Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

p-ISSN: 0972-6268
e-ISSN: 2395-3454

Vol. 18 | No. 4 | pp. 1249-1255 | 2019

Original Research Paper | Open Access

Development of Hybrid Membrane from Clay/TiO_2-PVA for Batik Wastewater Treatment

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Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 27-02-2019
Accepted: 30-05-2019

Key Words:
Hybrid membranes
Clay/TiO_2
PVA polymer
Batik wastewater

ABSTRACT

Hybrid membranes are currently being developed to find the membrane that is having good chemical and thermal resistance. This research devotes to the development of hybrid membrane from clay/TiO_2 with PVA polymer and its application for colour wastewater filtration. The results show that the optimum concentration of PVA is 5%. At this condition, the hybrid membrane has a bulk density of 2 g/cc and porosity of 23.13%. The hybrid membrane produces the coefficient rejection of 79.48%. At the higher concentration of PVA, the filtration becomes not effective because the flux of membrane is very low.

INTRODUCTION

The growth of batik clothing in Indonesia rises very significantly. The production of batik clothing is done on a household scale. From an economic aspect, this would be good as it could improve the economy of the community, but in terms of environment is not interesting. The production of batik clothing in a household, causes problems in terms of the management of the colour liquid wastewater produced.

There are several processes to treat colour wastewater. Coagulation process can be used to treat colour wastewater using coagulant. Malakootian & Fatehizadeh (2010) treated the colour wastewater by coagulation process using caustic soda and lime. Mohamed et al. (2014) treated the dye wastewater by coagulation process using aluminium sulphate (alum), polyaluminium chloride (PAC) and magnesium chloride ($MgCl_2$).

Adsorption process can also be used to reduce the dye contaminant in the wastewater. There are kinds of adsorbent that can be used as adsorbents such as zeolite (Wang et al. 2009), activated carbon (Malik 2004) and microbial biomass (Rahman & Akter 2016, Lata et al. 2008).

Membrane separation process is extensively applied in process industries to concentrate, purify, improve the final product and wastewater treatment. Ultrafiltration, nanofiltration and reverse osmosis processes are effective for dye removal (Abid et al. 2012), Lau & Ismail 2009, Kawiecka-Skrowron & Majeska-Nowak 2011, Majeska-Nowak & Kawiecka-Skowron 2011). The characteristics of textile effluents are a very wide range of composition in terms of pH, acidity/alkalinity, type of dyes and other contaminants and may be quite hot (50-80°C). Hence, the membrane to be used for such an application should have good chemical as well as thermal resistance.

The composite membranes of ceramic/polymer are currently being developed to find the membrane that have good chemical and thermal resistance. Gongping et al. (2012) developed the ceramic/polymer composite by dip coating process for pervaporation. Biron et al. (2015) developed ceramic/polymer membrane for protein separation. The polymer used was polyamide 66 (PA66) deposited by dip coating on the inner surface of α alumina-based (Al_2O_3) microporous tube.

This research will explore the development of hybrid membrane from clay/TiO_2 ceramic and polyvinyl alcohol (PVA) by dip coating process and its characteristics. The application of the membrane for separation of batik wastewater also will be deeply studied.

MATERIALS AND METHODS

Materials

Clay was obtained from Kebumen district, Indonesia. TiO_2 was purchased from Merck. Rice starch and methylene blue were purchased from the local market at Purwokerto, Indonesia.

Ceramic Membrane Support Preparation

Clay was crushed to the size of < 45 μm. The crushed clay was then mixed with TiO_2 (0, 5 and 10%w). The mixture was then placed at O-ring casting with the diameter of 3.2 cm and the thickness of 1 cm and pressed at 5 tons for 30 minutes. The mixture was then calcinated at the temperature of 900°C for 6 hours.

Hybrid Membrane Development

The hybrid membrane was developed by dip coating process. PVA polymer and citric acid (crosslinker) were dissolved in water and then homogenized and heated by ultrasound bath at 60°C for 30 minutes. Ceramic membrane support was dip coated at the polymer solution for 24 hours. The hybrid membrane was drying at 60°C for 6 hours then at 120°C for 2 hours. The development step of hybrid membrane production is shown in Fig.1.

