# The Optimization of Silica-Based Composite Membrane from Volcanic Ash of Mount Sinabung, Titanium Dioxide, and Polyvinyl Alcohol for River Water Treatment through Photocatalyst Process

**Moraida Hasanah[1,2], Timbangen Sembiring[1], Zuriah Sitorus[1], Syahrul Humaidi[1*], Fynnisa Zebua[3], and Rahmadsyah Rahmadsyah[2]**

[1]*Postgraduate Program (Physics), Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Jl. Bioteknologi No. 1 Padang Bulan, Medan 20155, Indonesia*

[2]*Department of Mechanical Engineering, Universitas Asahan, Kisaran Timur, Kisaran 21216, Indonesia*

[3]*Department of Civil Engineering, Universitas Asahan, Kisaran Timur, Kisaran 21216, Indonesia*

* ***Corresponding author:***

*tel: +62-82361351902*
*email: syahrul1@usu.ac.id*

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**Abstract:** *The application of composite membranes consisting of $SiO_2$ from the volcanic ash of Mount Sinabung, $TiO_2$, and PVA on a laboratory scale has been investigated to improve the Silau River's water quality in Asahan Regency. The purpose of this study is to determine the optimal combination of $SiO_2$, $TiO_2$, and PVA for treating river water to minimize its heavy metal content and color intensity to achieve clean water requirements. The membranes were prepared by drop-casting with varied compositions of PVA/40$TiO_2$/60$SiO_2$, PVA/60$TiO_2$/40$SiO_2$, PVA/80$TiO_2$/20$SiO_2$, and PVA/100$TiO_2$/0$SiO_2$. PVA was dissolved in aquadest, mixed with $SiO_2$ and $TiO_2$, then imprinted and dried for 24 h at 50 °C. A photocatalyst test was performed on each composition variation to see how the Silau River water's color changed over time. The PVA/80$TiO_2$/20$SiO_2$ membrane's composition fluctuated the highest during photocatalyst testing, with 45.95% degradation. The parameter results on the Silau River water test, namely turbidity, color, and chromium values, were reduced by photocatalysis of a PVA/80$TiO_2$/20$SiO_2$ composite membrane to 16 NTU, 30 TCU, and 0.013 mg/L, respectively. These results met the clean water quality criteria specified by Minister of Health of the Republic of Indonesia Decree No. 416/MENKES/PER/IX/1990.*

**Keywords:** *silica-based composite membrane; photocatalyst; river water treatment*

## INTRODUCTION

The Silau River is a vast river that flows from Asahan Regency's southern edge to the city of Tanjung Balai. The Silau River is the second biggest river in Indonesia, next to Asahan, and plays a significant role in the people who live along its banks. The Silau River benefits from abundant agricultural goods such as sand mining, fish, and shellfish. The Silau River watershed is also adjacent to community settlements and numerous community activities that significantly influence the Silau River water as a source of pollution. The Silau watershed provides numerous benefits to the surrounding community. However, it is feared that the Silau watershed area and its surroundings will become polluted due to community and industrial activities near the river. Hence, monitoring and evaluation of the condition of the waters in the community are necessary as a form of prevention [1].

According to the Ministry of the Environment of the Republic of Indonesia data year 2014, residential garbage contaminated more than 60% of waterways [2]. Numerous techniques for resolving the pollution problem caused by liquid waste are being explored, one of which is the photocatalyst process. Photocatalysis is a chemical reaction that happens in the interaction between light and a photocatalyst. Due to its efficacy and adaptability, photocatalytic degradation has become an increasingly attractive solution for water pollution concerns [3-4]. Photocatalysts are a favorable method in treating dirty water and textile waste. Titanium dioxide ($TiO_2$) is a frequently used photocatalyst material due to its high stability and non-toxicity. $TiO_2$ is a photocatalyst that stands out for its photodegradation of organic dyes [4].

