

# The Activity of PVDF-TiO<sub>2</sub>/ZnO/CoO Nanofiber Photocatalyst for Degradation of Humic Acid Solution

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**Abstract.** Peat water sources could be found in many lowland and marshy areas in Indonesia such as in Sumatra, Kalimantan, and Papua. The water could be a problem for residents living around it because it formed from decayed plants, animals, and microbes. The main component of it is humic acid which is a complex of organic compound and natural polymer. This research aims to conduct the activity of PVDF-TiO<sub>2</sub>/ZnO/CoO nanofiber photocatalyst for degradation of humic acid solution. Photocatalytic activities were studied inside a photoreactor with artificial UV radiation with 254 nm wavelength. The percentage of degradation was determined by measuring humic acid solution before and after degradation using UV-Vis spectrophotometer with maximum lambda is 219 nm. The study of kinetic for a photocatalytic reaction was calculated with rate constant 4,29 x 10<sup>-5</sup> min<sup>-1</sup> ppm<sup>-1</sup> and the kinetic of photodegradation on this research was pseudo second-order kinetic model.

**Keywords:** Nanofiber, Photocatalyst, Photocatalytic Activity, TiO<sub>2</sub>, Humic Acid

## 1 Introduction

Indonesia is a country that has quite extensive peatlands which spread across several large islands such as Sumatra, Kalimantan, and Papua. The total area of peatlands in Indonesia is estimated at about 14,90 million hectares which places Indonesia into the fourth country that has extensive peatlands after Canada, Russia, and the United States [1],[2]. The largest peatland area is found on Sumatra Island. One of the problems that often experienced by residents living in peatland areas is the lack of availability of clean water as peatlands produce peat water. Humic acid is one of the main components contained in peat water and a complex organic compound formed from the degradation of plants, animals, and microbes. Generally, humic acid has acidic properties, colored in brown-yellowish, and is dissolved in surface water and groundwater. The acidic property is derived from the carboxylic group function and hydroxyl phenol groups [3].

Some research has been carried out to treat humic acid in biological, physical, or chemical treatment. For an instant, some of the research that has been done to treat humic acid is degradation of humic acid by the litter-decomposing basidiomycete *Collybia dryophila* [4], adsorption by modification of activated carbon [5], and photocatalytic degradation [6],[7]. However, biological processes are ineffective and other processes only change the liquid waste phase into solid-phase so further processing is needed [8]. One of the effective wastewater

treatments is by using photocatalyst. The process of photocatalysis has great potential as an inexpensive technology that complies with the concept of zero waste. In the photocatalytic process, light energy is converted to chemical energy to produce hydroxyl radicals which will oxidize organic compounds into carbon dioxide and hydrogen dioxide [9]. This process produces compounds that environmentally friendly and harmless reaction products. Titanium dioxide is commonly used as a semiconductor material for photocatalysis process as it is relatively inexpensive, very efficient, has high stability, and low toxicity [10]. Previously, studies of photodegradation of PVDF/TiO<sub>2</sub> and PVDF-ZnO/Ag<sub>2</sub>CO<sub>3</sub>/Ag<sub>2</sub>O nanofiber were reported to degrade toxic pollutants [11],[12]. As a result, these materials have maintained a relatively high photocatalytic activity, which made them as promising candidates for photocatalytic applications and degrading organic pollutants. In this work, PVDF-TiO<sub>2</sub>/ZnO/CoO nanofiber photocatalyst activity was studied for the photodegradation of humic acid solution.

