



Photocatalyst with Various Ratios and Concentrations of $\text{TiO}_2\text{-Fe}_3\text{O}_4$ to Remove Humic Acid Pollutants

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Abstract. Humic acid is naturally generated from aerobic decomposition of organic matter by organisms. Treatment of humic acid by photocatalyst have some advantages, such as no saturation point, inexpensive, non-toxic and environmentally friendly. Photocatalyst is a photochemical process which involved catalyst and light illumination to generate radicals. This study was aimed determine the ability of photocatalysts to degrade humic acid using various ratios (1:1, 1:2 and 2:1) and concentrations of $\text{TiO}_2\text{-Fe}_3\text{O}_4$ (2000, 6000, 10000 ppm) with UVC light as energy source. This research was carried out using the photocatalytic method, which determine optimum ratio and concentrations variation of $\text{TiO}_2\text{-Fe}_3\text{O}_4$. The degradation data were obtained using a spectrophotometer UV-Vis with a wavelength of 254 nm. The optimum degradation percentage in the ratio variation test was 84,08%, at a ratio of 2:1. It caused by the ratio of 2:1 contains more TiO_2 than Fe_3O_4 . The optimum degradation percentage in the concentration variation test was 93,35%, at a 2000 ppm concentration. Due to, too much catalyst uses could be cause turbidity and block the light for absorption by the photocatalyst so that the photodegradation process becomes less effective.

Keywords: Concentration · Humic Acid · Photocatalyst · Ratio · $\text{TiO}_2\text{-Fe}_3\text{O}_4$

1 Introduction

Humic acid is one of the compounds that gives peat water its unique brown color, and these toxins naturally interact with organic materials, including metals, oxides, hydroxides, minerals, and other toxic impurities, making them difficult to remove [1]. Due to its organic substances, it could form disinfection by product (DBPs) when it contacted with disinfectant. DBPs is considerate carcinogenic and harmful to the body when consumed by humans although very small concentrations (ppm/ppb) [1]. Treatment of water containing humic acid is usually carried out by the filtration method [2]. However, the filtration method can reach a saturation point so that the filtration device is no longer able to filter the humic acid compounds. Treatment of humic acid by photocatalyst have some advantages, such as no saturation point, inexpensive, non-toxic and environmentally friendly. Photocatalyst is a photochemical process which involved catalyst and light illumination to generate radicals.

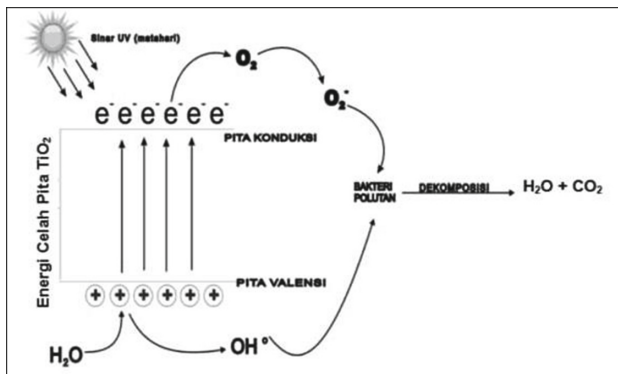


Fig. 1. Photocatalyst TiO₂ Activity Schematic

Photocatalysts that only use pure TiO₂ will be less than optimal and difficult to separate the catalyst from the solution because it can form a suspension [3]. Therefore, TiO₂ needs to be attached to an adsorbent. One of the adsorbents that can be applied to TiO₂ was Fe₃O₄ (magnetite). The addition of magnetite allowed the separation of photocatalyst solids from solution easily by an external magnetic. When a semiconductor catalyst exposed with UV light, electrons (e^-) in the valence band are moved to the conduction band and then holes (h^+) were left in valence band. Hole (h^+) will interact with H₂O and OH⁻ on the surface of the catalyst to form OH radicals (OH[•]) which function as a strong oxidants. Electrons (e^-) will react with O₂ in the catalyst to form superoxide radicals (O₂^{•-}) which act as reducing agents. These oxidizing and reducing agents attack the dye to produce CO₂ and H₂O and some low acid concentrations [4] (Fig. 1).

TiO₂ was a white titanium dioxide compound that was rust-resistant and non-toxic. TiO₂ was one of the most widely used and most stable catalysts compared to other catalysts [5]. In order to extend the use of TiO₂ in visible light and harness solar energy, different strategies have been developed by doping precious metals such as Au, Pt, Ag and Fe to enhance photocatalytic activity. In fact, TiO₂ photocatalysts will face obstacles such as difficulties in catalyst separation and recovery. Incorporation of magnetic Fe₃O₄ into catalysts based on TiO₂ nanocomposites has an effective way to overcome problems such as particle agglomeration during recovery and increase photocatalyst durability. By applying an external (outside) magnetic, the magnetic catalyst can be removed and can be recycled by providing a suitable magnetic separation method [6].

2 Methods

2.1 Research Location

This research was conducted at the Environmental Technology Laboratory, Faculty of Engineering, Mulawarman University, Gunung Kelua, Samarinda, East Kalimantan and sample analysis was carried out at the Chemical Engineering Laboratory, Faculty of Engineering, Mulawarman University, Sambaliung street, No. 9, Gunung Kelua, Samarinda, East Kalimantan.