RESULTS AND DISCUSSION

Characteristics of the Ceramic Support

The characterization of the prepared ceramic membrane was designed to evaluate the effect of TiO_2 content on the profile of the ceramic rheology. Fig. 2 shows the influence of TiO_2 on the bulk density of the ceramic membranes. The optimum addition of the TiO_2 is 5%w and will produce the bulk density of 1.8 gr/cm^3. At the addition of the TiO_2 of 10%w, the bulk density of the membrane will decrease. Hristov et al. (2012) reported the density of ceramic membrane developed from natural zeolite was 1.86 g/cm^3 at temperature calcination of 900°C. Bhattacharyya et al. (2005) showed that the bulk density of ceramics is influenced by sintering temperature. At the sintering temperature of 1200-1250°C, the bulk density will increase with the addition of TiO_2. But, the bulk density will decrease at the sintering temperature more than 1250°C.

The porosity of the membranes was determined by the gravimetric method using water as the wetting liquid (Singh & Bulasara 2013). To take into account the variation in the dimensions of membranes, their thickness and diameter were measured at different locations and the average values were used for calculating the membrane porosity. The porosity of ceramic membrane was determined by the equation:

$$Porosity, \% = \frac{\left(w_w - w_d\right)}{V_b} \text{ x } 100\% \qquad \ldots(1)$$

Where, w_w is the wet weight of the ceramic membrane; w_d is the dry weight of the ceramic membrane; and V_b is volume bulk of the ceramic membrane.

Fig. 3 shows the value of porosity of ceramic membranes. The porosity of the ceramic membranes will increase slightly due to the addition of TiO_2 powder. The optimum value of TiO_2 is 5%w. At this condition, the porosity

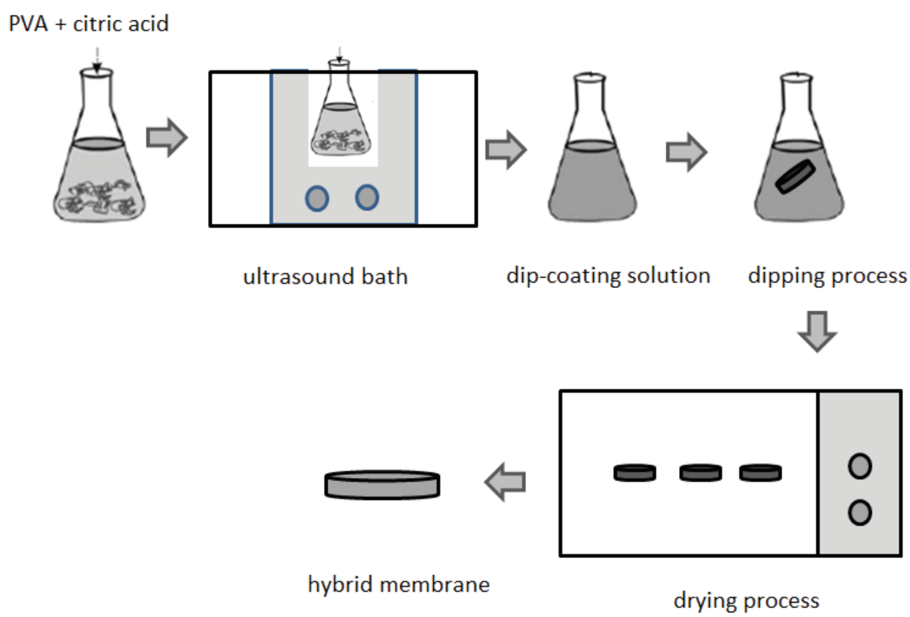

Fig. 1: The procedure of hybrid membrane production.