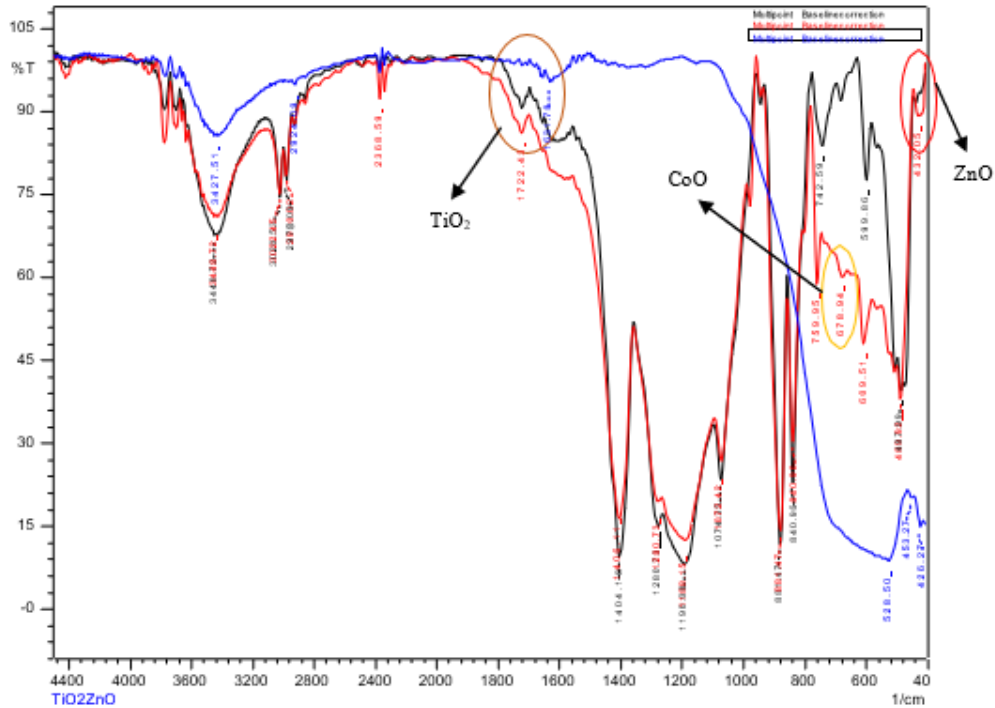
## 2 Experimental

Nanofiber photocatalyst that used in this research was obtained from the laboratory of Analytical Chemistry, Department of Chemistry, Bandung Institute of Technology. It was contained 24% PVDF and 4% TiO<sub>2</sub>/ZnO/CoO nanocomposite. In this research, PVDF-TiO<sub>2</sub>/ZnO/CoO nanofiber photocatalyst was contacted to humic acid solution under UV light source inside a photoreactor system [13]. A total of 50 mL of 25 ppm humic acid solution at pH 3 was put into a breaker glass. An amount of 0,03 gr of nanofiber PVDF-TiO<sub>2</sub>/ZnO/CoO was added to the breaker glass that contained humic acid solution. The breaker glass was put inside a photoreactor system. The solution of humic acid was stirred under the dark conditions for 20 minutes. After that, the solution was irradiated under 30 Watt of UV light sources with monochromatic rays in 254 nm wavelength. The distance of the light source to the surface of humic acid solution was 20 cm. After photodegradation process, the remaining of humic acid solution was determined by using UV-Vis spectrophotometer. The maximum lambda of humic acid was 219 nm.

## 3 Results and Discussions

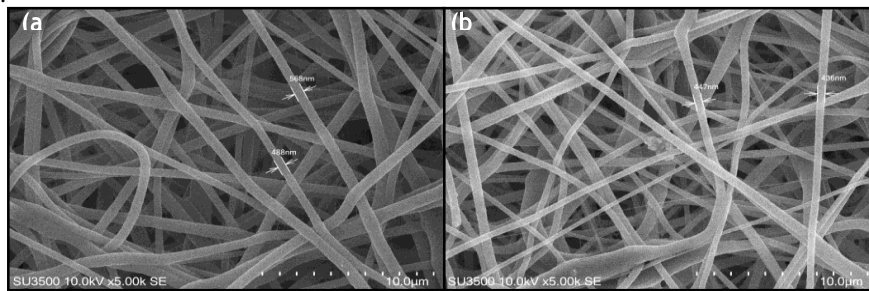
### 3.1 The Characteristics of Nanofiber Photocatalyst

Nanofiber photocatalyst of PVDF-TiO<sub>2</sub>/ZnO/CoO has been characterized by FTIR and SEM analysis. The result of FTIR spectrum and SEM images can be seen in **Figure 1** and **Figure 2** respectively. As a result of the analysis, it shows that nanofiber photocatalyst has been successfully synthesized.



**Fig. 1.** FTIR Spectrum.

From FTIR spectrum, the black line refers to pure PVDF, the blue line refers to TiO<sub>2</sub>/ZnO/CoO nanocomposite and the red line refers to PVDF-TiO<sub>2</sub>/ZnO/CoO nanofiber. The peak of cubic CoO after heat treatment at 800°C appeared at 687,94 cm<sup>-1</sup>[14]. The peak at 1722,43 cm<sup>-1</sup> was related to TiO<sub>2</sub>. The peak of stretch vibration of ZnO was observed at 432,05 cm<sup>-1</sup>[15].



