Effect of chitosan-zinc oxide coated in PVDF membrane; morphology and performance testing

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Abstract. PVDF membrane modification has been done by coating it using chitosan which is mixed with zinc oxide. This study was conducted to determine the effect of chitosan-zinc oxide hybrid on PVDF membrane’s hydrophobicity and performance. The coating has been processed by immersing PVDF membrane into a chitosan-zinc oxide hybrid solution with a ratio chitosan: zinc oxide of 1: 0 (M1), 6: 1 (M2), 4: 1 (M3), and 2: 1 (M4). Membrane morphology characterization was carried out by FE-SEM and FTIR. Water contact angle analysis and performance test was conducted to determine the effect of chitosan and zinc oxide on the hydrophobicity, permeability, percent rejection, and antifouling performance of PVDF membrane. The result of water contact angle analysis shows that the more zinc oxide was added to chitosan-zinc oxide hybrid, the hydrophobicity of membrane was decreased. Membrane performance test shows that the most stable membrane permeability to time is membrane M4, while the membrane with the most stable permeability to pressure is PVDF membrane without coating (membrane M). The best rejection performance and flux recovery ratio of membranes is shown by membrane M4.

1. Introduction

Currently the development of membrane technology is still interested according to its application, whether for waste water separation, gas separation, biodiesel separation, and others. Poly-vinylidene fluoride (PVDF) is a polymer commonly used as a membrane base polymer. PVDF has the advantage that it is stable against chemicals, it also has good mechanical strength and thermal stability. PVDF membrane applications can be used both for ultrafiltration, microfiltration, membrane bioreactor, and gas separation. One of the weaknesses of pure PVDF membranes and membrane-based polymers in general is that it is easy to foul on the membrane surface which causes significant flux reduction in the compound transport process. The fouling is caused by the deposit of both chemical and microbiological substances on the membrane surface [1]. In this article modification on flat sheet PVDF membrane was carried out using chitosan and Zinc oxide to overcome the weakness of fouling on membranes [2]. Chitosan is a natural polymer which is the result of deacetylation of chitin which can be obtained from the skin of shrimp or crab. Chitosan has been widely used for the pharmaceutical industry, but currently many also examine the benefits of chitosan as an adsorbent for processing wastewater. Benavente (2008) examined chitosan as an adsorbent for metal ions, Oktari (2014) examined chitosan in the form of composite films modified with κ-Karaginan for the adsorption of
methylene blue, and many more studies on chitosan with its application as adsorbents. Chitosan has the potential as a good adsorbent because it has chelating groups [3]. Goy et al. (2016) also reported the ability of chitosan in its activity as an antibacterial. With this consideration, chitosan is chosen as one of the substances used as coatings on PVDF membranes to prevent microbial buildup on the membrane surface [4]. Zinc oxide is a particle that has antimicrobial ability so that it can disperse bacteria that accumulate on the membrane surface. In addition, zinc oxide also has the ability to reduce the wetting effect that can occur on the membrane surface. Several types of nanoparticles have been studied that have potential in the process of degradation of organic matter and bacteria. Kumar et al. (2013) examined the potential of zinc oxide nanoparticles in the process of degradation of methyl orange dyes [5]. Sanna et al. (2016) also examined that the efficiency of degradation of organic dyes with zinc oxide nanoparticles was quite high in the sun [6]. And there are many more studies regarding the potential degradation of nanoparticles against organic matter. In addition to organic substances, Barnes et al. (2013) that titanium oxide and zinc oxide nanoparticles have the potential to degrade E. coli, S. aureus, P. aeruginosa, and B. subtilis bacteria [7]. It can be concluded that zinc oxide nanoparticles can have the potential to be applied in the waste treatment process. Research by combining polymeric membranes with nanoparticles is expected to not only stabilize polymer [4], the function of nanoparticles is also used as antifouling and anti microbacterial agents on membranes [8].

2. Materials and methods

2.1 Synthesis of zinc oxide.

A total of 50 grams of zinc acetate were dissolved in 100 mL of 0.5 M hydrochloric acid, then ammonium hydroxide 0.5 M was added. The pH of the solution was adjusted to pH 9 using concentrated ammonia. The solution was stirred with a hot plate at 85 °C for 5 hours. The precipitate formed was filtered and washed with distilled water. Then the sediment was dried in an oven at 130 °C and characterized by FE-SEM (JSM-7100F) [9].

