PVDF/PEG/TiO_2 Hollow Fiber Membrane for Lead(II) Removal

Shabrina Adani Putri[1], Fithri Yatul Humairo[1], Chi Siang Ong[2], Nurul Widiastuti[1], Juhana Jaafar[2], and Ahmad Fauzi Ismail[2]

Abstract*–Polyvinylidenefluoride-Polyethyleneglycol Titanium dioxide (PVDF/PEG/TiO_2) mixed- matrix hollow fiber membranes were prepared via phase inversion induced by dry-jet spinning method. The composition of the dope solution were PVDF 18 gram, PEG 2 gram, N, N-dimethylacetamide (DMAc) 80 mL and TiO_2 varied from 0 to 4 gram. The PVDF/PEG/TiO_2 mixed-matrix hollow fiber membranes were characterized using XRD, SEM-EDX and TGA. Results indicate that TiO_2 addition affects the performance of membrane such as hydrophilicity, pure water flux, porosity and antifouling properties. 2 gram TiO_2 addition was found to be the optimum amount based on the results of hydrophilicity, pure water flux, porosity and antifouling properties. Furthermore, PVDF/PEG/TiO_2 membranes with xx g TiO_2 were used to study the adsorption of Pb(II) on the membrane at various concentration from 20-100 ppm. Results show that the membrane demonstrates good performance with best capacity adsorption of 1.512 mg/cm^2 at Pb(II) concentration of 100 mg/L.

***Index Terms*-Polyvinylidene fluoride, Titanium dioxide, Hollow Fiber Membrane, Pb(II) removal.**

Introduction

Heavy metal pollution from industrial wastewaters is one of serious problems in water quality nowdays. The fact that Pb concentration of 0.1 to 0.2 ppm can cause toxicity in marine biota. To reduce the heavy metals in the water, several methods have been used such as ion exchange, liquid-liquid extraction and solid phase extraction. Solid phase extraction method has advantages over liquid-liquid extraction method, which is more perfect extraction process, using less organic solvent and analyte fraction obtained more easily collected. Excess use of nanoparticles of TiO_2 as an adsorbent which has adsorption process is simple and showing fast adsorption rate [1]. The problems that need to be considered in using nano-sized metal oxide is the agglomeration, which can lower the activity of adsorption [2]. Effective approach to solve this problem is to make TiO_2 nanoparticles is entrapped in a supporting material, which has a larger pore size [3]. The addition of PVDF as support to the TiO_2 was resulted in increasing mechanical resistance at high pressures and temperatures compared to pure PVDF membrane, increasing the metal ion adsorption capability, improving antifouling properties, increasing the thermal resistance, and improving hydrophilicity.

The main purpose of this study is to improve the performance of PVDV/PEG hollow fiber membrane by addition of various amount of TiO_2 for Pb(II) adsorption at various concentrations of Pb(II). The PVDF/PEG/TiO_2 membrane was called as mixed-matrix membrane.

Material and Methods

A. Materials

PVDF Kynar ®740) purchased from Arkema Inc. Philadelphia was used for matrix membrane. Polyethylene glycol (PEG3400) as additive membrane was purchased from Sigma-aldrich. TiO_2 nanoparticles (Degussa P25) purchased from Evonik GmbH (Germany) and N,N-dimethylacetamide (DMAc) as solvent was purchased from Merck. Albumin from bovine serum, Glyserol and lead(II) nitrate were purchased from Sigma Aldrich J.T.Baker (USA), and Sigma-Aldrich (Singapore), respectively.

B. Methods

In this research, phase inversion induced by dry-jet spinning method was used to prepare hollow fiber membrane. First, dope solution was prepared by disperse TiO_2 in DMAc and PEG solution.The composition of the dope solution and the amount of TiO_2 added were shown in Table 1. The PVDF 18 gram was dissolved into the solution. The solution was then stirred at 600 rpm for 24 hours. After the dope solution completely dissolved, the dope solution was placed on an ultrasonicator for 30 minutes. The hollow fiber membrane at various amount of TiO_2 were prepared by spinning methode, then immersed in destiled water with 10% glycerol for 3 days. Finally, the membrane were dried in air at room temperature of 25°C for 24 hours. The membrane performace such as antifouling properties, hydrophilicity, porosity and pure water flux were determined. Characterized using XRD and SEM-EDX were conducted.

[1]Shabrina Adani Putri, Fithri Yatul Humairo, and Nurul Widiastuti are with Department of Chemistry, Faculty of Mathematics and Science, Institut Teknologi Sepuluh Nopember, Surabaya, 60111, Indonesia Email : shabrina.adani@gmail.com; fitri.humairo@gmail.com; nurul_widiastuti@chem.its.ac.id.