**Fig. 2.** SEM images: (a) pure PVDF and (b) PVDF-TiO<sub>2</sub>/ZnO/CoO.

### 3.2 The Photodegradation Activity of Humic Acid Solution

After contacted PVDF-TiO<sub>2</sub>/ZnO/CoO nanofiber photocatalyst to humic acid solution, the remaining humic acid concentration was determined by using UV-Vis spectrophotometer at certain times. The graph of degradation percentage against degradation times is shown in **Figure**

3. It shows that as the time of degradation increases, the percentage of humic acid degradation also increases.

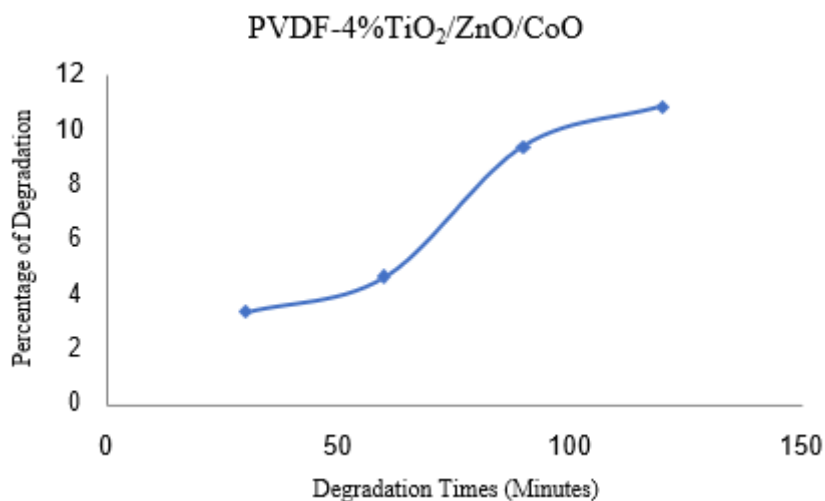


Fig. 3. The graph of photodegradation activity of the humic acid solution.

### 3.3 Kinetic Study of Photocatalytic Degradation

The kinetics study of photocatalytic degradation is one of the factors that have an important role in determining the optimum conditions for photodegradation process. From analyzing kinetic models, the rate constant will be known. The higher value of rate constant, the more effective photocatalytic degradation process. The kinetic study of photocatalytic reaction was carried out by calculating pseudo first-order kinetic model and pseudo second-order kinetic model reactions using Lagergren's model. First-order reaction formula is expressed through equation (1)

$$\ln C_0 - C = \ln C_0 - K_{\text{photocatalytic}} t \quad (1)$$

and as for second pseudo order reaction shows at equation (2)

$$\frac{t}{C} = \frac{1}{K_{\text{photocatalytic}} C_0^2} + \frac{t}{C_0} \quad (2)$$

In this equation, C is referred to the absorbed concentration of humic acid solution in ppm, C<sub>0</sub> is the concentration of initial humic acid solution in ppm, and t is the degradation time in minutes.

**Figure 4** depicts the plots of the t/C against the degradation time for nanofiber PVDF-TiO<sub>2</sub>/ZnO/CoO photocatalyst, whereas **Figure 5** shows the plots of t ln (C<sub>0</sub>-C) against the degradation time for nanofiber PVDF-TiO<sub>2</sub>/ZnO/CoO photocatalyst.

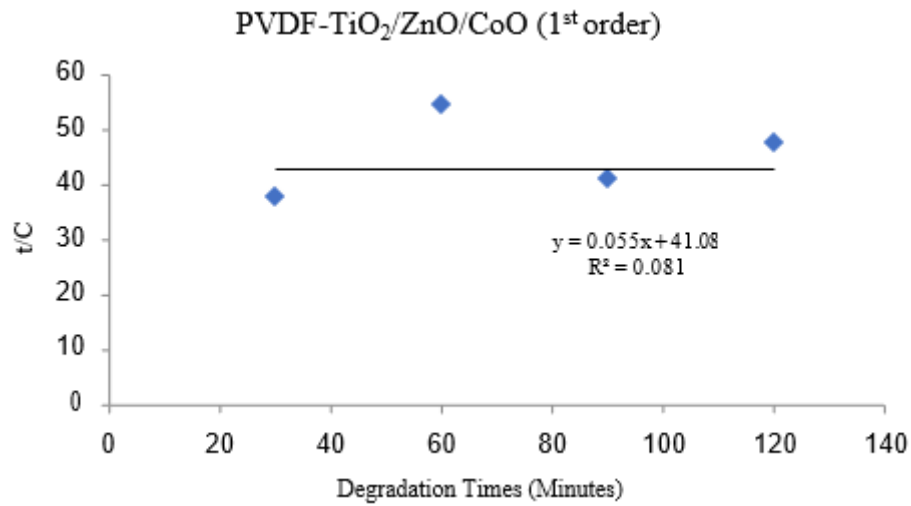


Fig. 4. The graph of pseudo first-order kinetic model.