2.2 Hybrid synthesis of chitosan-zinc oxide

A number of chitosan was dissolved in 2% acetic acid with a ratio of 1: 50, then stirred and heated at a temperature of 60 °C. After the chitosan solution is homogeneous, then mixed with zinc oxide with a weight ratio of chitosan and zinc oxide respectively; 2:1, 4:1, and 8:1. Stirring the solution is done at 1300 rpm for 30 minutes. Then the solution was taken 50 mL to be printed with Teflon mold and dried in an oven at 60 °C. After the membrane is formed then it is characterized. [2]

2.3 PVDF membrane coated with chitosan-zinc oxide

PVDF flat sheet membrane coated with chitosan-zinc oxide by immersion method. PVDF flat sheet was immersed in a mixture of chitosan-zinc oxide for 12 hours with a variety of chitosan-zinc oxide comparisons; 1: 0 (M1), 6:1 (M2), 4:1 (M3), and 2:1 (M4). Then the membrane was dried in an oven at 60 °C. The membrane that has been dried was then morphologically characterized by FE-SEM (JSM-7100F), EDS mapping, FTIR, and water contact angle. PVDF membrane without layers (M) is also characterized as control.

2.4 Performance test with methylene blue

This application and performance test was conducted to determine the effect of application time on the flux value, the effect of pressure on the flux value, calculate the percent rejection of the membrane to the target compound, and calculate the flux recovery ratio (FRR) to determine the antifouling properties of the membrane. Calculation of percent rejection is done using the following formula

\[ R (%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \]  

(1)

Where \(C_p\) and \(C_f\) are the concentration of the target compound in the permeate solution and the feed solution. Whereas to find out the FRR value, the following formula is used:
\[ FRR \% = \left( \frac{J_{w2}}{J_{w1}} \right) \times 100 \] (2)

Where \( J_{w1} \) is the value of membrane flux when the target compound is passed, and \( J_{w2} \) is the value of flux after the backwash membrane uses demineralized water. [10]

3. Result and Discussion

3.1 Morphological characterization

FE-SEM and EDS mapping identify morphological differences in each membrane M, M1, M2, M3, and M4 based on variations in membrane coating levels with chitosan and zinc oxide particles. Figure 1 shows the differences in PVDF membrane morphology before and after coated by chitosan (M and M1).

Figure 1. FE-SEM characterization results on M and M1 membranes

In Figure 1, membrane M pores appear more clearly than M1 membranes. M1 show that chitosan coats the pores of the PVDF membrane so that the PVDF membrane pore becomes faint. This will certainly affect the membrane filtration process. PVDF membrane has a pore size of 0.1 µ. After coating, the surface of the membrane becomes multilayer with the first layer is more dense than the second layer which is porous (anisotropic membrane)[11].

Coating membrane results with mixed matrix chitosan-zinc oxide can be seen in Figure 2 (red for the distribution of Zn elements and green for oxygen element distribution). SEM membrane images M2, M3, and M4 show different morphological structures in the EDS membrane M2, M3 and M4 mapping results showing the distribution map of zinc oxide particles in each membrane based on the ratio of chitosan and zinc oxide to the solution coated on the membrane surface. The distribution of Zn elements in the EDS map is proportional to the membrane surface roughness shown in the FESEM image. FESEM results on the M4 membrane show a kind of particle that is spread like a needle. It can be assumed that these particles are zinc oxide particles.
Fig. 2. Results of FE-SEM and EDS mapping characterization for M2, M3 and M4 membranes. Red color represent Zn elements, green color represent oxygen elements.

Zinc oxide particles on the membrane are propagated and immobilized on the surface of the membrane with the aim that the antifouling function is obtained optimally. Zinc oxide on the membrane surface is expected to degrade deposited substances on the surface so that the backwash process can produce membranes that are free of substances that cause fouling and reduce membrane permeability. From the results of FESEM, we can conclude that the process of immobilizing zinc oxide particles on the membrane surface was successfully carried out. Mainly indicated by the M4 membrane in which zinc oxide particles are seen to spread evenly on the surface of the membrane.

Fig. 3. FTIR spectra of membranes

FTIR spectra of membranes M2, M3, and M4 can be seen in Figure 3. It can be seen that the peak at wave number 840 cm\(^{-1}\) shows the beta phase vibration of PVDF polymer, the number 2300-2400 cm\(^{-1}\) shows the vibration of C and N double bonds asymmetry in chitosan, wave numbers 2700-2978 show CH\(_2\) bonds in chitosan [12][13]. The greater the intensity of the peak in the wave number between 300 and 400 cm\(^{-1}\) where in the wave number Zn element is detected [2]
Figure 4. Water contact angle of membranes M, M1, M2, M3, M4

Water contact angle analysis on the membrane surface shows how much influence the coating of chitosan and zinc oxide has on the hydrophilicity properties of PVDF membrane surface. From Figure 4, it can be seen that the addition of chitosan (M1) can improve the hydrophilic properties of the membrane surface due to the chitosan properties that are easily bonded to water molecules. The addition of zinc oxide (M2, M3, and M4) further increases the surface hydrophilicity of PVDF membranes due to ionic properties in zinc oxide so that it is easy to bind to water. A slight increase in M4 is due to the uneven distribution of zinc oxide on the membrane surface [13][14].

