ZIF-8/Cellulose Acetate Based Mixed Matrix Membranes (MMMs) Synthesis and Characterization

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Abstract. Mixed matrix membranes (MMMs) have gained much interest in the last two decades to be used as water, waste water, and gas separation membranes. MMMs combine polymer matrix and inorganic filler to improve the performances of pure polymeric membranes. However, the choice of filler should be conducted carefully to avoid the formation of microvoids that can decrease the membrane's performances. Hence, in this study the synthesis and characterization of Zeolitic Imidazolate Framework-8 (ZIF-8) based MMMs were conducted in which the ZIF-8 has organic component that can improve the particle dispersion and avoid the formation of microvoids. Experimental results showed that ZIF-8 incorporation improved the degree of crystallinity of MMMs and also enhanced the particle dispersion compared to pure inorganic fillers, such as TiO_2.

Introduction

Textile is a raw material that is needed for clothing manufacturing. Many textile industries are built to fulfill these needs. The biggest problem that these industries face is dye wastewater. Consequently, the treatment plant to treat this wastewater should be well considered. From the former study, the concentration of dye wastewater was ranging from 10-15%, the wastewater was unrecyclable and must be discarded [1]. In general, the dye wastewater is consisted of organic dye molecules, which are difficult to degrade in nature. Thus, it is important to choose proper treatment in order to reduce the negative impact on nature [2] that removes the dye molecules before it is discarded to the environment [3].

Methylene blue is the most common tartrazine dye molecule that is used in the textile industry because it is inexpensive and easy to use in the dyeing process [4]. This molecule is very stable. Therefore, it is difficult to degrade in natural circumstances. In addition, the dye is very soluble in water, thus improper use can lead to disruption of the aquatic ecosystem, such as low dissolved oxygen (DO), it can be irritating to the digestive tract or skin if swallowed or touched, and also can cause cyanosis if inhaled or exposed [5].

The treatment processes that are commonly used in treating dye wastewater are adsorption, coagulation-flocculation, and the use of biological agent. These processes have their own advantages and disadvantages. First process is adsorption; this process is simple, highly efficient, and environmentally friendly [6]. Despite all these advantages, this process needs a large number of adsorbents to handle large capacity of wastewater as this method only transfer the contaminants into the adsorbent until the adsorbent becomes saturated. Second process is the coagulation-flocculation; this process is simple, easy to operate, relatively cheaper, and able to fulfill the effluent quality standards. However, this process needs chemical that may increase the cost and yield high quantity residues.

The last process is using biological agent; this process was developed because the other options are expensive. One of the biological treatments that exist uses *Marasmius sp.* fungi as the biological agent, which produces laccase enzyme. This enzyme can degrade dye wastewater but has some drawbacks, such as unstable activity, low concentration, and longer detection time.

In order to tackle these disadvantages, another method must be introduced. One of the potential methods is membrane separation. This method offers some features such as simple process, able to run in mild condition, no chemicals needed, energy saving, recyclable, and more compact. The compactible properties enable the membrane to be designed as a module with capability to handle a large number of wastewaters that needed small spaces. However, a membrane strongly depends on its material components, consequently, a membrane has a lifetime due to its brittle property and structural deterioration by feed chemicals.

Many researchers have tried to synthesize mixed matrix membranes (MMMs) in order to remove membrane's shortcomings. The incorporation of inorganic and organic particles as membrane constituents enhances permeability, selectivity, thermal, and mechanical strength also chemical stability of membrane. Therefore, these improvements make the membrane separation method in industrial-scale profitable. However, most of the recent studies about the mixed matrix membranes that have been done are about gas separation, meanwhile studies of the liquid-solid membrane separation are still lacking [5].