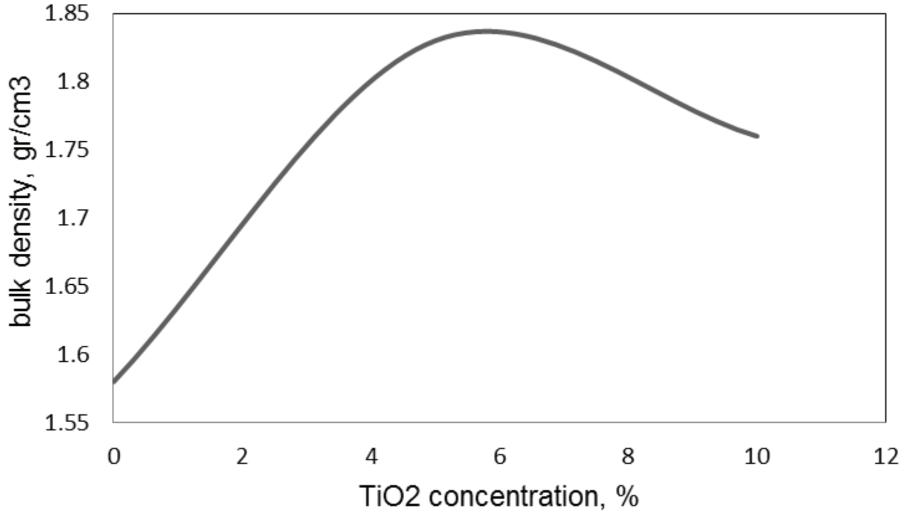

Fig. 2: The influence of TiO_2 concentration on the bulk density.

of the membrane is 28.67%. Singh & Bulasara (2013) reported the porosity of ceramic membrane from fly ash as 34.8% at the optimum sintering temperature of 900°C. Talidi et al. (2011) reported that the porosity of ceramic membranes developed from pyrophyllite clay decreased from 47% at 900°C to 31% at 1200°C.

Fig. 4 illustrates SEM pictures of ceramic membranes at the sintering temperature of 900°C in this work. Observation of the SEM pictures indicates that the membranes did not possess any cracks or surface defects. The SEM image analysis is a simple and reliable method to determine the pore size distribution of ceramic membranes in microfiltration range. Fig. 4 also shows that addition of TiO_2 influences the porosity of the membranes. The ceramic membrane becomes more porous due to the addition of TiO_2 powder.

Characteristics of Hybrid Membrane

The dip-coating process of the ceramic membrane will affect the bulk density of ceramic membrane (Fig. 5). This phenomenon can be explained that the polymers fill the

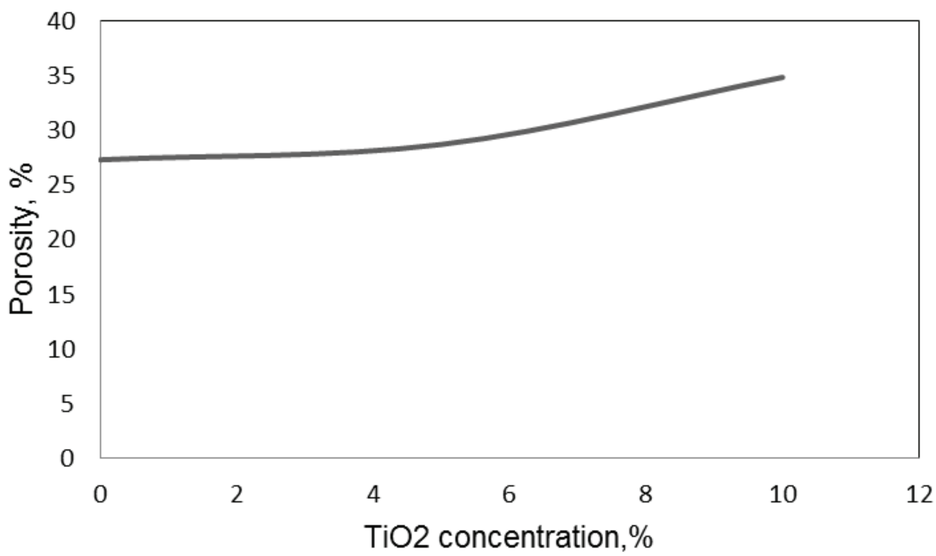

Fig. 3: The influence of TiO_2 concentration on the porosity.

