

Synthesis, Characterization, and Performance of TiO₂-N as Filler in Polyethersulfone Membranes for Laundry Waste Treatment

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Abstract—The synthesis of TiO₂-N has been done by the sol gel method. The results of XRD characterization of TiO₂ doping cannot destroy the anatase structure because the TiO₂-N diffractogram represents peaks similar to TiO₂. In the N-doped TiO₂, peaks around 1160, 1274, 1430, 1340, and 1490 cm⁻¹ represent to nitrogen atoms which are processed as substitutes for the interstitial form of the TiO₂ lattice. From the results of processing data from UV-DRS characterization, it was found that the TiO₂ bandgap energy value was 3.33 eV, whereas the TiO₂-N photocatalyst of the band gap energy was 3.08 eV. BET results state that TiO₂ has a higher surface area compared to TiO₂-N. In this study, the highest results of pure water flux and laundry waste flux were found in PES/PEG/TiO₂-N membrane, which was 116.91 L/m².h in the first 2 minutes for pure water flux and 98.636 L/m².h in the first 2 minutes for waste flux and rejection produced reached 84.328% for COD and 82.75% reduction values for BOD reduction values so that the addition of TiO₂-N to the membrane can improve membrane performance for ultrafiltration.

Keywords—Synthesis, TiO₂-N, Membrane.

I. INTRODUCTION

TITANIUM dioxide with anatase phase is a photo catalyst having a band gap of 3.3 eV which is effectively applied to UV light. Doping on TiO₂ photo catalyst semiconductors is one way to increase the absorption of light in the visible wavelength region [1]. The function of dopants as electron trapping can increase photocatalytic activity [2]. To insert a dopant in TiO₂ there are many ways that can be done including coprecipitation methods, hydrothermal method and sol-gel method. The sol-gel method can be applied to the preparation of nanoparticles, because it can control particle size and homogeneity [3]. Compared to the sol-gel method, the coprecipitation method was considered to have a disadvantage, namely the uneven distribution of dopants [4]. Therefore using the sol-gel method will be more profitable.

One of the excellent membranes to be used in wastewater treatment is polyethersulfone (PES) membranes. Polyethersulfone is a material that is widely used in the manufacture of asymmetrical membranes, because of its good performance, high mechanical strength, and high thermal stability [5]. PES is widely used in ultrafiltration, reverse osmosis and pervaporation membranes [6]. However, PES membranes have poor permeability and high fouling tendency due to inadequate hydrophilic properties [7]. Antifouling on the membrane can be increased by adding inorganic compounds such as



Figure 1. Dead-end mode ultrafiltration Reactor.

TiO₂ [6]. Some authors specifically conducted research to modify PES membranes with TiO₂ to increase their hydrophilicity and to reduce the tendency for fouling. TiO₂ is preferred over other semiconductors due to good physical and chemical properties, availability, photocatalytic activity, hydrophilic and desired antifouling potential [8]. Modified PES composite membranes of TiO₂ nanoparticles show good quality of water separation and higher flux compared to unmodified membranes, improve thermal stability, and increase hydrophilicity [5]. TiO₂ can degrade dyes and organic substances in liquid or gas phases with sunlight as a source of photons and can be used repeatedly [8]. However, the use of TiO₂ is only active in ultraviolet light and it can be modified to be active in the visible light so that the membrane performance will have better performance. Modification of TiO₂ involves the introduction (doping) of metals and non-metals. The nitrogen element is the most effective dopant. Nitrogen dopants can be obtained from urea with high nitrogen content, easy to obtain, and relatively inexpensive so that it is quite potential to be used as a nitrogen source for the production of N-propelled TiO₂ which is expected to be active in visible light regions [9]. From all the above explanations, this study aims to synthesize TiO₂-N to improve membrane performance, because TiO₂-N can degrade or compounds of waste compounds and dangerous surfactants without the help of UV light because it's active in visible light.

II. MATERIALS AND METHOD

A. Materials

The material that used in this research such as PEG 6000 Carbowax, DMAc Merck, Polyethersulfone Merck, TiO₂ Pro Analysis Merck, Urea Merck.