From the previous studies [3-5], the application of inorganic particles for mixed matrix membranes synthesis has been investigated. Some researchers have interest in inorganic particles such as TiO_2 and metal organic framework (MOF) such as ZIF-8. The addition of TiO_2 for membrane enhancement was demonstrated by using PES (polyethersulfone) as the polymer in wastewater separation. Their results showed the influence of TiO_2 particles increased the permeability, molecular weight cut-off (MWCO), porosity, and anti-fouling behavior as the concentration of particles increased. Furthermore, the other group researchers confirmed the similar effects of TiO_2 particles such as the addition of TiO_2 inside the PVDF (polyvinylidene fluoride) membrane for methylene blue separation and TiO_2 inside the PSF (polysulfone) membrane for forward osmosis application. These researches also showed the increased flux of the membrane were accompanied by reduced rejection. Furthermore, these phenomena were occurring because of the hydrophilicity properties of TiO_2 particles. Another hydrophilic particle, ZSM-5 was studied with polyphenylsulfone (PPSU) and also showed the same results as TiO_2 mixed matrix membranes, which flux and anti-fouling were enhanced with increasing the concentration of inorganic particle. This confirms that hydrophilicity of TiO_2 can improve the membrane properties. However, the structural studies of the membrane still limited. On the other hand, the usage of ZIF-8 as MMMs was studied in gas separation [7]. The result showed the trade-off between permeability and selectivity, in which the particle only improved membrane permeability. On the other hand, another report showed decreased permeability and increased selectivity when the ZIF-8 or ammonia modified ZIF-8 particles are combined with polysulfone (PSF) membrane for CO_2/CH_4 separation. Besides the ZIF-8 application for gas separation studies, the liquid-solid separation studies using ZIF-8 MMMs are still limited.

The incorporation of inorganic particles inside the membrane introduces some difficulties, which are caused by the property difference between polymer and particles. The inorganic particles can be hydrophilic or hydrophobic, which can affect the interaction and performance of the membrane. The TiO_2 particle was reported to have hydrophilic and oxidative behavior meanwhile the ZIF-8 particle had hydrophobic behavior. Besides, only a few works studied the structure and image of membranes. Hence, this work wants to investigate the influences of TiO_2 and ZIF-8 particle concentrations with cellulose acetate as the matrix. The performance of the membrane to run methylene blue separation is tested by permeation test to determine flux and rejection of each particle concentration. Meanwhile, for imaging, elemental and crystallinity scanning purposes are examined using XRD and SEM.

The Material and Method

Materials

Cellulose acetate (CA) was supplied by Sigma Aldrich and was used as the polymer matrix of mixed matrix membranes (MMMs), the membranes were prepared using a phase inversion process.

Formamide and acetone was supplied by Sigma Aldrich were used as polymer solvents for membrane preparation. Besides, phase inversion process used water as non-solvent. Zeolitic imidazolate framework-8 (ZIF-8) and titanium oxide (TiO_2) were used as the inorganic fillers. Zinc nitrate hexahydrate and 2-methylimidazole supplied by Sigma-Aldrich were used as reactants for ZIF-8 preparation and water was used as the solvent. Another inorganic filler, TiO_2 was supplied by Sigma Aldrich. All chemicals were used without any further purification.

Synthesis of ZIF-8

ZIF-8 was prepared by room temperature technique. The 2-methylimidazole solution was prepared by dissolving 3.7 g solids into 32.5 ml of water and then mixed with 32.5 ml zinc nitrate hexahydrate solution containing 0.18 g solids. The mixture was reacted and stirred for 1.5 hours until the mixture turned cloudy. The suspension was then separated using Beckman centrifuge for 15-20 min at 13,000 rpm. Centrifuge precipitate was dried using oven at 85°C for 24 hours.

Synthesis of mixed matrix membranes

The membrane manufacturing applied the immersion precipitation technique (phase inversion process). The cellulose acetate polymer solid was dissolved in acetone and then formamide was added into the mixture by composition 14.9 wt.% polymer, 50 wt.% acetone, and 35.1 wt.% formamide. Then one of the inorganic fillers (ZIF-8 or TiO_2) was added into the mixture with composition 0, 3, 5, and 10 wt.% respect to the polymer dry weight. The membrane solution was stirred 24 hours to ensure the homogeneity of the mixture. Then the solution was left for the degassing step in 24 hours. After degassing, the solution was poured and casted with thickness about 0.21 mm on the surface of flat glasses. The thin film was formed after casting, then the film was left alone at room temperature until the solvent evaporated. After the solvent evaporated, then the film was immersed for 24 hours in a coagulant basin contained water and the film started to solidify. After 24 hours, the membrane was stored before performance tests and structure determination.

