsorption of heavy metal ions, it is not possible to use them directly in water treatment processes; that is related to the small size of metal oxides which result in high pressure drops. Another problem is the requirement of additional post-treatment process for the separation of these very fine particles from water. Therefore, many researchers investigated the impregnation of metal oxide nanoparticles into porous media such as zeolite (Li et al., 2011), cellulose (Guo et al., 2007) and polymer (Pan et al., 2009; Wang et al., 2011) to overcome these disadvantages and to develop their application in heavy metals removal.

Thus, by creating a relationship between adsorption and membrane based separation processes, a novel technique known as mixed matrix membranes (MMMs) has been developed which takes the advantages of both systems and overcomes the aforementioned problems (Ghaemi et al., 2015; Jamshidi Gohari et al., 2013; Mukherjee et al., 2016; Nayak et al., 2015). Among the various polymeric materials used in preparation of membranes, polycarbonate (PC) can be considered as a good candidate for the membrane fabrication due to its excellent physical properties, good toughness, high heat and chemical resistances and low cost.

The main objective of this work is to develop novel UF mixed matrix membranes (MMMs) by impregnating inorganic nanoparticles into porous polycarbonate (PC) membranes to represent an efficient and applicable treatment process for Cd^{2+} and Cu^{2+} removal. In this study, MMMs were prepared from the casting solutions consisted of different weight percent of in-house made HMO nanoparticles (fabricated via chemical co-precipitation methods) and commercial Al_2O_3. Then, the Cd^{2+} and Cu^{2+} removal performance of the fabricated PC-HMO and PC-Al_2O_3 MMMs were compared. Also, the effects of operating conditions such as feed concentration, pH and temperature on heavy metal removal efficiency of the fabricated MMMs were studied.

2. Experimental

2.1. Materials

Polycarbonate (grade: 0710) was purchased from Khuzestan Petrochemical Company (Iran) and was used as the base polymer for membrane fabrication. *N*-methyl-2-pyrrolidone (NMP) was used as the solvent and cellulose acetate (CA) and glycerol were used as the nonsolvent additives to the casting solution. Manganese sulfate monohydrate ($MnSO_4{\cdot}H_2O$), potassium permanganate ($KMnO_4$) and sodium hydroxide (NaOH) were purchased from Merck and were used in the synthesis of HMO nanoparticles. Commercial γ-Al_2O_3 (with the purity of 99.99% and average particle size of 10 nm) supplied by Tecnan Navarrean Nanoproducts Technology (Spain) and was used for fabrication of mixed matrix membranes. Hydrochloric acid (HCl) was purchased from Merck and was used for the regeneration of saturated PC-HMO MMMs. To prepare aqueous feed solutions containing specific concentrations of Cd^{2+} and Cu^{2+}, $Cd(NO_3)_2{\cdot}4H_2O$ and $CuSO_4{\cdot}5H_2O$ were purchased from Merck, respectively. The determination of Cd^{2+} and Cu^{2+} concentrations was carried out using a UV–vis spectrophotometer (Lee and Choi, 2001). Hence, ammonium pyrrolidine dithiocarbamate (APDC), Tween 80 and KH_2PO_4 were purchased from Merck for the preparation of standard solutions described in that method. All the chemicals used in this study were of analytical grade and used without further purification.

2.2. Synthesis of HMO nanoparticles

The HMO nanoparticles were synthesized via the coprecipitation method described by Parida et al. (1981). Initially, two solutions named solution A and solution B were prepared as follows:

Solution A: 8% (w/v) $KMnO_4$ aqueous solution; 80 g of $KMnO_4$ were dissolved in 1000 ml deionized water.

Solution B: 12% (w/v) $MnSO_4$ aqueous solution; 120 g of $MnSO_4{\cdot}H_2O$ were dissolved in 1000 ml deionized water.

In this study, the HMO nanoparticles were synthesized according to the following procedure where the manganese ion is oxidized by $KMnO_4$. 50 ml of solution A was taken and the pH of this solution was adjusted to 12.5 by 1 M NaOH solution. Then, 50 ml of solution B was added drop-wise to the pH-adjusted solution A at room temperature and under vigorous stirring, using a magnetic stirrer. Mixing was continued for 2 h and in the meantime, the brownish precipitates were formed in the solution. After that, the resulting solution containing HMO nanoparticles was filtered and washed three times with deionized water to ensure the removal of residual