$TiO_2$ with an anatase structure has high photocatalytic activity [5-7]. One of the properties of $TiO_2$ is determined by its crystallinity, crystal size, and crystal phase. Increasing the capability of $TiO_2$ material can be done by adding oxides substances such as $Fe_2O_3$ [6], $SiO_2$ [8], and other oxides. Since $TiO_2$ has a limited surface area, it can affect the performance of $TiO_2$ materials [9]. To address this issue, it is required to incorporate an oxide material with a high surface area, such as $SiO_2$. Silica with the chemical formula of $SiO_2$ may be produced by extracting volcanic ash from Mount Sinabung, where it is known that the silica concentration after extraction is 48% [10]. $SiO_2$ that is combined with $TiO_2$ has several benefits, including being one of the most promising heterogeneous photocatalytic options for the degradation of various chemical molecules, heavy metal reduction, and selective oxidative processes [9].

## ■ EXPERIMENTAL SECTION

### Materials

The materials used to fabricate $SiO_2$ composite membranes included volcanic ash extracted from Mount Sinabung as a silica source, polyvinyl alcohol (PVA; Sigma-Aldrich, Mw = 145,000) as a matrix, $TiO_2$ (Sigma-Aldrich) as an active photocatalyst, and Silau River water from Asahan Regency, North Sumatera as a sample in the photocatalyst process.

### Instrumentation

Fourier transform infrared (FTIR) spectroscopy (Shimadzu, IR Prestige 21), scanning electron microscope-energy dispersive X-ray (SEM-EDX, FEI, Inspect-S50), and X-ray diffractometer (XRD, PANalytical, X'Pert PRO) were employed to characterize the composite membrane samples. Furthermore, ultraviolet-visible (UV-Vis) spectrophotometer (Analytik Jena, Specord 200 Plus) was used to monitor the degradation process.

### Procedure

A 10% PVA solution was prepared by dissolving 1.111 g of PVA in 10 mL of distilled water and heating it for 1 h at 90 °C. Then, using a 100-mesh sieve, $SiO_2$ and $TiO_2$ were sieved. As a filler, $SiO_2$ was combined with $TiO_2$ in this research. PVA and filler are combined in a 4:1 ratio. The mixture was then molded and dried for 24 h at 50 °C. The following table summarizes the differences in the composition of the filling material (Table 1).

After fabricating the PVA/$TiO_2$/$SiO_2$ composite membrane, the next stage was to test the membrane material, precisely the degree of the swelling test, which was used to determine the membrane's resistance to water absorption. The degree of swelling was determined by submerging it in aquadest for varying periods. Additionally, FTIR and SEM analyses were performed to identify the functional groups and morphology of the PVA/$TiO_2$/$SiO_2$ composite membrane.

Additionally, the photocatalyst test was conducted to ascertain how the color content of Silau River water may be decreased by adding a PVA/$TiO_2$/$SiO_2$ composite membrane. The photocatalyst process was carried out in a box fitted with a ten-watt ultraviolet lamp for 1, 2, 3, 4, 5, 6, and 8 h. The solution's absorbance was determined following the treatment using a UV-Vis spectrometer. Eq. (1) was applied to calculate the percentage of watercolor decrease in the water sample.

$$\%\ \text{Decrease in water content} = \frac{c_o - c_t}{c_o} \times 100 \quad (1)$$

**Table 1.** Variations of Filler Composition as $TiO_2$:$SiO_2$

| Sample | $TiO_2$ (%) | $SiO_2$ (%) |
|---|---|---|
| I | 100 | 0 |
| II | 80 | 20 |
| III | 60 | 40 |
| IV | 40 | 60 |

where $c_o$ denotes the initial concentration of Silau River water, and $c_t$ is the concentration after t time of the photocatalyst process.

The characterization of river water was conducted at the Environmental Health Engineering Center of Class I in Medan. The purpose of this test was to investigate the effect of adding a PVA/$TiO_2$/$SiO_2$ composite membrane towards river water content parameters.

## ■ RESULTS AND DISCUSSION

### FTIR Characterization

FTIR was used to visualize the composite membrane's functional groups. A functional group is a collection of one or more atoms with distinct chemical characteristics covalently connected to other compounds [11]. The FTIR spectra are presented in Fig. 1. The band around 3500 and 1700 $cm^{-1}$ corresponds to the absorption of the O–H stretching and bending functional groups, which are the hydroxyl groups present in PVA [12]. A C–H stretching functional group with an absorbance of around 2900 $cm^{-1}$ suggests the existence of residual organic molecules. An absorption at a wavenumber of around 1100 $cm^{-1}$ was assigned to C–O bonds from PVA [13]. This peak overlap with Si-O-Si asymmetric stretching vibration [14]. The absorption of about 960 $cm^{-1}$ is owing to the stretching of Si–O–Ti, which suggests the presence of a covalent bond between $TiO_2$ and $SiO_2$, rather than Van der Waals attraction [6]. However, this peak fuses with other peaks so that it looks unclear. Moreover, absorption at approximately 770 $cm^{-1}$ is due to the Si-O stretching functional group as well as Ti–O [14-15].

