Preparation of PVA/TiO$_2$ Composites Nanofibers by using Electrospinning Method for Photocatalytic Degradation

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Abstract. PVA/TiO$_2$ composites nanofibers have been prepared by using electrospinning method. Electrospinning was performed at a voltage of 15 kV, with a tip-collector distance of 14 cm. The PVA/TiO$_2$ composites nanofibers were characterized by FTIR, SEM, and EDAX. The results showed that PVA/TiO$_2$ composites nanofibers were successfully formed. SEM observation showed that the nanofibers has hundreds of nanometers with a smooth surface and have TiO$_2$ nanoparticle distributed in the nanofibers. FTIR result shows a functional group of PVA and EDAX result demonstrates the presence of TiO$_2$ in the nanofibers. The photocatalytic activity of PVA/TiO$_2$ composites nanofibers were investigated for the degradation of methylene blue under UV light. The PVA/TiO$_2$ composite nanofibers suspending in the dye solution have dye removal of 70% dye was degraded in 5 h. As a comparison, the TiO$_2$ powder that has dye removal of 95% dye was degraded in 5 h. Photocatalytic activity of PVA/TiO$_2$ nanofiber was lower than TiO$_2$ powder, but PVA/TiO$_2$ nanofiber was more efficient than TiO$_2$ powder regarding process treatments photocatalytic.

Keywords: electrospinning, nanofibers, PVA, TiO$_2$, photocatalytic.

1. Introduction
Titanium dioxide has been widely studied for its ability to photocatalytic and applications have high performance for photovoltaic applications [1]. It also shows chemical stability, low toxicity, low pollutant load, and availability at low cost. TiO$_2$ size has been reduced to increase the reactive surface area to improve efficiency [2]. Wastewater treatment for environmental preservation based TiO$_2$ photocatalytic has been proven to degrade many organic pollutants effectively. This case, however, still leaves some problems when it is applied in environments such as rivers, lakes, and sea [3]. The main problem is the difficulty of recovery after photocatalytic treatment process, namely how to separate TiO$_2$ particles from the liquid waste that is already degraded. Several ways have been made to overcome this problem include the use of TiO$_2$ particle filtration system with ceramic materials, stainless steel, and activated carbon. It is less effective because it can cause new problems as the precipitation and cause further pollution [4].
The solution to this problem is the development of photocatalytic based nanofibers were synthesized by using electrospinning methods. TiO$_2$ has been widely used as photocatalytic due to its chemical stability and availability in the commercial. Many forms of TiO$_2$ nanomaterial have been prepared including nanoparticle, nanotube, nanofiber, and nanosheet [5]. Electrospinning is a unique spinning technique using electrostatic force to produce fine fibers from a polymer solution. Fibers produced from this electrospinning have a thinner diameter (in order of nanometers) and a surface area which is greater than that obtained from conventional spinning process [6]. The electrospinning process is a method to produce polymer fibers from polymer solutions, with diameters in the range of 10 - 500 nm and high surface areas per unit mass. Nanofibers were due to their high ratio of surface area to mass and extraordinary small diameters around 100 nm. Electrospinning has received considerable attention in recent years in various applications due to the ease of forming fibers with different properties. Electrospinning offers some unique advantages such as a high ratio of surface to volume, porosity that can be adapted to the structure of electrospun, and flexibility to electrospinning into various shapes and sizes [7]. Nanofiber has excellent characteristics such as the ratio of surface area to volume ratio is vast and high porosity with small pore sizes. Therefore, the nanofibers are very promising materials for many biomedical applications such as tissue templates, medical prostheses, artificial organs, wound dressings, bone tissue engineering, drug delivery, pharmaceutical compositions, a formation of filter and sensing applications [8]. Compared to conventional TiO$_2$ particles, TiO$_2$ fibers have greater surface-to-volume ratios, and their porous structures provide a higher number of active surface sites for effective photocatalytic [9-10].

Many efforts are focused on the application of TiO$_2$ in the wastewater treatment system. However, it is hard to remove TiO$_2$ from wastewater after treatment using conventional separation methods due to the nanosized structures. This limitation worked as the main drawback for TiO$_2$ to be widely used as adsorbents and photocatalysts in the environmental protection. In this paper, TiO$_2$ nanoparticles have been bounded into nanofiber composites by using Polyvinyl alcohol as fiber template. The primary purpose why TiO$_2$ was bounded into a nanofiber waste prevent TiO$_2$ particles not became a new pollutant in the water, as we know TiO$_2$ particles are very dangerous for an organism living in the water. In this paper, we study about electrospinning process of PVA/TiO$_2$ composites nanofibers and morphology of the fiber. The photocatalytic activity of PVA/TiO$_2$ composites nanofibers were investigated for the degradation of methylene blue under UV light and compared with the photocatalytic activity of TiO$_2$ nanopowder.