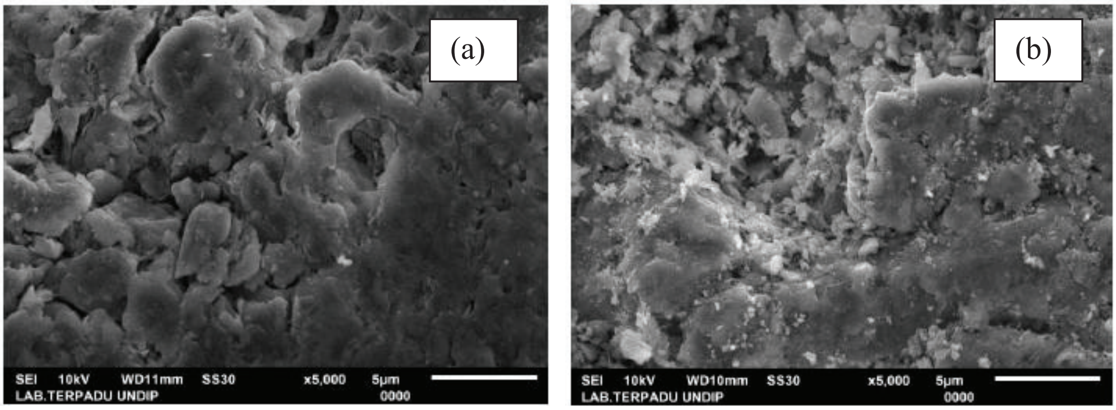

Fig. 4: SEM images of ceramic membranes. (a) 0% TiO_2; (b) 10%TiO_2.

pores of the ceramic membrane. Consequently, the porosity of the hybrid membranes will decrease (Fig. 6). It can be seen that the porosity of hybrid membrane is only 6.66% at the concentration of PVA of 10%. PVA is soluble in water, so the utilization of PVA as coating solution need crosslinker materials. In this research, citric acid was used as a crosslinker (Lusiana et al. 2016, Shi et al. 2015).

Fig. 7 shows the morphology of hybrid membrane. From the figure, the polymer coated the clay particles. The PVA polymer besides fills the pores of the ceramic membrane, and also strengthens the linkage of clay particles. The membrane becomes non fragile. The visualization of hybrid membranes at various concentrations of PVA can be seen in Fig. 8. At higher concentration of PVA polymer, the membrane becomes denser and strengthen.

Ultrafiltration of Colour Wastewater Using Hybrid Membranes

A synthetic solution of colour wastewater was prepared by dilution of 1 gram of methylene blue (wantex) into 1 L water. The concentration of dye was analysed by TDS meter. The filtration process was done at the pressure of 5 bars. Fig. 8 shows the water before and after filtration process. The hybrid membranes successfully separate the dye contaminant of the water.

Based on total dissolved solids (TDS), rejection coefficient (R) can be calculated by the equation:

$$R,\% = \left(1 - \frac{Cp}{Cf}\right) x100\% \quad \ldots(2)$$

Where, Cp is the concentration of permeate and Cf is

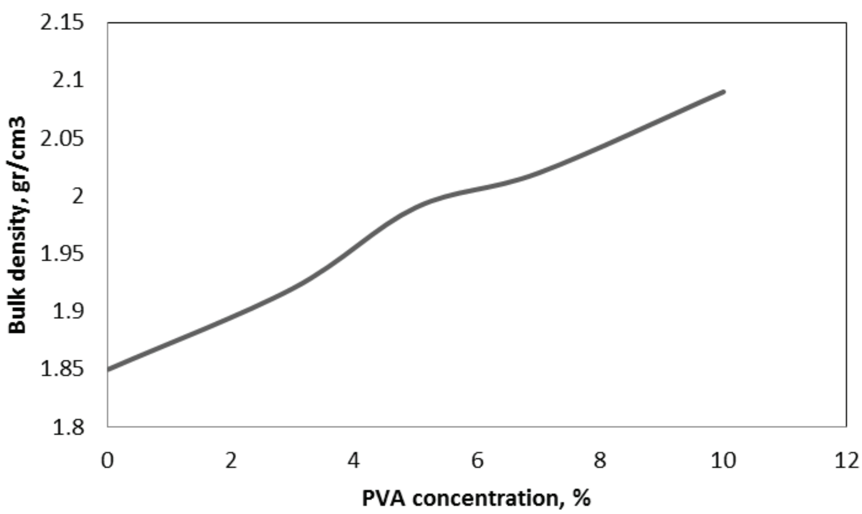

Fig. 5: The bulk density of the hybrid membranes.