### SEM-EDX Characterization

The morphology of the PVA/$TiO_2$/$SiO_2$ composite membrane was observed using SEM. The SEM test results are depicted in Fig. 2. The PVA/$TiO_2$/$SiO_2$ composite membrane appears to have a uniform distribution of $TiO_2$ and $SiO_2$ fillers [16]. The morphology of the PVA/60$TiO_2$/40$SiO_2$ and PVA/80$TiO_2$/20$SiO_2$ samples was more homogenous than that of the filler material, whereas the PVA/40$TiO_2$/60$SiO_2$ and PVA/100$TiO_2$/0$SiO_2$ samples exhibited an agglomeration [17].

Agglomeration may occur due to the uneven mixing of the PVA matrix with the $TiO_2$ and $SiO_2$ fillers [18]. Agglomeration decreased the surface area of $TiO_2$

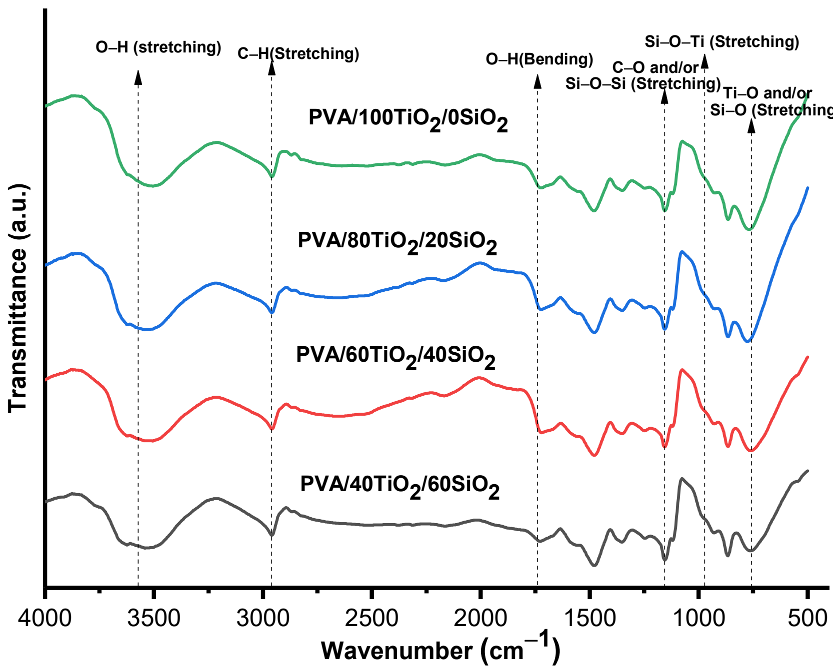


**Fig 1.** FTIR spectra of (a) PVA/40$TiO_2$/60$SiO_2$, (b) PVA/60$TiO_2$/40$SiO_2$, (c) PVA/80$TiO_2$/20$SiO_2$, and (d) PVA/100$TiO_2$/0$SiO_2$ composite membrane