2. Experimental Method

The material used in the research were: PVA (Mw: 89.000-98.000 g/mol, 99% hydrolyzed), Titanium (IV) oxide, anatase, nanopowder < 25 nm particle size, 99.7% trace metal basis, Glutaraldehyde solution 50 wt% in H$_2$O, and methylene blue powder, all of them purchased from Sigma-Aldrich. Characterizations of PVA/TiO$_2$ nanofibers by using FTIR and SEM-EDAX. FTIR (Shimadzu, Type: IR Prestige21) were used to determine the functional group of PVA/Chitosan/TiO$_2$ nanofiber. The nanofibers surface morphology was studied by using SEM-EDAX (FEI, Type: Inspect-S50). Image processing software was used to measuring the diameter of the nanofibers captured in the SEM micrograph.

PVA/TiO2 electrospun solution was prepared by dissolving TiO$_2$ nanoparticle in deionized water at 90 °C for 1 hour in magnetic stirrer. TiO$_2$ dispersion was added with PVA powder and then the PVA and TiO were blended at a ratio of 4:1. They were then stirred for 1 hour at 90 °C. The prepared PVA/TiO2 solution was then loaded into a 12-mL plastic syringe equipped with a 0.4-mm needle diameter. A high voltage of 15 kV, with a tip-collector distance of 14 cm, was applied to the solution and fiber collected on the plane collector. Electrospun nanofibers were crosslinked by immersing in a solution of 2.5 wt% Glutaraldehyde solution (volume ratios of Glu (aq): acetone: HCl (aq) = 1:2:0.01 ) at 40 °C for 24 h.

Photocatalytic activities of nanofiber membrane PVA/TiO$_2$ were investigated by observing degradation of methylene blue (MB) under UV light. The experiment was set up with conditions of 4 x
10 W lamp as the UV light source (365 nm). The reaction was prepared by using 0.1 g of PVA/TiO$_2$ nanofibers mat into the beaker containing 10 ppm of Methylene blue solution (10mL). Degradation of methylene blue was observed by UV-vis spectroscopy each 1 hour during 5 hours which suggested PVA/TiO$_2$ composites nanofibers could degrade the methylene blue solution.

3. Results and Discussion

The SEM image of electrospun nanofibers and TiO$_2$ nanopowder is shown in Figure 1. The morphology of PVA nanofibers as depicted in Figure 1.(a) is clearly fine and smooth. Its average diameters are uniform about 355 nm. On the other hand, PVA nanofibers containing TiO$_2$ as in Figure 1.(b) has some TiO$_2$ nanoparticles in the fiber. TiO$_2$ in the nanofibers has agglomeration, same as TiO$_2$ nanopowder in Figure 1.(c). The SEM image showed that the fiber has several hundred nanometers with a smooth surface and have TiO$_2$ nanoparticle distributed in the fibers. The average diameters of PVA/TiO$_2$ nanofibers are about 160 nm. If we compare those two nanofibers, we find that adding TiO$_2$ gives rise to reduce the fiber’s diameter. The presence of TiO$_2$ causes to decrease the solution’s viscosity and increase the conductivity of the electrospun solution. A reduction in fiber diameter is very helpful to increase the active surface area to improve the ability of the photocatalytic.

![Figure 1](image1.png)

**Figure 1.** SEM image of (a) PVA/TiO$_2$ nanofibers, (b) PVA nanofibers, and (c) TiO$_2$ nanopowder.

The FTIR spectrum of PVA/TiO$_2$ nanofibers is shown in Figure 2. The Broadband at 3200-3550 cm$^{-1}$ indicates the O-H stretching. The peaks at 2910 cm$^{-1}$ indicate the C-H stretching. The peaks at 1330 and 1377 cm$^{-1}$ indicate the C-H group. The broad absorption bands at 1095 cm$^{-1}$ indicate the C-O stretching. C-H group vibration peaks were observed at 1230 and 1323 cm$^{-1}$. For the PVA/TiO$_2$ nanofibers adsorbents, a new broadband around 550–800 cm$^{-1}$ is attributed to the Ti-O-Ti band [11].
Figure 2. FTIR spectra of PVA/TiO$_2$ nanofibers.