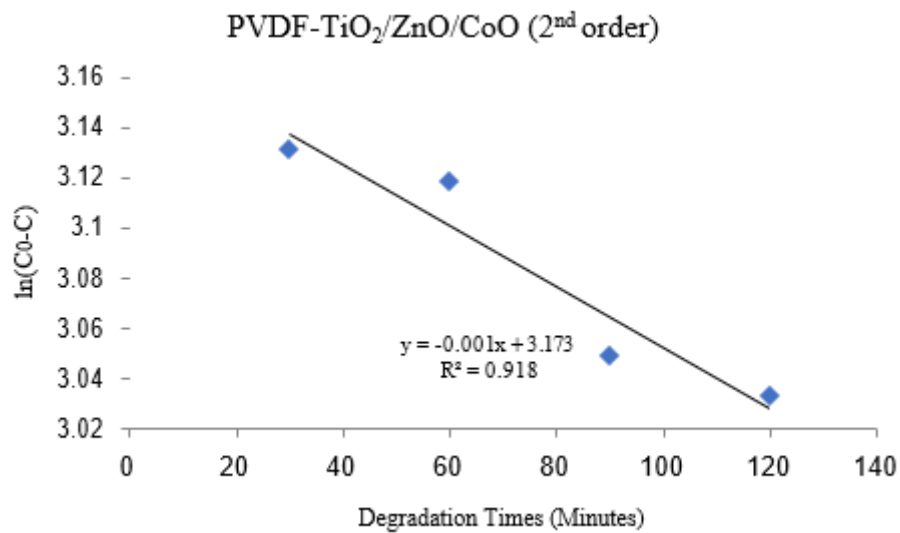


Fig. 5. The graph of pseudo second-order kinetic model.

From the **Figure 4** and **Figure 5**, it shows that the value of R<sup>2</sup> for pseudo second-order kinetic model is greater than the pseudo first-order kinetic model so by that it can be concluded that the photocatalytic activity of PVDF-TiO<sub>2</sub>/ZnO/CoO nanofiber photocatalyst follows the pseudo second-order kinetic model. The rate constant of photocatalytic reaction could be calculated from the slope and the intercept of the graph. The rate constant was calculated and the result was  $4.29 \times 10^{-5} \text{ min}^{-1} \text{ ppm}^{-1}$ .

To compare with other materials, Table 1 shows several studies of photocatalytic degradation of humic acid solution. From the table, it concluded that the rate constant of photocatalytic degradation of humic acid on this research might be lower than other literature. Furthermore, study the optimum condition has to be done for further research.

**Table 1.** Kinetic studies of humic acid photocatalytic degradation.

Materials	$k$	References
PMMA/PVDF	0,049-0,128 g.mg <sup>-1</sup> .min <sup>-1</sup>	[16]
iron-modified pillared montmorillonite powder	0.00903 ± 1.07462 10 <sup>-4</sup>	[17]
100 kDa HA, NPOC <sub>i</sub> : 4.67 mg L <sup>-1</sup> Ce-doped ZnO	2,18x10 <sup>-2</sup> min <sup>-1</sup>	[18]

## 4 Conclusions

In summary, humic acid solution has been contacted to PVDF-TiO<sub>2</sub>/ZnO/CoO nanofiber photocatalyst under UV light source inside a photoreactor system. The photodegradation of humic acid increases with increasing the time of degradation. The kinetic study of photodegradation of humic acid by using PVDF-TiO<sub>2</sub>/ZnO/CoO nanofiber as photocatalyst described by the pseudo second-order kinetic model with rate constant is 4,29 x 10<sup>-5</sup> min<sup>-1</sup> ppm<sup>-1</sup>. From this preliminary study, the PVDF-TiO<sub>2</sub>/ZnO/Co nanofiber photocatalyst can be used as photocatalyst to degrade humic acid solution but for further research, the amount of nanocomposite should be added up to various percentage to increase the degradation activity and the optimum condition of photocatalytic degradation must be studied.

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