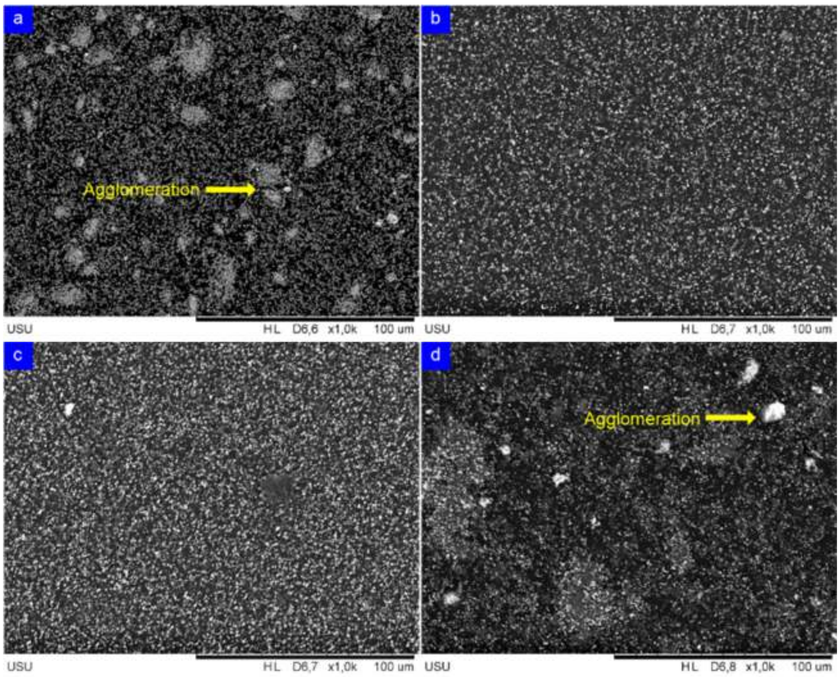


**Fig 2.** SEM images of (a) PVA/40$TiO_2$/60$SiO_2$, (b) PVA/60$TiO_2$/40$SiO_2$, (c) PVA/80$TiO_2$/20$SiO_2$, and (d) PVA/100$TiO_2$/0$SiO_2$ composite membrane

and $SiO_2$, both of which act as degrading agents in river water. This can affect the membrane's performance during the photocatalytic testing process. The bigger the surface area of the particles, the higher the surface area of contact between the membrane and the test sample in the form of river water, resulting in a quicker rate of color degradation of river water.

The distribution of the components that comprise the PVA/$TiO_2$/$SiO_2$ composite membrane is depicted in Fig. 3. As can be observed, the filler in $TiO_2$ and $SiO_2$ particles is dispersed equally. This will impact the photocatalyst process's outcome later. PVA/$TiO_2$/$SiO_2$ composite membranes are composed mainly of C and O elements, also found in PVA [16]. The contents of the membrane elements are determined using EDX, as stated in Table 2.

## XRD Characterization

The crystal structure of the PVA/$TiO_2$/$SiO_2$ composite membrane was characterized using XRD. The diffractogram in Fig. 4 illustrates the XRD test results. Two crystal structures were identified in the XRD analysis, namely the Anatase and PVA peaks.

The XRD analysis reveals a crystal structure in the form of anatase for $TiO_2$ [19]. Anatase's crystal structure in Fig. 4 shows a tetragonal crystal system with lattice parameters of a = 3.7845 and c = 9.5143 Å, corresponding to COD:9015929. According to Jiang et al. [20], the anatase phase was found in this study at angles of 2θ = 25.12°; 36.80°; 37.64°; 38.48°; 47.98°; and 53.70° with Miller indices of (011), (013), (004), (112), (020), and (015). As indicated by the XRD pattern,

**Table 2.** Composition of PVA/$TiO_2$/$SiO_2$ Composite Membrane

| Composite Membrane | Percentage (%) | | | |
|---|---|---|---|---|
| | C | O | Si | Ti |
| PVA/40$TiO_2$/60$SiO_2$ | 59.58 | 35.26 | 2.74 | 2.43 |
| PVA/60$TiO_2$/40$SiO_2$ | 63.94 | 32.33 | 0.72 | 3.01 |
| PVA/80$TiO_2$/20$SiO_2$ | 62.26 | 33.97 | 0.07 | 3.70 |
| PVA/100$TiO_2$/0$SiO_2$ | 62.78 | 33.17 | NA* | 4.05 |