Fig. 2. Box Reactor

2.2 Research Procedures

This research uses a photocatalytic method, using a semiconductor catalyst $\text{TiO}_2\text{-Fe}_3\text{O}_4$ to degrade humic acid compounds. The catalyst used in this study was $\text{TiO}_2\text{-Fe}_3\text{O}_4$ which was obtained from the synthesis of $\text{TiO}_2\text{-Fe}_3\text{O}_4$ by the sol-gel method. This research used humic acid with a concentration of 15 ppm with a neutral pH (7). Box reactor made from plywood with a size of $40 \times 40 \times 45$ cm, equipped with a UVC lamp with 8 watts for humic acid degradation process. The absorbance value was tested using a spectrophotometer UV-Vis with a maximum wavelength was 254 nm.

2.3 Preparation of Fe_3O_4

Synthesis of Fe_3O_4 was carried out using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with a mole ratio of 1:2, both of it was dissolved in 25 mL with distilled water. Mixed $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ on a magnetic stirrer and then added 100 mL of 1 M NaOH slowly until the solution turned dark black. Added 100 mL of distilled water and stir until homogeneous. The solution was allowed to stand for 24 h to form a sol. Next the black solids were separated from the solution and then transferred into a porcelain dish to placed in the oven. The drying process lasted for 5 h at a temperature of 105°C . Crushed Fe_3O_4 with a mortar and pestle to get Fe_3O_4 powder.

2.4 Synthesis of $\text{TiO}_2\text{-Fe}_3\text{O}_4$

$\text{TiO}_2\text{-Fe}_3\text{O}_4$ synthesis was carried out by sol-gel method using 2-propanol, ti-butoxide, Fe_3O_4 and distilled water. The sol-gel process was divided into four stages there was hydrolysis, condensation, aging, and drying. Started from the synthesis of TiO_2 by mixing 100 mL of 2-propanol and 100 mL of ti-butoxide. Then 200 mL of 2-propanol was added to obtain a total of 400 mL of precursor solution. Next 100 mL of the precursor solution was taken and 10 g of Fe_3O_4 powder was added to obtain a ratio of 1:1, the

same thing was done with a different ratio of 1:2 and 2:1. Then it was hydrolyzed by adding 100 mL of distilled water using a burette and stirred using a magnetic stirrer to form a sol. At the aging stage, let the solution stand for 24 h to form a gel. Next, separate the black solid and the liquid formed, then the black solid was put into a porcelain to be dried using an oven. In this drying stage, it was dried for 4 h at a temperature of 105°C. After that, it was ground in a mortar and pestle until become a powder and transferred to a crucible to be calcined in a kiln at 250°C for ± 2 h. This research used $\text{TiO}_2\text{-Fe}_3\text{O}_4$ as much as 3 g.

2.5 Photocatalytic Activity Test

Prepared 3 samples of 15 ppm humic acid compound solution with aneutral pH (7) as much as 500 ml and put into a beaker glass with a bar stirrer and then added $\text{TiO}_2\text{-Fe}_3\text{O}_4$ to the three glasses with a ratio of 1:1, 2:1 and 1:2. Stirred using a magnetic stirrer at 100 rpm for 15 min and irradiated with UVC for 5 h with take 5 mL of sample every 30 min. This photodegradation process was repeated for three times. The dye concentration was determined from a standard curve using the absorbance value measured by a spectrophotometer UV-Vis with a wavelength of 254 nm (the wavelength corresponds to the maximum absorption of AH). A similar procedure was carried out for testing variations in the concentration of $\text{TiO}_2\text{-Fe}_3\text{O}_4$ with the concentrations variation were 2000, 6000 and 10000 ppm. The optimum $\text{TiO}_2\text{-Fe}_3\text{O}_4$ ratio obtained from the previous test was used.

2.6 Data Analyst

The efficiency of the process is evaluated in terms of the percentage of color removal, which is calculated using the following Eq. (1):

$$\% \text{ Organic Substance Degradation} = \left(\frac{(C_o - C_t)}{C_o} \right) \times 100\% \quad (1)$$

C_o and C_t are the initial concentration and the concentration at t time.

3 Result and Discussion

3.1 Effect of $\text{TiO}_2\text{-Fe}_3\text{O}_4$ Ratios

Based on Fig. 2, can be seen in that figure the variations ratio of $\text{TiO}_2\text{-Fe}_3\text{O}_4$ 1:1, 1:2 and 2:1 was able to degrade organic substances in the sample of humic acid solution using UVC light and pH 7 there ratio 1:1 the percentage of degradation was 31,15%, ratio 1:2 the percentage of degradation was 23,80% and ratio 2:1 the percentage of degradation was 84,08%. The results of the percentage degradation with three ratio variations on the graph are quite stable after 60 min. It could see from the graph that the longer irradiation time, had the higher percentage of degradation. On the curve, the optimum ratio was 2:1. Because the ratio of 2:1 contains more TiO_2 than Fe_3O_4 so that the level of degradation is greater than other ratio variations. TiO_2 when mixed or charged will reduce the level of degradation, but easier to separate the solid and the solution. Due to the magnetic properties of the $\text{TiO}_2\text{-Fe}_3\text{O}_4$ catalyst so that it is easier to separate from the water after being used for the photocatalytic process [2].