Characterizations of pure polymeric membrane and MMMs

The characterizations of pure polymeric membrane and MMMs were conducted using scanning electron microscopy (SEM), x-ray diffraction, and water drop test (hydrophilic and hydrophobic test). The top surface of flat membrane was Pd/Au coated and was examined using Evo MA 10 Carl Zeiss SEM. The crystallinity of MMMs and pure polymeric membranes were analyzed using Empyrian XRD for 2θ ranging from 5° to 50°.

Results and Discussion

Synthesis of pure cellulose acetate membrane

In this work, the synthesis of cellulose acetate membrane and mixed matrix membranes was conducted using the phase inversion method. This technique produces membranes with compact and porous morphology. In addition, this method compatible when it is used to synthesis polymeric membranes (Wenten, 1996). The figures of pure cellulose acetate membrane were produced in this work is shown in Fig. 1. From Fig. 1a, the top surface of the membrane had a glossy appearance, meanwhile Fig. 1b, the bottom surface of the membrane had doffed surface. These phenomena occurred because of the phase inversion method. The method causes the top surface of membrane to turn into a glossy surface. When membrane has been cast, then free diffusion of solvent to the air is occurred on the surface. This leads to the solvent deficiency on the membrane surface (Setiasih, 2009).

(a)

(b)

Figure 1 Cellulose acetate membrane: (a) top surface and (b) bottom surface.

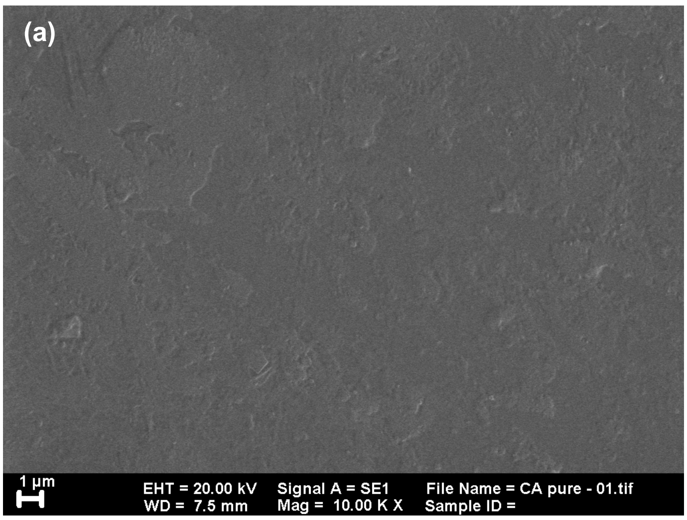
Hydrophilicity and hydrophobicity test of mixed matrix membranes (MMMs)

The inorganic fillers were used in this work are titanium oxide (TiO_2) and zeolitic imidazolate framework-8 (ZIF-8). These particles have different properties i.e. TiO_2 is hydrophilic besides ZIF-8 is hydrophobic. Hydrophilicity and hydrophobicity test were conducted by dripping water to the membrane surfaces. The hydrophilicity and hydrophobicity test results are shown in Fig. 1a-c. From these figures, the water droplet of each membrane had different progression. Compared to CA-ZIF-8 membrane, water droplet on the CA-TiO_2 membrane showed a significant change that the droplet was more widespread. These phenomena confirm that CA-ZIF-8 membrane is hydrophobic and CA-TiO_2 membrane is hydrophilic.

Characterization of pure cellulose acetate membrane and mixed matrix membranes (MMMs)

The structure of membranes was analyzed using scanning electron microscopy (SEM) and x-ray diffraction (XRD). Only three samples were analyzed such as pure cellulose acetate membrane (CA), CA-TiO_2 5% membrane, and CA-ZIF-8 5% membrane. The 3% and 10% materials concentration were not analyzed because the 3% concentrations are too small to affect the structure of membranes, meanwhile, agglomeration of particles could form at 10% materials concentration.