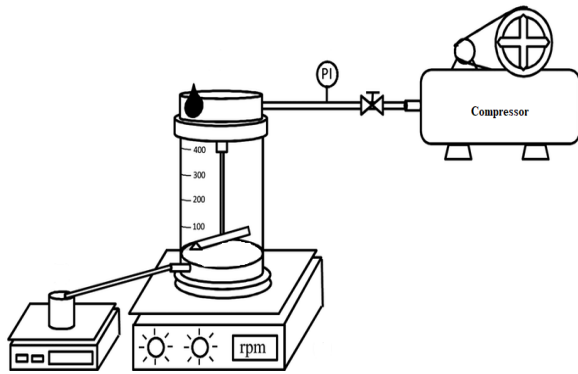
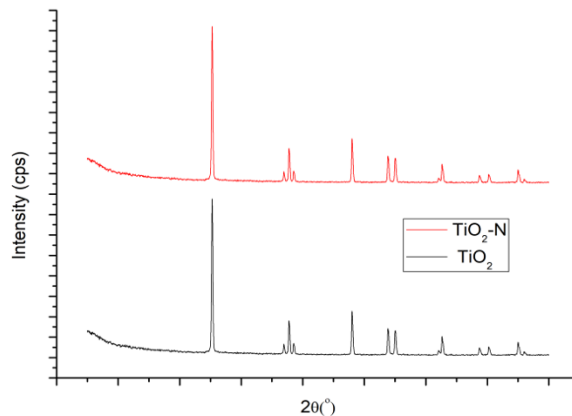


Figure 2. Schematic diagram of ultrafiltration system.

Figure 3. XRD Pattern of TiO₂ and TiO₂-N.

B. Synthesis of TiO₂-N

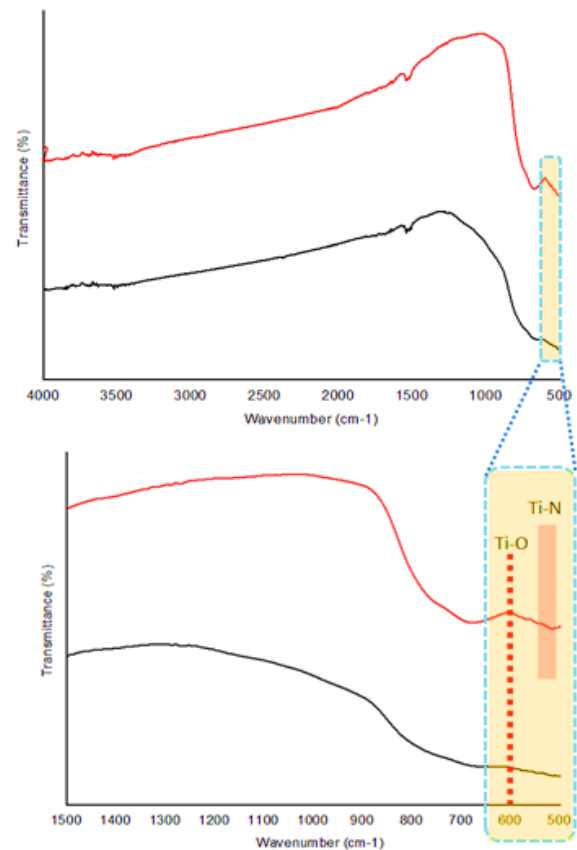
4 grams of urea as a nitrogen source on N-deposition of anatase TiO₂ dissolved in 10 mL deionized water under magnetic stirring and stirred for 1 hour. Furthermore, the suspension is sonicated for 30 minutes. The stable suspension is then dried at 100°C in the oven for 24 hours. Then, calcination was carried out at 400°C for 1 hour at a heating rate of 5°C/minute (Kalantari et al., 2016). TiO₂-N was characterized by *Fourier Transform Infrared Spectroscopy* (FTIR) SHIMADZU, *X-ray diffraction* (XRD), *UV-Vis Diffuse Reflectance Spectroscopy* SHIMADZU, and *BET Quantachrome ASWin™*.

C. Preparation of PES/PEG/TiO₂-N

23.56 ml of DMAc as a solvent were put into a Durant bottle, then 0.4 grams of TiO₂-N was added as a membrane filler. Then stirred with a magnetic stirrer with a temperature of 50 °C until homogeneous. After that, PEG 6000 was added for 1.5 grams while in the stirrer until it is homogeneous. After the solution is mixed until it is homogeneous, it is sonicated for 20 minutes which aims to disperse the mixture and homogenize it. Then after being sonicated, 6 grams of PES are added and stirred at 50°C until the solution is completely homogeneous for 8 hours. It was called as dope solution. The dope solution is casted onto glassplate, then it was immersed into DI water for solidification process.