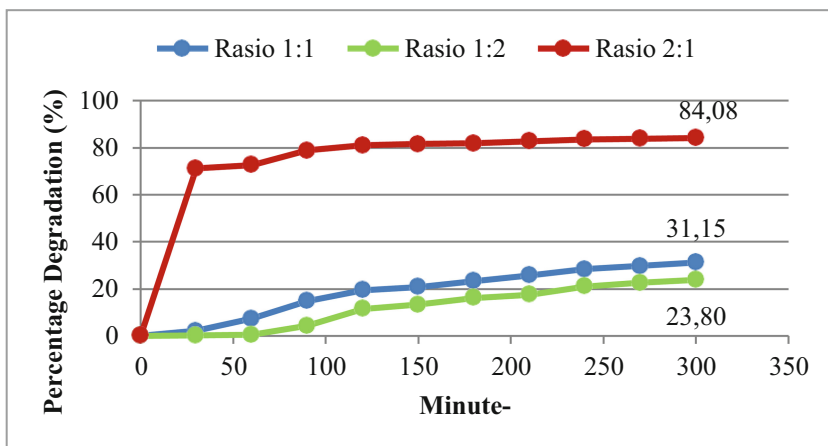


Fig. 3. Comparison Percentage of Photocatalyst Degradation With Variations Ratio

3.2 Effect of $\text{TiO}_2\text{-Fe}_3\text{O}_4$ Concentration

Based on the Fig. 3, the percentage of degradation can be seen that the concentration of 2000 ppm had the largest and optimum degradation percentage, which was 93,35% compared to the concentration of 6000 ppm which was 84,08% and 10000 ppm which was 63,52%. This decrease in the percentage of degradation occurs due to the lack of UV light hitting the sample solution as a result of the suspended catalyst. This causes the percentage of degradation to decrease [3]. For a result, the addition of $\text{TiO}_2\text{-Fe}_3\text{O}_4$ photocatalyst further (more) will reduce the percent degradation of organic matter and color. This because the increasing number of photocatalysts, the turbidity of the solution increases. Thus, reducing the transmitted light for the photodegradation process. If used too much TiO_2 powder will made turbidity and block the absorption of light by the photocatalyst so that the photoreduction and photooxidation processes become less effective [3]. So, the degradation percentage results are optimum at the $\text{TiO}_2\text{-Fe}_3\text{O}_4$ with 2000 ppm (Fig. 4).

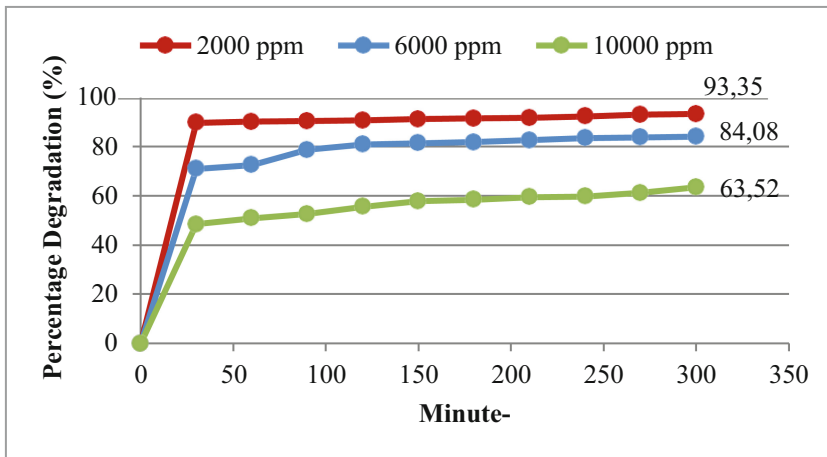


Fig. 4. Comparison Percentage of Photocatalyst Degradation With Variations Concentration

4 Conclusion

At a ratio of 1:1, the percentage of degradation was 31,15%, at a ratio of 1:2, the percentage of degradation was 23,80%, and at a ratio of 2:1, the percentage of degradation was 84,08%. The optimum ratio was 2:1. Because the ratio of 2:1 contains more TiO_2 than Fe_3O_4 so that the degradation rate was greater than other ratio variations. At this 2:1 ratio, the degradation rate will increase but it will be more difficult to separate the solid and the solution. The concentration of $\text{TiO}_2\text{-Fe}_3\text{O}_4$ which had the optimum percentage degradation was 2000 ppm. Because the results of the degradation percentage touched 93,35% compared to other $\text{TiO}_2\text{-Fe}_3\text{O}_4$ concentration variations were 84,08% and 63,52%. The optimum concentration of $\text{TiO}_2\text{-Fe}_3\text{O}_4$ obtained was 2000 ppm, this because if too much catalyst used will cause turbidity and block the absorption of light by the photocatalyst so that the photodegradation process becomes less effective.

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