[2]Chi Siang Ong, Juhana Jaafar, and Ahmad Fauzi Ismail are with Advanced Membrane Technology Research Centre, University Technology Malaysia, Malaysia. Email : ongchisiang@gmail.com; juhana@petroleum.utm.my; afauzi@utm.my.

TABLE 1. COMPOSITION OF DOPE SOLUTION AND TiO_2 DOSAGE

Membrane	Dope solution composition			TiO_2 (gram)
	PVDF (gram)	PEG (gram)	DMAc (mL)	
M_0	18	2	80	0
M_1	18	2	80	1
M_2	18	2	80	2
M_3	18	2	80	3
M_4	18	2	80	4

The optimum membran composition at certain amount of TiO_2 was then used for batch adsorption of Pb(II). PVDF/TiO_2 hollow fiber membrane with length 3 cm was added into 50 mL of Pb(II) solution in erlenmeyer flask 250 mL at various initial concentration of 20, 40, 60, 80 and 100 mg/L. The erlenmeyer flask then was placed in a rotary shaker at rotation speed 120 rpm for 48 h. The equilibrium concentration of Pb(II) solutions was determined using atomic absorption spectrometer (AAS).The amount of Pb(II) adsorbed by the membrane was calculated by :

$$q_e = \frac{(C_0-C_e) \times V}{A} \quad (1)$$

where q_e is the adsorption capacity per membrane area (mg/cm^2), C_0 and $C_e$are the initial concentration (mg/L) and equilibriumconcentrations (mg/L) of Pb(II) in the solution, respectively, V is the total volume (L) of Pb(II) solution and A is surface area membrane.

RESULTS AND DISCUSSION

Performace of PVDF/PEG hollow fiber membrane was lower than performance of PVDF with TiO_2 hollow fiber membrane. The antifouling properties, pure water flux, and porosity of membranes were improved due to changing the membrane surface properties from hydrophobic to hydrophilic after TiO_2 addition at 2 gram TiO_2 addition. PVDF/PEG/TiO_2 membrane with the amount of TiO_2. 2 gram, showed the optimum result for contact angel of 63.73, porosity of 34.65%, antifouling properties of 1.236 mg/cm^2 and pure water flux of 72.49 L/m^{2}h.

The cross section SEM images of membrane with different TiO_2 composition show that membrane without TiO_2 had bigger macrovoid size than membrane with TiO_2 2 gram. It was noticed that TiO_2 nanoparticles were dispersed across the surface of membranes made of 1 and 2 wt.% of TiO_2 but at higher concentration of TiO_2 (i.e. 3 and 4 wt.%), these nanoparticles tended to agglomerate and form bigger size of nanoparticles. Although the number of pores appeared more in the membrane with increasing TiO_2 concentration from 3 to 4 wt.%, the agglomerated TiO_2 nanoparticles would have blocked the pores, resulting in lower water flux.

Adsorption capacity of Pb(II) increased with increasing of initial concentration of Pb(II)**.** The adsorption isotherm result indicated that Freundlich model provided the best fit for equilibrium. The FTIR spectra of PVDF/TiO_2 hollow fiber membrane before and after adsorption experiments is helpful to clarify the interaction between the adsorbed Pb^{2+} and hybrid membranes, and the results were shown there has no obvious difference between the two spectra; it proved a physical adsorption was occurred in the adsorption process of Pb^{2+}.

CONCLUSION

Addition of TiO_2 on PVDF/PEG hollow fiber membrane affected hydrofilicity, pure water flux, porosity and antifouling properties of the membranes. 2 gram TiO_2 indicated the best performance, and therefore the membrane was selected for Pb(II) adsorption study at various Pb(II) concentration. The highest adsorption capacity was up to 1.512 mg/cm^2 at Pb(II).

REFERENCES

[1] Rashidi.F, Reza.S, Zinab.G, Seif.A (2010), "Kinetic, Equilibrium and Thermodynamic Studies for The Removal of Lead(II) and Copper(II) Ions From Aqueous Solutions by Nanocrystalline TiO_2",*Superlattices and Microstructures*, Vol 48 page 577-591.

[2] Cumbal. L., Sengupta. A.K. (2005), "Arsenic Removal using Polymer-Supported Hydratediron (III) Oxide Nanoparticles: Role of Donnan Membrane Effect", *Environ SciTechnol*. 39 6508–6515.

[3] Jang. M., Chen. W.F., Cannon. F.S (2008), "Preloading Hydrous Ferric Oxide into Granular Activated Carbon for Arsenic Removal", *Environmental Science Technology*, Vol 42 page 3369–3374.