D. Performance test for laundry waste treatment

The membrane ultrafiltration process uses a dead-end ultrafiltration stirred cell mode (Model XFUF076). The membrane is cut into a circular shape and placed into the reactor (Figure 1). Laundry waste water is obtained in Keputih area, Surabaya which has been tested before hand including BOD and COD. Flux permeate from laundry

Figure 4. FTIR Spectra of TiO₂ and TiO₂-N.

wastewater is calculated the same as water flux in 2 minute intervals. The rejection test was carried out by calculating COD and BOD before and after ultrafiltration.

$$J (\text{flux}) = \frac{V}{A \times \Delta t} \quad (1)$$

$$\text{Rejection (\%)} = 1 - \left(\frac{C_p}{C_f} \right) \times 100 \quad (2)$$

III. RESULTS AND DISCUSSION

A. Structural analysis of TiO₂ and TiO₂-N

Synthesis of N-doped TiO₂ was carried out using anatase TiO₂. N-doped TiO₂ was carried out by the sol-gel method using an ultrasonicator to disperse nitrogen evenly. The effect of nitrogen deposition is to reduce band gap energy and its material can more active under visible light [10]. The XRD diffractogram in Figure 3 shows the appearance of typical TiO₂ peaks. This is indicated by the successful impregnation of TiO₂ or TiO₂-N. Doping process into TiO₂ also cannot destroy the anatase structure, because the TiO₂-N diffractogram represents peaks similar to TiO₂. However, based on previous research, it was explained that the doping process could make a crystal lattice defective and its effect made N-doped TiO₂ have greater photocatalytic activity due to the lower band gap energy [10].

B. FTIR Characterization

The FTIR spectra results in Figure 4 show the spectra of TiO₂ and N-doped TiO₂. In the FTIR spectrum, a wide and strong peak in the range of 500-800 cm⁻¹ can be associated with Ti-O and Ti-O-Ti bonds in N-doped TiO₂ and TiO₂ [11]. In the case of N-doped TiO₂, peaks around 1160, 1274, 1430, 1340, and 1490 cm⁻¹ represent to nitrogen atoms which are processed as substitutes for the interstitial form of the TiO₂ lattice. This creates N-Ti-O

Table 1.
Specific surface area and pore's size of TiO₂ dan TiO₂-N

Sample	S _{BET} (m ² /g)	Surface Area (m ² /g)		Pore Volume(cc/g)			Average Radius Pore (nm)
		S mikro	S meso	V mikro	V meso	V total	
TiO ₂	267.434	27.345	240.089	0.089	0.106	0.195	1.9142
TiO ₂ -N	172.638	63.104	109.534	0.140	0.127	0.267	1.82561

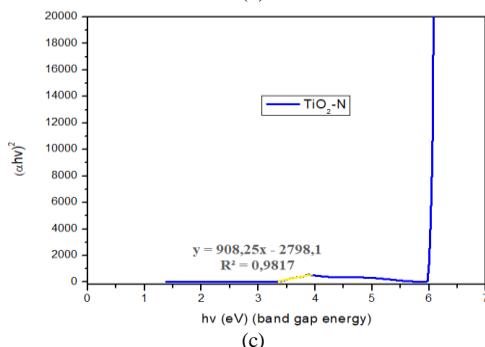
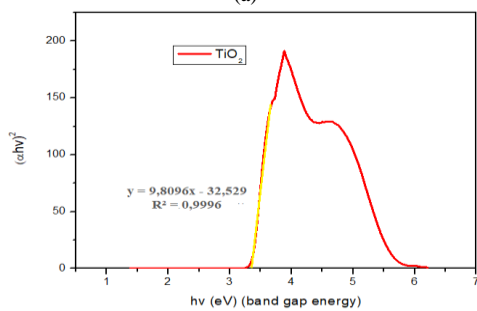
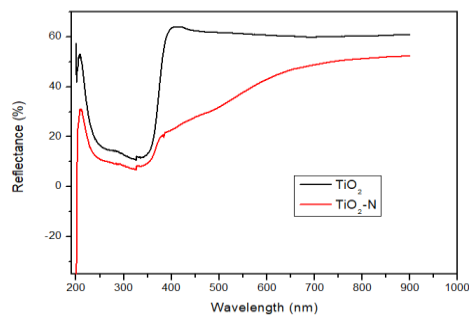