Morphological analysis



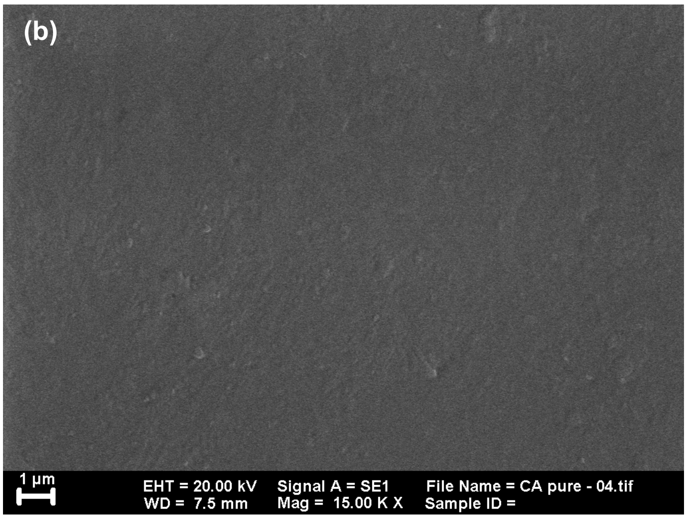


Figure 2 SEM images of pure cellulose acetate membrane of (a) 10,000x magnification and (b) 15,000x

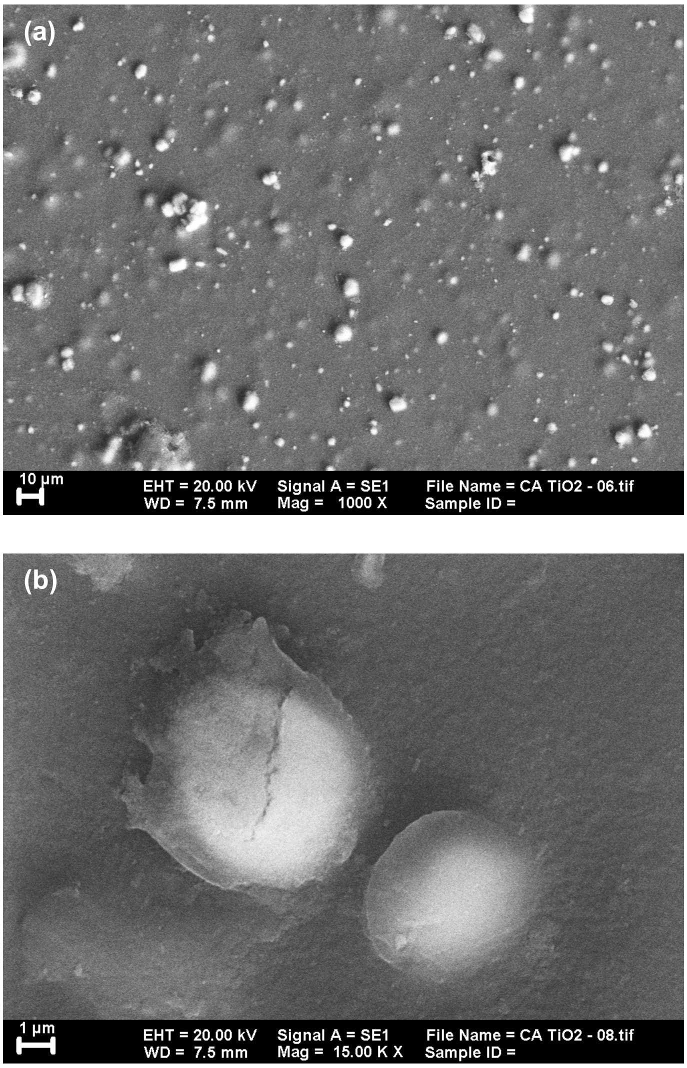


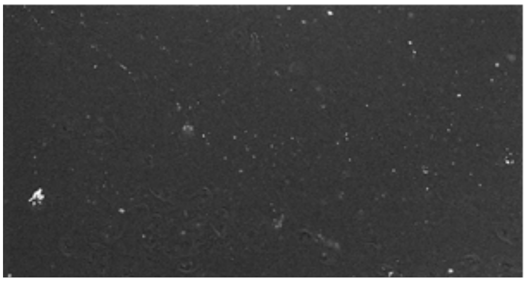
Figure 3 SEM Images of CA-TiO_2 5% membrane of (a) 1,000x and (b) 15,000x magnification

calibration image 5537Date:9/17/2018 1:47:03 PMImage size:512 x 384Mag:10000xHV:20.0kV