3.2 Performance test of membranes

In this performance test, variations in pressure and time are taken to see the permeability capability of the membrane.

Figure 5. Membrane permeability test for flux value pressure variations

Graph on the figure 4 shows a fairly low and stable flux value of membrane M. The value of flux increases with the addition of chitosan and zinc oxide on membranes M1, M2, M3, and M4, this is because chitosan and zinc oxide make the surface of the membrane more hydrophilic, so that water is more easily absorbed to the membrane surface [15].

There are several factors that cause membrane flux values to go down or increase. The lower membrane flux indicates fouling caused by deposit of substances on the surface of the membrane. While the increase in membrane flux is usually caused due to membrane imbalance to the pressure applied. The increase in flux that occurs significantly in the M2 membrane is due to membrane instability to the pressure applied.
From the graph we can see that the pressure applied to the membrane actually affects the instability of chitosan and zinc oxide in membrane particles, therefore the application of the synthesis synthesis membrane should be carried out at a low pressure range of 1-2 bar.

![Figure 6. Membrane permeability test time](image)

The permeability test is then carried out using 7 ppm methylene blue solution to determine the stability of membrane permeation over time. In this test, it was found that M3 membrane had the most significant decrease in flux compared to other membranes. While the membrane that appears to be stable with time is the M4 membrane.

As we discussed earlier, that membrane flux can be reduced due to fouling that occurs on the surface of the membrane. This is a normal condition as the phenomenon of fouling on the surface of the membrane cannot be avoided. Membrane stability over time can be influenced by several factors, including the appropriate operating pressure and antifouling performance on the membrane surface.

In this study we try to immobilize zinc oxide particles on the membrane surface in the hope that the membrane can reduce the percentage of fouling by itself so that it can reduce the time and water requirements for the backwash process.

![Figure 7. The percent rejection graph of membranes](image)

The percent rejection graph in Figure 6 shows the performance of M, M1, M2, M3, and M4 membranes in rejecting methylene blue compounds with an initial concentration of 7 ppm. The highest percentage of rejection at the initial minute is owned by the M3 membrane, where the membrane is a PVDF membrane coated with chitosan-zinc oxide with a ratio of 4:1. However, the percentage of rejection on this membrane decreased although not significant, this indicates that fouling affects the membrane rejection process against methylene blue compounds from the initial minute. While membrane M4 also has a high percentage of rejection compared
to other membranes and tends to rise. This shows that at the initial minute, the rejection process can still increase even though the transport process has been going on for 1 hour. Excessive and inequality addition of zinc oxide to the coating process can also potentially damage the membrane because of its ability to degrade organic compounds. So it requires optimal levels of zinc oxide and the selection of polymers that are quite stable such as PVDF [16]

The level of flux recovery ratio (FRR) on the membrane shown in Graph 5.7 above identifies the antifouling performance of each membrane. Overall the membrane FRR value is below 50, which means that the membrane antifouling performance is still quite low. The effect of zinc oxide is seen in the increase in FRR values in M2 and M4 membranes. Zinc oxide is thought to reduce fouling on the surface of the membrane because of its ability to degrade pollutants deposited on the surface of the membrane [17]. However, this effect is not too significant. This condition can be caused due to lack of reactivity of zinc oxide particles so that the degradation efficiency of zinc oxide particles against methylene blue is less optimal. Degradation particles such as zinc oxide will be more reactive if they are in smaller sizes such as nano size. Although it is feared that the more reactive zinc oxide particles will actually cause membrane instability itself because the membrane is made from organic polymers. Therefore the choice of the stability of the membrane material against the degrading agent itself is very necessary

4. Conclusions

PVDF membrane coating with chitosan-zinc oxide has been done by immersion method. The effect of chitosan-zinc oxide was identified by morphological characterization, water contact angle analysis, and performance test. The results of morphological characterization with SEM-EDS show that the spread of zinc oxide particles is most evenly distributed on the M4 membrane (membranes coated with chitosan-zinc oxide in a ratio of 2: 1). Analysis of water contact angle shows that more zinc oxide is added to the coating process, the higher the hydrophilicity of the membrane surface. Membrane performance test shows that the most stable membrane permeability to time is membrane M4, while the membrane with the most stable permeability to pressure is PVDF membrane without coating (membrane M). The best rejection performance of membranes is shown by membrane M4. While the antifouling performance of the coated membrane is not too significant compared with PVDF membrane (M) despite it has increased.

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