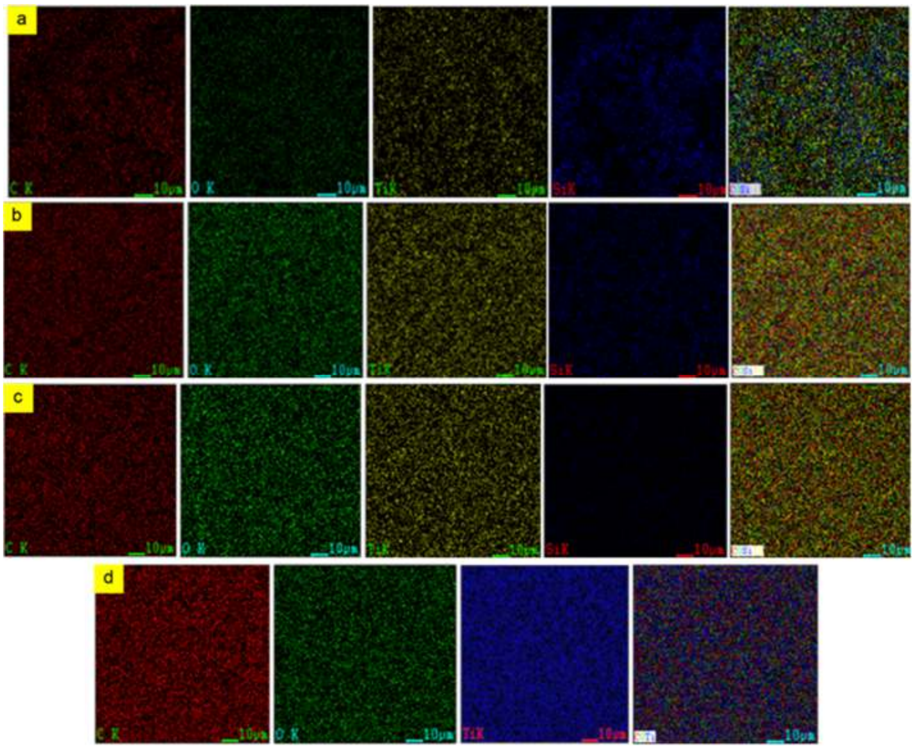


**Fig 3.** Elemental mapping of (a) PVA/40$TiO_2$/60$SiO_2$, (b) PVA/60$TiO_2$/40$SiO_2$, (c) PVA/80$TiO_2$/20$SiO_2$, and (d) PVA/100$TiO_2$/0$SiO_2$ composite membrane

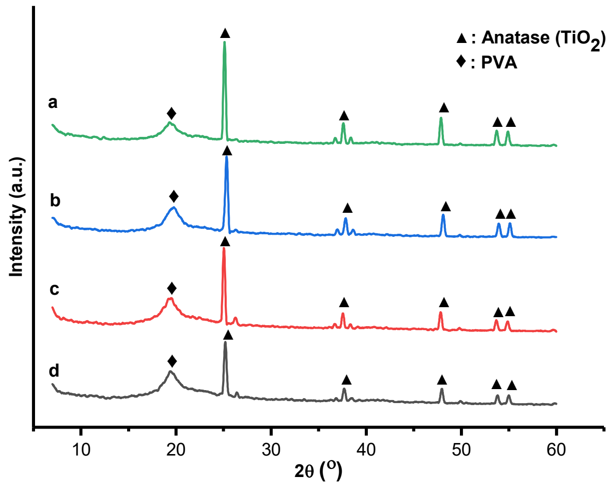


**Fig 4.** XRD patterns of (a) PVA/100$TiO_2$/0$SiO_2$, (b) PVA/80$TiO_2$/20$SiO_2$, (c) PVA/60$TiO_2$/40$SiO_2$, and (d) PVA/40$TiO_2$/60$SiO_2$

no peak indicates the structure of $SiO_2$. The structure of $SiO_2$ is amorphous, and as a result, the peak does not exist in this diffractogram. This is consistent with the findings in Ref. [21].

Meanwhile, the amorphous peak visible in the XRD results corresponds to the PVA peak. PVA is an amorphous polymer. With a Miller index of (101), PVA was found at an angle of $2\theta = 21.92°$. These findings were supported by the previous research [22]. Moreover, the intensity of the anatase was observed to increase with the addition of $TiO_2$.

## Swelling Characterization

Swelling is a property that may be used to assess the rate of membrane absorption and the saturation point of solution absorption [23]. The swelling test results are depicted in Fig. 5.