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
C	6	K-series	53.06	53.06	62.60	16.7
O	8	K-series	39.84	39.85	35.30	51.3
Ti	22	K-series	7.10	7.10	2.10	0.2
N	7	K-series	0.00	0.00	0.00	0.0
		Total:	100.00	100.00	100.00	

Figure 4 SEM-EDX analysis of CA-TiO_2 5%

Information about morphology, structure, and pore size from the top surface of membranes were achieved. The results of SEM are shown in Fig. 2. The figures display the top surface of pure cellulose membrane. The membrane was smooth and continuous because of no particles were introduced. In contrast, Figure 3 shows the top surface of the CA-TiO_2 membrane where TiO_2 particles were quite dispersed. However, there were some particles form large clusters in some spots. The inorganic particles which have tendency to agglomerate with other inorganic particles can form interfacial void defect on the membrane. This defect increases permeability and decreases the selectivity at the same time [6]. Furthermore, from Fig. 4, SEM EDX shows the presence of a titanium element with the percentage 7.1%.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	62.32	48.09
8	O	Oxygen	20.94	21.52
11	Na	Sodium	10.34	15.28
17	Cl	Chlorine	5.89	13.42
19	K	Potassium	0.27	0.67
30	Zn	Zinc	0.24	1.01

Figure 5 SEM EDX analysis of CA-ZIF-8 5%

SEM and SEM EDX images of CA-ZIF-8 5% are shown in Fig. 5. Compared to Fig. 4, Fig 5 shows that the ZIF-8 particles were more distributive than TiO_2 particles on the membrane. The well dispersed of ZIF-8 particles were caused by organic linkers. Hence, the compatibility between cellulose acetate and ZIF-8 are increased by strong interactions [7]. This phenomenon leads to the polymer rigidification defect, where the strong interactions form polymer layers near to the particles. In addition, the polymer chain mobility in the vicinity of particle surface is less than bulk polymer. Hence, the lower permeability and higher selectivity can be expected [6,7].

Fig. 5 shows the elements on the top surface of CA-ZIF-8 membrane. The zinc element, one of the building blocks of ZIF-8 particles, was observed and only had 1.01% on the top surface of the membrane. The small number of ZIF-8 particles indicate the particles tend to distribute into the inner membrane. Further observation of the cross-sectional SEM images is needed to see the distribution of particles in the inner membrane. Another element, such as sodium and chlorine, were detected on the top surface by SEM EDX. These elements indicate a contamination when synthesizing membrane.

XRD analysis

Table 1 Crystalline/amorphous peak locations of membranes and particles

2θ					
Previous studies			**This work**		
Pure CA (Hong et al., 2013) (Mohiuddin et al.,2015)	**TiO_2 (Rahmawati et al., 2017)**	**ZIF-8 (Sutrisna, 2017)**	**Pure CA**	**CA-TiO_2**	**CA-ZIF-8**
Amorphous	Crystalline	Crystalline	Amorphous	Amorphous	Amorphous
5 – 15	25	7	5 - 13	5 – 15	5 – 13
15 – 25	36, 37, 38	11	13 - 25	15 - 25	13 – 25
35 -50	48	13	35 -50	35 -50	35 -50
	54, 55	14	Crystalline	Crystalline	Crystalline
	63	16	21	21	21
	68	18	23	24	23
	71	19	24	25	24
	75	22		38	
		24		48	
		26			
		27			

