Fabrication of High Performance PSf-rGO/TiO2 UF Membrane for Ruberry Wastewater Treatment

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Abstract. Membrane technology is commonly used because it is one of the most effective and efficient technologies in producing clean water. The PSf-rGO / TiO2 UF (Ultra Filtration) membrane was synthesized using the phase inversion NIPS method. The membrane was synthesized by modifying the membrane surface by adding rGO / TiO2 nanoparticles to achieve the best performance. The membrane matrix used was the polymer of Polysulfone (PSf) with 0, 0.5, 1, and 1.5 wt% nanoparticles addition and UV irradiation time of 0.5, 1, 3, and 5 minutes. The higher concentration addition of rGO / TiO2 at 1.5% resulted in the best permeability. Meanwhile, the UV irradiation time of 3 and 5 minutes were the lowest time to gain permeability value.

1. Introduction
Indonesia is an agricultural country, especially in Sumatra island, which has one of the most extensive rubber plantations in PTPN VII Bengkulu. Rubber cultivation is beneficial for the economy and fulfills rubber availability, both domestically and abroad. According to [1], Indonesia's rubber exports can reach 2.6 million tons and domestically 0.49 million tons. Even though the rubber industry is doing well economically, rubber processing produces ± 400 m³ of wastewater every day [2]. This wastewater is a problem for the environment because it will pollute the clean water if it is directly discharged into the environment. Clean water is the most crucial source in life [3]. Rubber wastewater content that is still above environmental quality standards, according to [4], will endanger the balance of the ecosystem in the environment.

Efforts to treat wastewater have been carried out conventionally, for example, flocculation and filtration [1], BDB plasma reactor [4], and HRF filtration [5]. Nevertheless, the problem remains unsolved. The use of high technology in wastewater treatment requires a lot of energy consumption. In recent years, the industry has focused on minimizing energy consumption during processing [6]. The factors that need to be considered in the use of technology, especially in the separation process, are operating costs, construction, and energy consumption [7]. The membrane is a separator between the two phases that have good effectiveness and efficiency [8]. Thus, membrane technology is to choose. It has other advantages as well. It is a continuous process, consume low energy, easy to scale up, and highly compatible to add another material to achieve better performance. It also does not require a large area, additional chemicals, or...
extreme conditions [8]. According to [9], membrane separation is a technology that consumes less energy. The ease of membrane technology operation makes it very good in treating wastewater [10]. Many recent studies discussing synthetic membranes instead of natural membranes for better physical properties [25], [11].

In terms of mechanical, thermal, hydrolytic, and chemical stability, a membrane made of PSf is suitable for UF and RO membrane applications [11]. UF is known as a membrane widely applied in the wastewater treatment, oil, food, and pharmaceutical industries [7]. The nature of the membrane is influenced by the polymer materials used as a matrix membrane, such as polysulfone (PSf) [12], polyethersulfone (PES) [13], cellulose acetate (CA), and polyvinylidene fluoride (PVDF) [6], [14]. PSf has high intensity, good thermal stability, and good chemical resistance to attract attention in its utilization. However, the weakness of PSf, which is hydrophobic, makes the fouling process easier to occur [7]. Hydrophilic membranes have been studied and can reduce the occurrence of fouling [14].

Fouling is a major problem that is very difficult to avoid in membrane technology operation [26], [15]. This size difference-based separation process is influenced by the driving force, which allows the accumulation of solution on the membrane surface. The fouling process occurred when there is irreversible contaminant accumulation in the solution, which then is adsorbed by the membrane surface and adsorbed into the membrane pores afterward [12]. Efforts to reduce fouling are by modifying the membrane surface. Thus, in this study, the modification of the membrane surface was carried out by adding nanoparticles with the influence of UV irradiation time. The nanoparticles added were rGO / TiO2. Reduced Graphene Oxide (rGO) is a 2D carbon nanomaterial as thick as atoms and has good solubility in organic solvents [16]. TiO2 was added because its nanoparticles had hydrophilic properties against membrane polymers and maintained adequate hydration and mechanical properties [17]. According to [18], TiO2 has good compatibility with organic solvents when casting PSf membranes. Adding TiO2 to the polymer matrix can improve thermal stability and hydrophilicity. This study is different from previous studies conducted by [19], which only used GO nanoparticles on the PSf matrix. Research by [27] also utilized rGO / GO with a PSf matrix but resulted in low flux because the membrane was still hydrophobic. Besides, [20] made a membrane using the NIPS method. The results obtained were good; the GO added was in accordance with the PES / SPSf matrix. Hence it reduced the E. coli colony, which initially 50, decreased to 12 as the GO concentration increased. However, by its viscosity, it can be known that viscosity contributed to the increase in kinetic energy. Low viscosity would result in high molecular kinetic energy at high temperatures. Whereas in this study, the higher concentration of the added GO resulted in higher viscosity. So that the molecular kinetic energy decreased with increasing GO concentration, this was because GO induced more generation by binding hydrogen to the electron donor. Therefore, in this paper, the addition of rGO / TiO2 nanoparticles would disperse on the membrane surface. Combining the two properties of rGO / TiO2 nanoparticles could achieve a good performance in rubber wastewater treatment.