The EDAX was used to investigate the content elements of electrospun fibers. EDAX result of the PVA/TiO$_2$ composite nanofibers is shown in Figure 3. The elemental analysis reveals the presence of TiO$_2$ nanoparticle on the fibers, the element ratio of C, O, and Ti are 68.03, 28.76 and 3.21% respectively in the entire area of PVA/TiO$_2$ composite nanofibers. It proves that the nanofiber contains TiO$_2$.

Figure 3. SEM-EDAX of PVA/TiO$_2$ nanofibers
Figure 4. Uv-vis spectrum dye Methylene Blue solution after 1 – 5-hours degradation by (a) PVA/TiO$_2$ nanofibers (b) TiO$_2$ nanopowders.

The UV-Vis spectroscopy was used to observe the concentration of Methylene Blue solution after photocatalytic treatment. The UV-Vis spectroscopy observed every 1 hour during 5 hours. Figure 4 shows that the Methylene Blue solution are degraded by (a) PVA/TiO$_2$ nanofibers (b) TiO$_2$ nanopowder. Degradation of Methylene Blue solution by PVA/TiO$_2$ nanofibers was less than TiO$_2$ nanopowder. Comparison of photocatalytic activity to degrade Methylene Blue solution between PVA/TiO$_2$ nanofibers and TiO$_2$ nanopowder is shown in Figure 5.

Figure 5. Removal of dye Methylene Blue by (a) PVA/TiO$_2$ nanofibers (b) TiO$_2$ nanopowder.

The plot of dye concentration on exposure time is shown in Figure 5. The results indicate that the PVA/TiO$_2$ composite nanofibers suspending in the dye solution and having dye removal of 70% dye was degraded in 5 h. In another research, PAN-based fibers contain TiO$_2$ particles removal 80% of the dye was degraded in 38 h [3]. PVA/PAAc/TiO2/CNTs composite nanofiber showed 30% of dye removal after 350 min at pH 7 and 80% of dye removal after 350 min at pH 10 [12]. TiO$_2$/PVA/PDMA-PAAm composite nanofiber showed 50% of dye removal after 300 min at pH 7 and 90% of dye removal after 300 min at pH 2 [2]. As a comparison, the TiO$_2$ powder suspending in the dye solution and having dye removal of 95% dye was degraded in 5 h. Photocatalytic activity of PVA/TiO$_2$ nanofiber was lower than TiO$_2$ powder, but PVA/TiO$_2$ nanofiber was more efficient than TiO$_2$ powder regarding photocatalytic treatments. The treatments process of TiO$_2$ powder in photocatalytic should be done by using stirrer to mix the TiO$_2$ powder with methylene blue solution.
after treatments process we must separate TiO\textsubscript{2} powder that has been dissolved in a methylene blue solution conducted by centrifuge and filtration. On the other hand, for nanofiber photocatalytic does not need to do it. This phenomenon proves that the process of photocatalytic with PVA/TiO\textsubscript{2} nanofiber is more efficient than TiO\textsubscript{2} powder. The result reveals that PVA/TiO\textsubscript{2} composite nanofibers could be applied for environmental field effectively.

4. Conclusion
The PVA/TiO\textsubscript{2} nanofibers were successfully fabricated by electrospinning method. The result of FTIR and EDAX shows that PVA and TiO\textsubscript{2} nanoparticles exist in PVA/TiO\textsubscript{2} nanofibers. SEM observation shows that the fiber has several hundred nanometers with a smooth surface and have TiO\textsubscript{2} nanoparticle distributed in the fibers. It also shows that by adding TiO\textsubscript{2} in the electropun solution resulted in reducing the diameter of the fiber due to reducing the solution's viscosity and increasing the conductivity of the electropun solution. Photocatalytic activity of PVA/TiO\textsubscript{2} nanofiber is lower than TiO\textsubscript{2} powder, but PVA/TiO\textsubscript{2} nanofiber is more efficient than TiO\textsubscript{2} powder regarding photocatalytic treatments. The result reveals that PVA/TiO\textsubscript{2} composite nanofibers could be applied for environmental field effectively.

5. References
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Acknowledgement
This research was supported by a research grant of “PUPT (Penelitian Unggulan Perguruan Tinggi), Contract No:157/LPPM/2015” by the General Directorate of High Education (DIKTI), Ministry of Education and Culture, the Republic of Indonesia. The authors would also thank Mr. Kunto Wandono for maintaining the electrospinning machine.