the concentration of feed. The calculation shows that the maximum rejection is 79.48% (Fig. 10). It can be achieved by using a hybrid membrane with concentration of PVA as 5%. Fig. 11 shows the flux of the hybrid membranes during the filtration process. The flux of the hybrid membrane ranges from 0.0102 to 0.0037 mL/cm^2.minute (PVA 5%). At the higher concentration, the flux of membrane is very low and it can not be done.

CONCLUSION

The hybrid membrane developed from clay/TiO_2 and PVA is applicable for colour wastewater treatment. At higher concentration of PVA polymer, the membrane becomes denser and strengthen. The maximum concentration of PVA solution is 5%. The coefficient rejection that can be achieved is 79.48%.

ACKNOWLEDGMENT

The authors acknowledge the Ministry of Research Technology and Higher Education of Indonesia for funding this research.

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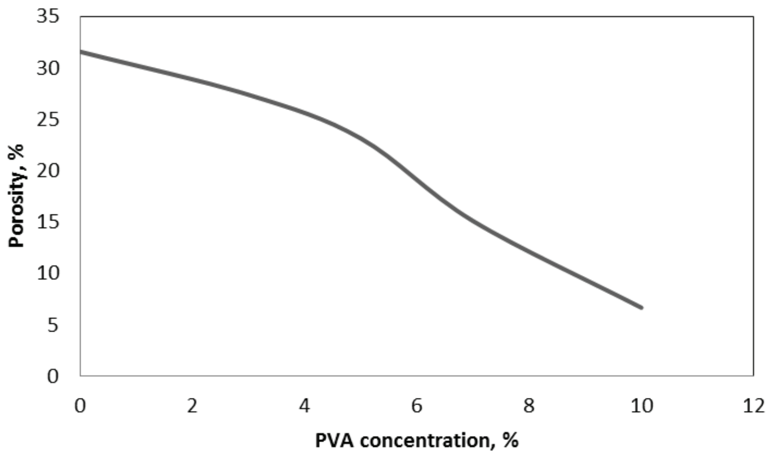

Fig. 6: The porosity of the hybrid membranes.

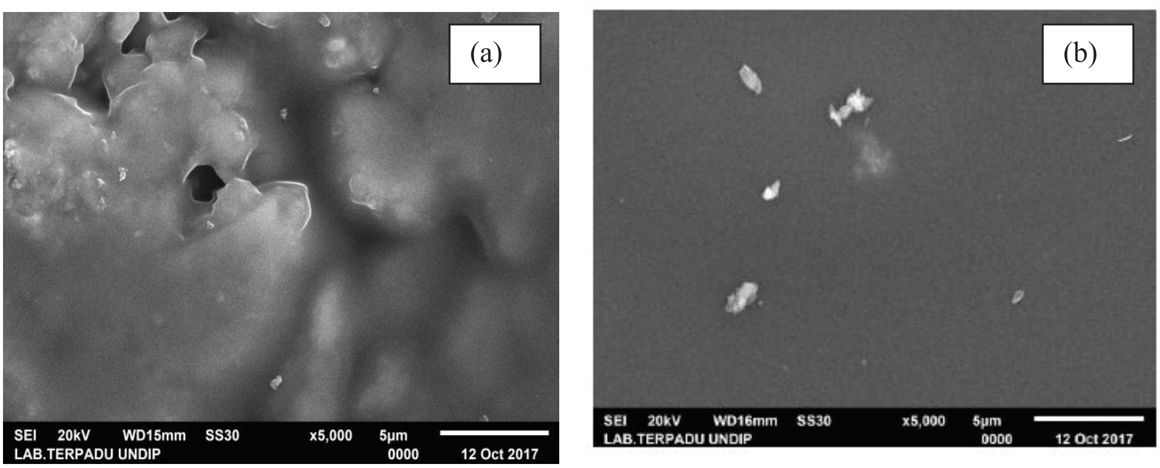

Fig. 7: The morphology of the hybrid membrane: (a) PVA 5%; (b) PVA 7%.