2. Materials and Methods

2.1. PSf-rGO / TiO2 Membrane Preparation

Materials for the membrane preparation were Polysulfone (PSf) from Solvay Advanced Materials (USA), N-methyl-2-pyrrolidinone (NMP) (Merck) as a solvent, composites of nano rGO (Malaysia Technology University) as the membrane properties modifier. TiO2 supplied from Nano Center Indonesia was also used as an inorganic nanofiller to modify the membrane surface as membrane coating and ion-free water.
The membrane preparation process's primary tool was a casting knife. Other supporting tools used were stirrers, magnetic rods, beakers, measuring glass, measuring pipettes, volumetric flasks, glass plates, glass funnels, coagulation bath, analytical scale, oven, ultrasonic, and membrane filtration cell.

The PSf-rGO / TiO₂ membrane was synthesized with 16% PSf using 84% NMP solvent. The two ingredients were mixed until they were homogeneous. Then the PSf solution was used to dissolve rGO (0%, 0.5%, 1%, and 1.5%) and to dissolve TiO₂ (0%, 0.5%, 1%, and 1.5%). All materials were dissolved until homogeneous using a magnetic stirrer. After this, sonification was carried out for one hour to remove bubbles from the stirring process and dissolve the PSf solution's nanoparticles. The dope solution was rested for one night, after which the PSf-rGO / TiO₂ dope solution was cast at room temperature. The casting stage was carried out using the dry-wet phase inversion technique, namely by pouring the dope solution on a glass plate. Furthermore, the casting knife was used to form a thin layer on the glass plate with a thickness of 0.015 μm. The thin layer on the glass was UV irradiated with irradiation time varied from 0.5, 1, 3, and 5 minutes. Furthermore, the membrane layer was immersed in a coagulation bath containing ion-free water for one hour, and the last step was drying the PSf-rGO / TiO₂ membrane.

2.2. **PSf-rGO / TiO₂ Membrane Application**

PSf-rGO / TiO₂ membranes were used for rubber wastewater treatment. The wastewater was obtained from PTPN VII Bengkulu, Indonesia, because the rubber industry wastewater would be a problem if discharged directly into the environment. The PSf-rGO / TiO₂ membrane was mounted on a filtration cell with an area of 12.56 cm² and its operation was carried out at a fixed pressure of 6 bar at room temperature.

![Figure 1. Filtration Cell](image-url)

Figure 1 describes the process of treating wastewater using a filtration cell. First, the prepared membrane was placed in a membrane container with an effective cross-sectional area of 12.56 cm². The rubber seal was placed on the membrane, and the stainless-steel cylinder was attached on top of it. The cylinder was then closed, and the bolts on the cylinder cap were tightened. The rubber wastewater sample was put into the tank; then, the membrane filtration equipment was connected to the hose. The filtration process began with the first step of turning on the filtration tool at button B; the wastewater in storage tank A was fed using the pump H through pipe C. After that, the pressure setting at D was carried out as needed. The UF membrane was operated at a pressure of 6 bar. Wastewater passed through a flat membrane attached to E in a dead-end flow [21]. The filtered wastewater (filtrate) would be collected through the pipe K in container L. While the rejection (permeate) flowed back through the pipe J&K to the feedback tank. The filtration process continued for 2.5 hours by measuring the filtrate sample every 30 minutes.
2.3. Analysis

The membrane performance can be seen from the permeability parameter of rubber wastewater. It is also necessary to calculate the TDS rejection rate because it affects the fouling process due to the wastewater's solid content. The permeate flux was calculated using the following equation:

\[ J_w = \frac{Q}{A \cdot \Delta t} \]  

\( J_w \) (L.m\(^{-2}\).h\(^{-1}\)) is the flux of pure water, \( Q \) (L) is the permeate volume, \( A \) (m\(^2\)) is the membrane area, and \( \Delta t \) is the sample operating time [22]. Flux was calculated every 30 minutes of impregnation [14]. One of the parameters used to measure the membrane process's efficiency is solute rejection (R) [23]. R or rejection in% and \( C \) is the solute concentration in the solution (mg/L) (Safarpour, 2016).