Figure 5. (a) Wavelength Graph as function of reflectance, (b) Kubelka-Munk Graph as function of band gap energy(TiO₂), (c) Kubelka-Munk Graph as function of band gap energy(TiO₂-N).

bonds through substitution of several structural oxygen and Ti-O-N bonds through interstitial inclusion [12], [13]. Wavenumber 505.31-680.83 cm⁻¹ is a characteristic of Ti-N bond vibrations [13]. Wavenumber 680.83 cm⁻¹ is an absorption from Ti-O stretching vibration.

C. Band Gap Investigation Uses UV-Vis Diffuse Reflectance Spectroscopy

The characterization of TiO₂-N photocatalyst using UV-Vis Diffuse Reflectance Spectroscopy was to determine the photocatalyst band gap energy. The effect of N doping can decrease the photocatalyst band gap energy, band gap energy in pure TiO₂ is equal to 3.34 eV [9], whereas in the TiO₂-N photocatalyst the resulting band gap energy is 3.05 eV [14]. Graph of the relationship between the wavelengths of the reflectance of the TiO₂ photocatalyst is shown in Figure 5a. Based on Figure 5 a, it is known that each TiO₂ and TiO₂-N photocatalyst spectra have absorption in the wavelength region of 200-400 nm. However, on the absorption of the 400-800 nm wavelength range TiO₂ has a smaller absorption than

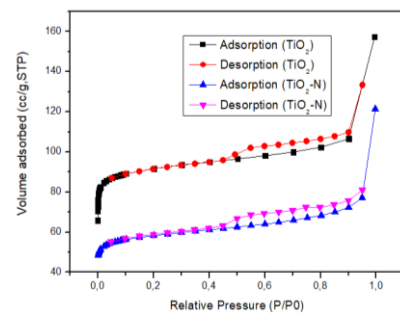


Figure 6. Isotherm adsorption-desorption of TiO₂ and TiO₂-N.

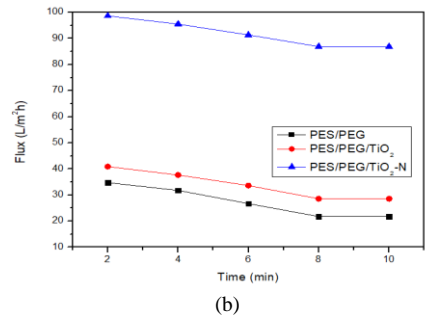
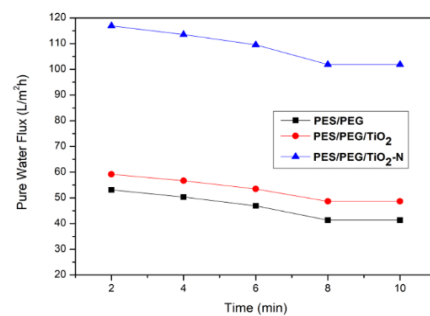


Figure 7. (a) Water Flux and (b) Waste Laundry Flux.

TiO₂-N. This shows that the addition of N dopants to the photocatalyst TiO₂ is capable of producing new energy levels. In addition to absorbance, UV-DRS characterization is able to provide information on the bandgap value of the photocatalyst. From the results of calculations and data processing results of UV-DRS characterization, the bandgap energy value of TiO₂ was 3.33 eV obtained from the line equation $y = 9,8096x - 32,529$ when $y = 0$ (Figure 5 b), while the TiO₂-N photocatalyst energy band the resulting gap is 3.08 eV (Figure 5 c). The decrease in bandgap energy is caused by a shift in wavelength to a longer area. The addition of N dopants to TiO₂ will provide a new energy level that makes it easier for electrons to excite from the valence band to the conduction band. By decreasing the bandgap energy from the photocatalyst, the photocatalyst activity will be optimal under visible light and will decrease under UV light [15].