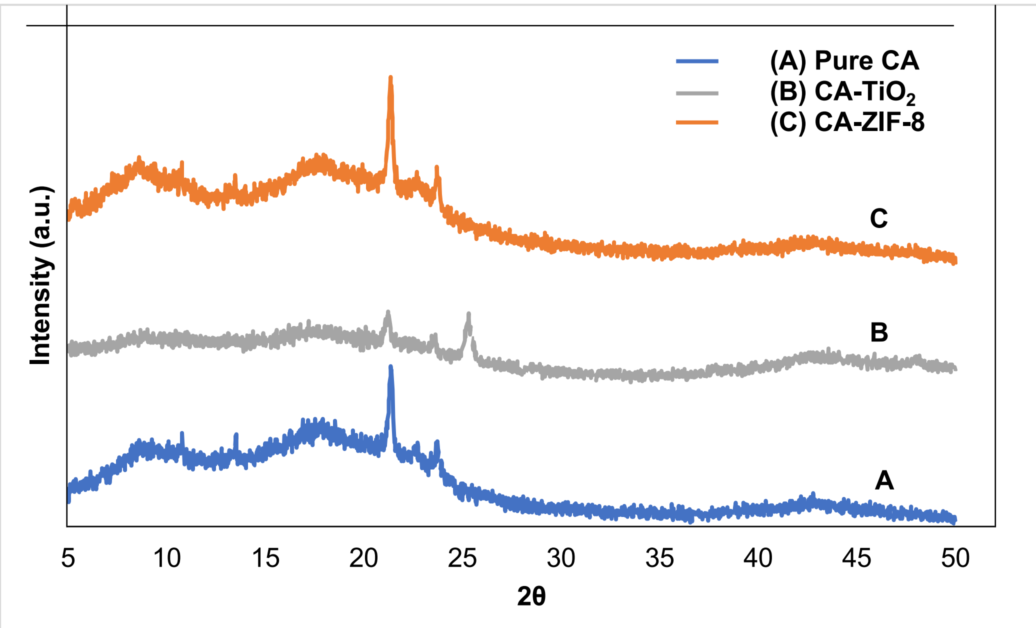


Figure 6 XRD patterns of membranes

Crystallinity and cell dimension of materials can be identified using XRD. The information is displayed in peaks that appear in certain angles. The results were 3 amorphous peaks detected for 5-15°, 15-25°, and 35-50°. Then, other studies in 2017 [7] showed TiO_2 and ZIF-8 particles had crystalline peaks that showed in Table 1. Similarly, the data of pure cellulose acetate, CA-TiO_2, and CA-ZIF-8 membrane of our study shows the angles for 5-15°, 15-25°, and 35-50° (Table 1). These discoveries confirm the membranes, that were investigated in this study, are cellulose acetate based membranes. However, few crystalline peaks appeared at 21°, 23°, and 24°. These crystalline peaks are predicted as cellulose's crystalline peaks which are formed at 20-25° angle.

The addition of inorganic fillers (TiO_2 and ZIF-8) for cellulose acetate membrane, were expected to showed the new crystalline peaks on the intensity vs 2θ graph of cellulose acetate. These peaks should not different with the former researchers result. One of MMMs, CA-TiO_2 membrane, shows XRD data in Fig. 6. The figure shows some new crystalline peaks at 24°, 25°, 38°, and 48° angles, which are not shown in pure cellulose acetate membrane. Moreover, these peaks are ranging in TiO_2 particle's angles at 25°, 36-38°, 48°, 54-55°, 63°, 68°, 71° dan 75°, which confirm TiO_2 particles presence on the membrane.

Another MMMs, CA-ZIF-8 membrane were also analyzed by XRD device. The result shows that there are no significant peak different between CA-ZIF-8 membrane and pure cellulose acetate membrane. Based on the previous study [7], ZIF-8 particle's peak angles are 7°, 11°, 13°, 14°, 16°, 18° ,19°, 22°, 24°, 26°, dan 27°. These angles were not shown in our CA-ZIF-8 membrane. The lower concentration of ZIF-8 particles on the top surface as shown in Figure , causes the ZIF-8 particle's peaks to not observed. Further SEM observation for cross sectional area of membrane is needed to confirm the presence of ZIF-8 particles. From Fig. 6 it can be implied that the incorporation of ZIF-8 particles will improve the crystallinity of the polymer matrix.

Conclusion

In this work, pure cellulose acetate membrane and mixed matrix membranes were synthesized and investigated. These results have led to a deeper understanding about how different inorganic particles interact with polymeric membrane. The results of CA-ZIF-8 membrane characterization showed uniform distribution of ZIF-8, which ZIF-8 has organic linkers to interact well with cellulose acetate. The interaction leads to polymer rigidification that reduced the fluxes and increased the rejections. These potential results can be a solution for wastewater treatment for textile industries. However, the further studies about particle concentrations are needed in order to find the optimal performance. In addition, mechanical properties of the membrane is should be examined, which are the basis knowledge to designing a wastewater filtration apparatus for industrial purposes.

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