After adding $SiO_2$ to the membrane composition, the degree of swelling was relatively modest. This demonstrates that the membrane is superior in terms of resistance to absorption but affects the photocatalytic process [23] since the catalyst process requires strong absorption when the membrane is put into the test solution to initiate a photocatalytic process [24-25]. The swelling values for the PVA/100$TiO_2$/0$SiO_2$ and the PVA/40$TiO_2$/60$SiO_2$ membrane composition were 171%

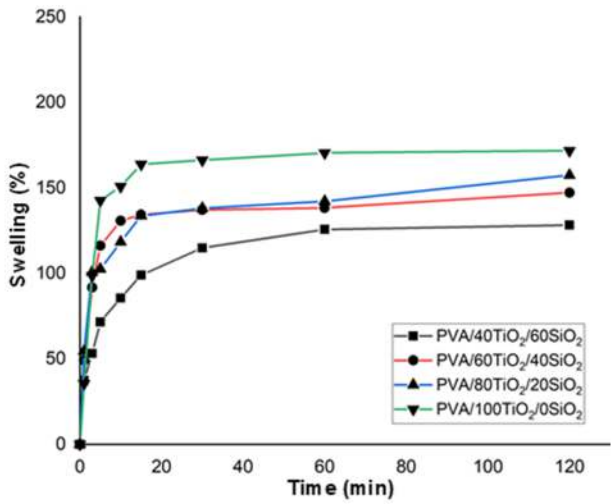


**Fig 5.** Swelling test of $PVA/TiO_2/SiO_2$ composite membrane

and 128%, respectively. It is reasonable to suppose that the amount of $SiO_2$ added is proportionate to the degree of swelling reduced [26]. The increased surface area of the $PVA/TiO_2/SiO_2$ composite membrane contributes significantly to its increased processing and swelling rates. Swelling also affects the membrane's mechanical properties [9].

### UV-Vis Analysis

UV-Vis spectroscopy was used to examine the color degradation. Water samples from the Silau River were passed over a membrane having a surface area of $1.5 \times 1.5$ cm$^2$. The water added to the membrane is then placed in a box equipped with a UV lamp, and the irradiation procedure is repeated for a specific duration. Fig. 6 illustrates the test results.

UV-Vis spectroscopy was used to measure the degree of color degradation in river water. The measurement results indicate that the optimal composition is $PVA/80TiO_2/20SiO_2$. As seen in Fig. 6, the cleanest water appears after 8 h, while the $PVA/40TiO_2/60SiO_2$ composite membrane produced the