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

3. Results and Discussion

Permeability is the filtrate volume that passes through each membrane area per unit time divided by the operating pressure [21]. In permeability assessment, it was necessary to carry out supporting assessments such as the TDS rejection rate. TDS analysis was intended to determine the membrane's performance capability in producing filtrate with low dissolved solids content.

**Figure 2.** Surface of PSf-rGO / TiO\(_2\) membrane

*Figure 2* shows the picture of the membrane surface result from the casting process. *Figure 2* shows the color of different membranes; the left one is the membrane with the addition of rGO / TiO\(_2\) nanoparticles at 0% and 0.5% concentration. The right side is the membrane with the addition of concentrations of 1% and 1.5%. The more rGO added, the darker the color it would be. The dark color was influenced by the presence of GO, which was a group of carbon compounds. The same study regarding GO's effect was carried out by [24], that pure polymer membranes had lighter color than membranes modified using GO.
The membrane filtration process could produce clean water that was safer when discharged into the environment, as shown in Figure 3. The filtrate (the result of the filtration process) was clearer because dissolved solids' content was lower than the wastewater before the filtration process.

3.1. rGO-TiO₂ Nanoparticles Addition on Permeability

In the PSf-rGO / TiO₂ membrane preparation, apart from being influenced by nanoparticles' addition, it was also influenced by the UV irradiation time. Figure 4 shows that the best result of membrane permeability was achieved by 1.5% addition of rGO / TiO₂ with the UV irradiation time of 30 seconds. The highest concentration added, at 1.5% rGO / TiO₂, increased the hydrophilicity of the membrane. Meanwhile, the longer the irradiation time, the lower the permeability. It was because UV irradiation could increase the density of the polymer of the PSf membrane and tightened the chain bonds of each polymer compound. UV irradiation would make polymer chains to rearrange spaces and fill gaps so that the volume between polymers was filled [21]. The lowest yield was at the no addition of rGO/TiO₂ treatment. The composition was dominated by PSf (pure), which made it very hydrophobic and produced the lowest permeability. The UV irradiation time of 3 minutes also supported the 0% 3 minutes variable to yield the lowest permeability because the chain between polymer compounds was tighter. It also happened at the concentration of 1.5% but at UV irradiation time of 1, 3, and 5 minutes. It can be concluded that the lowest irradiation time was 3 minutes and 5 minutes because both times produced low permeability compared to other irradiation times. The hydrophobic nature resulted in faster fouling occurrence and lower permeability. The addition of TiO₂ and rGO resulted in excellent dispersion that agglomeration did
not occur. The high affinity possessed by TiO$_2$ could hydrolyze water through the membrane by the formation of hydroxyl groups and some hydrophilic oxygen on the rGO/TiO$_2$ surface [24].

3.2. **TDS Rejection Rate (%) of PSf-rGO / TiO$_2$ Membrane**

Rejection is an indicator of a membrane's ability to reduce the pollutant in wastewater, for example, TDS. In this research, the membrane performance was supported by data on the TDS rejection rate of the PSf-rGO / TiO$_2$ membrane.

![Figure 5. %Rejection PSf-rGO / TiO$_2$ membrane](image)

In Figure 5, it can be seen that the longer the UV irradiation time, the higher the rejection rate. The best rejection rate was at 0% rGO / TiO$_2$ concentration (no rGO / TiO$_2$ addition) with the UV irradiation time of 3 minutes. The hydrophobic nature of pure PSf was good in removing TDS. Although fouling would be more accessible, the polymer chain's density, due to the long UV irradiation time of 3 minutes, inhibited the escape of dissolved solids in the rubber wastewater resulting in a low TDS value or the best TDS rejection rate of 79%. The lowest TDS rejection rate was 9% at the concentration of 1% rGO / TiO$_2$ addition and 1-minute UV irradiation time. Fouling due to the filtration process can be seen in Figure 6.

![Figure 6. Fouling of PSf-rGO / TiO$_2$ membrane](image)

4. **Conclusion**

The PSf-rGO / TiO$_2$ membrane was synthesized by modifying the membrane surface by adding rGO and TiO$_2$ nanoparticles. The best results were achieved by adding 1.5% rGO / TiO$_2$ because it had the highest permeability. The best permeability was achieved at UV 30 seconds of irradiation time of the PSf-rGO / TiO$_2$ membrane preparation, while the time which yielded the lowest was 3 minutes and 5 minutes. Membrane performance in TDS rejection was inversely proportional to permeability; the more hydrophobic the membrane, the more it removed the TDS, namely at the addition concentration of 0% and UV irradiation time of 3 minutes. Long-time UV irradiation would increase the polymer chain's density, and it would make it more difficult for the dissolved solids in rubber wastewater to pass.
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