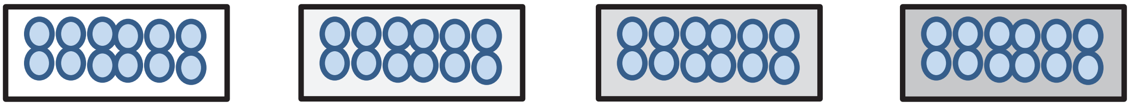

Fig. 8: The visualization of the hybrid membrane at various polymer concentrations.

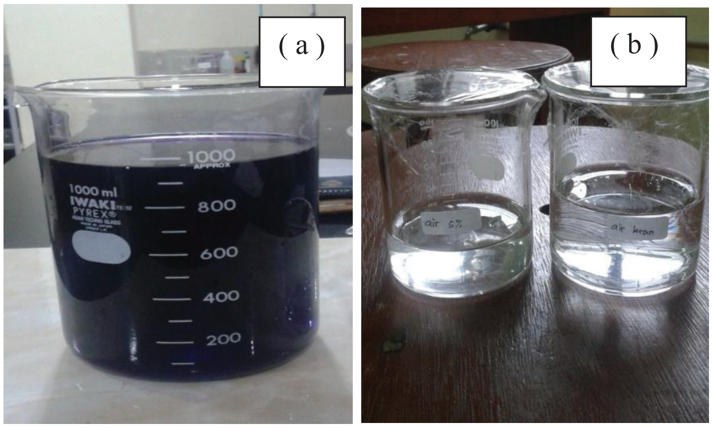

Fig. 9: Colour of batik wastewater: (a) before filtration; (b) after filtration.

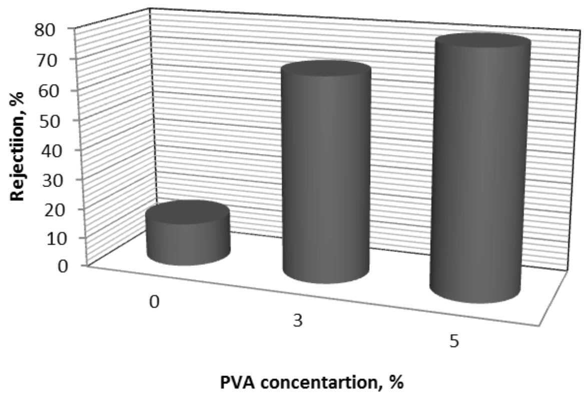

Fig. 10: Rejection coefficient of the filtration process.

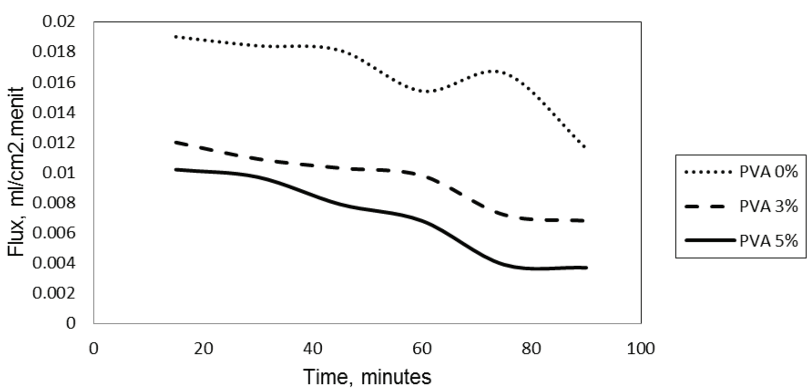

Fig. 11: Flux of hybrid membrane during the filtration process.

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