D. Isotherm N₂ adsorption-desorption

The analysis of nitrogen adsorption-desorption isotherms aims to determine the surface area and pore size

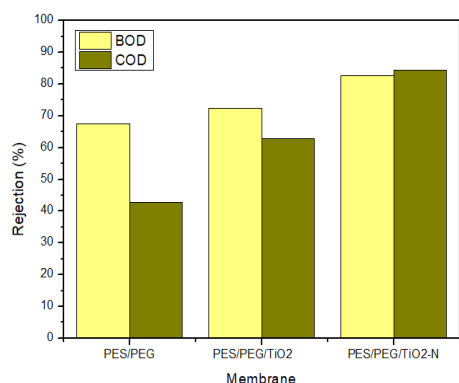


Figure 8. Rejection graph of membrane.

of TiO₂ and TiO₂-N materials. From the results of the characterization it was found that the synthesized material had micropore and mesoporous pore types. This is because at low pressure the material has adsorbed many adsorbates and during high pressure a hysteresis pattern occurs where the amount of adsorption is not the same as desorption. TiO₂ material has a higher surface area compared to TiO₂-N due to the doping effect can cover the pore surface. Addition of dopant N causes smaller pore size but larger pore volume size due to agglomeration.

E. Performance Test for Laundry Waste Treatment

In Figure 5a and b can be seen the relationship between the addition of TiO₂-N with flux and rejection. The membrane with the addition of TiO₂-N has a high flux and pure flux value compared to the others. But further additions will decrease pore size due to agglomeration. The graph of pure water flux is higher because pure water has no concentration of laundry waste so it can produce a higher flux value. The low flux value of the waste because the molecule surfactant in the feed solution will accumulate on the surface of the membrane so that it will affect the decrease in flux value. In the research of Damodar et al [16] which states that the value of pure water flux is greater than the value of the dye flux. This is because the organic material present in the coloring agent with increasing time will clog the membrane pores so that the resulting flux value is smaller when compared to pure water. The value of the rejection coefficient is inversely proportional to the value of the flux. More and more large flux value, the smaller the rejection value. In this study, the highest yield of pure water flux and laundry waste flux was found in the PES/PEG/TiO₂-N membrane, which was 116.91 L/m².h in the first 2 minutes for pure water flux and 98.636 L/m².h in the first 2 minutes for waste flux. This result can be compared with Zhang et al [17] which shows that the addition of additives can increase the flux value. On the rejection chart, PES/PEG/TiO₂-N membranes reached a COD reduction value of 84.388% and a BOD reduction value of 82.75%, whereas in PES/PEG membranes the efficiency of COD was 46.83% and PES/PEG/TiO₂ membranes had efficiency COD decrease 62.68% of flux value. On the rejection chart, PES/PEG/TiO₂-N membranes reached a COD reduction value of 84.388% and a BOD reduction value of 82.75%, whereas in PES/PEG membranes the efficiency of COD was 46.83% and PES/PEG/TiO₂ membranes had efficiency COD decrease 62.68%.

CONCLUSION

Based on the results of the research, N-doped TiO₂ synthesized using the sol-gel method was successful. The results of XRD characterization of TiO₂ with N dopant cannot destroy the anatase structure because the TiO₂-N diffractogram represents peaks similar to TiO₂. In the N-doped TiO₂, peaks around 1160, 1274, 1430, 1340, and 1490 cm⁻¹ represent to nitrogen atoms which are processed as substitutes for the interstitial form of the TiO₂ lattice. The effect of nitrogen deposition is to reduce the active band gap energy in ultraviolet (UV) light to become active in visible light. From the results of the calculation and processing of the results of UV-DRS characterization, the bandgap energy value of TiO₂ was 3.33 eV, whereas in the TiO₂-N photocatalyst the band gap energy produced was 3.08 eV. The decrease in bandgap energy is caused by a shift in the wavelength to a longer area. BET results state that TiO₂ has a higher surface area compared to TiO₂-N. This is because the doping effect can cover the pore surface. In this study, the highest results of pure water flux and laundry waste flux were found in PES/PEG/TiO₂-N membrane, which was 116.91 L/m².h in the first 2 minutes for pure water flux and 98.636 L/m².h in the first 2 minutes for the waste flux and rejection produced it reached 84.388% for the value of COD and 82.75% for the BOD reduction value so that the addition of TiO₂-N to the membrane could improve the performance of the membrane for ultrafiltration process.

ACKNOWLEDGMENT

This research was financed by Ministry of Research and Higher Education of Indonesia under "Program Kreativitas Mahasiswa 2019" grant. We also thank to Material Chemistry and Energy Laboratory of Chemistry Department, Institut Teknologi Sepuluh Nopember for providing research facilities.

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