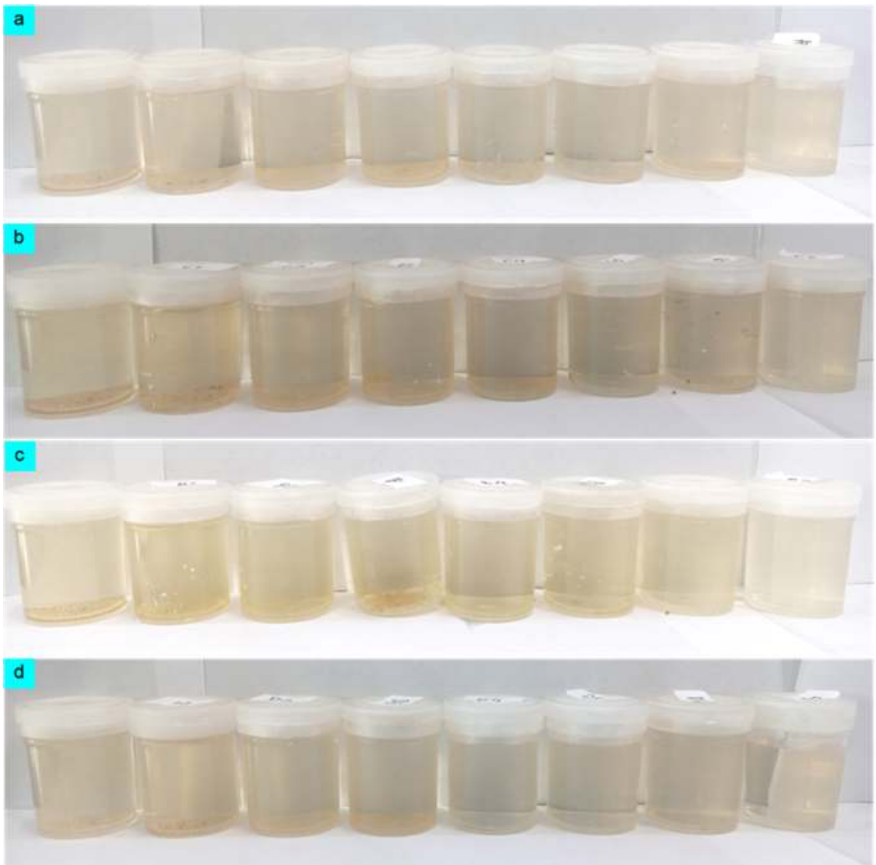


**Fig 6.** Images of Silau River water treated using (a) $PVA/40TiO_2/60SiO_2$, (b) $PVA/60TiO_2/40SiO_2$, (c) $PVA/80TiO_2/20SiO_2$, and (d) $PVA/100TiO_2/0SiO_2$ for 1–8 h (from left to right)

lowest yield. The longer the photocatalyst process continues, the more significant the decrease in watercolor levels [6], resulting in cleaner Silau River water.

Fig. 7 shows the percentage of color degradation of river water. The most optimum degradation occurs at a rate of 45.95% by PVA/80$TiO_2$/20$SiO_2$ composite membrane. According to the graph in the illustration, degradation will occur at a maximum rate over time.

The length of irradiation in the photocatalyst process indicates the time required for the PVA/$TiO_2$/$SiO_2$ composite membrane to interact with the inner light and form •OH radicals from river water. With increasing duration, the PVA/$TiO_2$/$SiO_2$ composite membrane absorbs more proton energy, making it simpler to lower the color content of river water. The longer the irradiation period, the more the photocatalyst process will continuously operate until the optimum condition is reached [27].

The matrix plays a role as a support for dye absorption in the absence of decomposition. Increased dye decomposition efficiency might be attributed to improved $TiO_2$ dispersion. Additionally, photodegradation's efficacy depends on the degree of swelling, enabling the lower $TiO_2$ concentration to degrade the color efficiently and rapidly. Moreover, the carboxylate anions increase the electrostatic and hydrophilic repulsion of the hydrogel's polymer chains. As a result, the PVA membrane increases

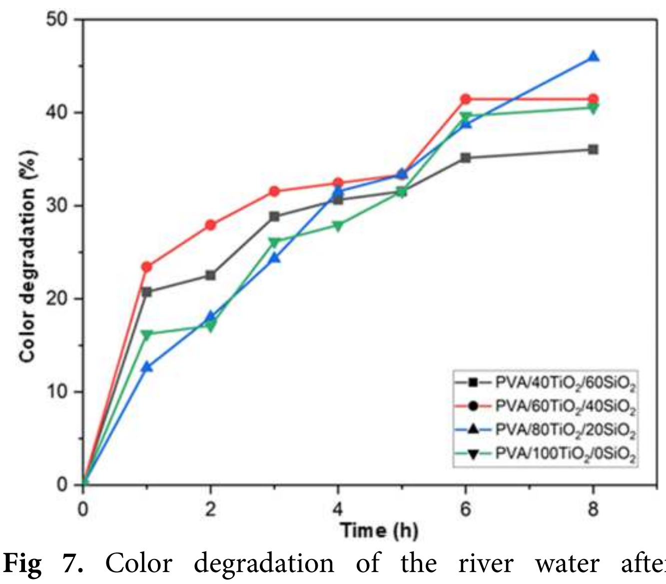


**Fig 7.** Color degradation of the river water after photocatalytic process

the surface area, allowing $TiO_2$ particles to come into contact with a greater degree of swelling [28]. On the other hand, excessive $TiO_2$ can cause this compound coating to thicken, which can cause obstruct light transmission and reduce the specific surface area [6].

### River Water Characterization Before and After Treatment by PVA/$TiO_2$/$SiO_2$ Composite Membranes

Following the photocatalyst test on river water, the best composition was used to determine its composition. Table 3 summarizes the test results. They can absorb heavy metals from river water due to the presence of $SiO_2$ particles. $SiO_2$ is a porous solid. The porous structure is proportional to the surface area: the smaller the silica particle, the higher the surface area. Hence, the more significant the adsorption capacity.

From the results of the FTIR characterization, there are silanol (Si–OH) and siloxane (Si–O–Si) groups that can bind specific metal ions [15] so that the levels of heavy metals dissolved in river water decrease. This silanol group has low acidity and oxygen as a weak donor atom. Two groups, namely straight-chain Si–O–Si, and siloxane groups, form a circular structure. Straight chain siloxanes are unreactive with common reagents but are highly reactive to alkali metal compounds. The siloxane group with a circular shape has high reactivity and can absorb water, ammonia, as well as methanol. The reaction of those with water will produce the Si–OH group [6].

Changes in functional groups are due to the transformation of certain silanol groups into others. Other groups should give advantages, such as interactions during the adsorption process. Other groups facilitate adsorption by creating compounds with metal ions. Adsorption can occur by ion exchange if the replacement group is ionic. This transformation enables interaction with metal ions. Adsorption of metal ions on $SiO_2$ can be used to separate metal ions present in a solution, such as industrial waste or wastewater [6].

Table 3 demonstrates that the test results indicate a change in the value of each parameter. The initial turbidity, color, and chromium parameter values were 115 NTU, 63 TCU, and 0.389 mg/L, respectively, which initially did not meet the clean water standard. After

**Table 3.** Characterization of river water before and after treatment by $PVA/80TiO_2/20SiO_2$ composite membranes

| Parameters | Units | Test results before treatment | Test results after treatment | Maximum content |
|---|---|---|---|---|
| Turbidity | NTU | 115 | 16 | 25 |
| Color | TCU | 63 | 30 | 50 |
| Dissolved solid | mg/L | 70.6 | 69 | 1000 |
| Taste | - | Tasteless | Tasteless | Tasteless |
| Scent | - | Odorless | Odorless | Odorless |
| Fe | mg/L | 0.19002 | 0.09002 | 1 |
| Hardness | mg/L | 67.02 | 59.1 | 500 |
| Mn | mg/L | 0.12451 | 0.11893 | 0.5 |
| Nitrite | mg/L | 3.3 | 2.3 | 10 |
| Detergent | mg/L | < 0.5 | < 0.5 | < 0.05 |
| Hg | mg/L | 0.00079 | 0.00043 | 0.001 |
| As | mg/L | 0.00024 | 0.00018 | 0.05 |
| Cd | mg/L | 0.00043 | 0.00037 | 0.005 |
| Cr(IV) | mg/L | 0.389 | 0.013 | 0.05 |
| Se | mg/L | 0.00093 | 0.00089 | 0.01 |
| Zn | mg/L | 0.00191 | 0.00178 | 15 |
| Pb | mg/L | 0.00067 | 0.00058 | 0.05 |
| Organic substance | mg/L | 15.848 | 2.139 | 10 |

treatment, the parameters of turbidity, color, and chromium values were reduced to 16 NTU, 30 TCU, and 0.013 mg/L, respectively, following the treatment with a $PVA/80TiO_2/20SiO_2$ composite membrane using the photocatalyst method. It demonstrates that after treatment, the test results for river water fulfilled the criteria for clean water quality established by Minister of Health of the Republic of Indonesia Decree No. 416/MENKES/PER/IX/1990 dated September 3, 1990.

## CONCLUSION

The composition of the $PVA/80TiO_2/20SiO_2$ membrane showed the most optimum composition in this study throughout photocatalyst testing. Degradation occurs at a rate of 45.95%. The membrane can effectively degrade the color of river water in this composition after 8 h. As for the Silau River water test results, it can be seen that each parameter has changed. The initial turbidity, color, and chromium parameter values were 115 NTU, 63 TCU, and 0.389 mg/L, respectively, which initially did not meet clean water standards. After being treated with a $PVA/80TiO_2/20SiO_2$ composite membrane by photocatalyst method, the turbidity, color, and chromium parameter values were changed to 16 NTU, 30 TCU, and 0.013 mg/L, respectively. These results indicate that the Silau River water test satisfied the clean water quality criteria established by Minister of Health of the Republic of Indonesia Decree No. 416/MENKES/PER/IX/1990 dated September 3, 1990. Additionally, given the results of this study shown that the watercolor could be degraded, it is expected that this composite membrane might be used to clean dye waste in regions with high river flow, such as Asahan Regency.

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## AUTHOR CONTRIBUTIONS

The first author prepared materials and conducted experiments. The second, third, and fourth authors applied the concepts and methodology, while the fifth and sixth authors processed and analyzed the data. The manuscript was written and revised by the first and fourth authors. All authors evaluated and discussed the results. All authors have approved the final version of this manuscript.

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