Preparation of TiO$_2$ thin layer on ceramics using dip coating method for degradation humic acid

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Abstract. TiO$_2$ thin layer on ceramic with dip coating method and photocatalyst activity test in humic acid. One of the photocatalysts used for the degradation of humic acid is TiO$_2$ because TiO$_2$ has several advantages, including non-toxic, stable, high activity, relatively inexpensive and environmentally friendly. This study was performed using TTIP as a precursor and MEA as an additive in isopropanol. Addition of MEA influences the stability of the titanium oxane solution. Ceramics were coated in a 0.5 M TiO$_2$ solution by a dip coating method, then dried in an oven at 110°C for 10 minutes and difugeice at 400 °C for 2 hours. Maximum degradation of 0.5 M TiO$_2$ is 59.94% over 24 hours using 8 watt fluorescent lamps with 4 TiO$_2$ coatings on ceramic.

1. Introduction

Peat water is surface water that is found in peat areas that spread in the lowlands. The properties of peat water have a high color intensity (brownish red), a high acidity (low pH), a high organic matter content and low concentrations of suspended and ionic particles [1,12-13]. Photolysis shows the potential for overcoming peat water. Addition of catalysts to the photolysis process can break down peat water into simpler compounds. Photocatalysts are chemical reactions that are carried out using a catalyst that is active when exposed to light [2,14-22].

The catalyst in the most commonly used photocatalyst process for water purification is TiO$_2$ [3,23-24]. This is because titanium oxide has favorable properties such as semiconductors, is stable, has a high activity, is resistant to wear, is relatively cheap and environmentally friendly [4]. Although, water purification can be done by absorption method, like using Spirogyra and some algae [25]. Some algae is very potential for anti bacterial and anti oxidant [26-28].

Titania has 3 main structures, namely anatase, rutile and brokite with a band gap of 3.0 - 3.2 eV [5]. To obtain these metals can be done by synthesis of TiO$_2$ powder or from precursors such as TTIP (titanium (IV) isopropoxide), TiCl$_2$ (titanium (II) chloride) or others. Synthesis of TiO$_2$ in the form of a thin film of the TTIP precursor [6].

The coating method used in this process is a coating method. Dip-coating methods or painting methods are often used because the process is simple and does not require expensive costs. The process that takes place is the substrate that is immersed in the solution and then lifted vertically at a constant speed. [7] In the dipping process, the substrate or material to be coated is vertically introduced into a container with a coating substance with a constant draw speed. The withdrawal
of the substrate from a high-viscosity solution will form a layer whose thickness depends on the withdrawal and dyeing speed. After solvent evaporation and drying, a thin layer will form on the surface of the substrate [8]. The radiation source for degrading humic acid and reducing the color intensity of humic acid in the mist water with a TiO$_2$ photocatalyst is UV light [9]. The test was performed using UV-Vis spectrophotometry. The principle of UV-Vis is based on the interaction between matter and light, the light in question is ultraviolet (UV) and visible light (Vis), while the material can be atoms and molecules with more role of valence electrons [10].

2. Tools and materials
Tool for the preparation of TiO$_2$ photocatalyst materials are: glass cup (pyrex), measuring cup, magnetic stirrer, volume pipette and spatula. Then the tools for making reactor design reactors, glass, 8 watt fluorescent lamps. The aid for characterizing TiO$_2$ photocatalysts is UV-Vis spectrophotometer. the materials used in this study were humic acid, titanium (IV) isopropoxide (TTIP), MEA (mono ethanol amine), isopropanol and nitrogen gas.

3. Experiment

3.1. Create reactor design
The making of the reactor starts with the installation of a transparent glass with a thickness of 3 mm and then the cutting of the glass with a height of 10 cm and a width of 6 cm, after which the glass is glued to form a hexagon form.

3.2. Photocatalyst Preparation of TiO$_2$ 0.5 M
A total of 22.6 ml of titania (IV) isopropoxide (TTIP) was mixed with 150 ml of isopropanol and then homogenized using a 3000 rpm magnetic stirrer for 30 minutes. then add a few drops of MEA (Mono Ethanol Amin) and homogenize again using a magnetic stirrer for ± 3 hours. During the process of making aliri with nitrogen gas.

3.3. Dip coating method
Prepare Ceramics that have been sharpened with a size of 4cm x 5cm, rinse the ceramic with detergent 2-3x, dry it, after that rinse with acetone, oven ceramic at 100°C for 10 minutes. Cleaned ceramics dyed into the container or place of 0.5 M TTIP solution, the plate is lifted using a coating tool with a lifting speed of 2mm / s, soaking time 3s and lifting speed of 2mm / s, ceramic coated with 2 layers heated with oven at 100°C - 110°C for 10 minutes, then the ceramic is put into the furnace with a temperature of 400°C for 30 minutes, then the ceramic layer is obtained.

3.4. Test of photocatalyst activity for degradation of humic acid
In carrying out this catalyst test, humic acid is used as a contaminant or material to be decomposed (degradation). This degradation process includes light to accelerate the reaction, commonly called
photodegradation. Humic acid was first made at a concentration of 20 ppm. This solution is obtained by weighing 0.02 grams of humic acid and then dissolving in 1000 ml of distilled water.

The first phase of the process starts with the intake of 500 ml of 20 ppm humic acid solution in the reactor that is placed ceramic after TiO$_2$ coating, the time variation used in the degradation process is 2 hours, 4 hours, 6 hours, 8 hours and 24 hours, the process is performed in under 8 watt fluorescent light and 8 watt purple UV lamp. After the degradation process the adsorption was measured with a UV-Vis spectrophotometer and the percentage of degradation calculated ($\%D$).

4. Results and discussion

4.1 Photocatalytic reactor

The reactor made is a radiation reactor, namely a reactor without a rotating tool. the photocatalysis process is performed in a box using 8 watt fluorescent light, a purple 8 watt UV lamp and a luminous flux measured from the side of each lamp and the top of the reactor with a light sensor.

4.2 Photocatalyst activity for degradation of humic acid

Absorption measurements were performed with UV-VIS spectrophotometry. In this method, the maximum wavelength of humic acid is determined at 20 ppm. Determination of the maximum wavelength can be seen in Figure 1 which has a wavelength of 265 nm.

![Humic acid spectra](image_url)

**Figure 2.** Humic acid spectra

Measurements are performed at 2 hour, 4 hour, 6 hour, 8 and 24 hour intervals and the chart results are obtained.
Figure 3. The decrease in humic acid activity with 2 layers of TiO$_2$ 400°C neon light

Table 1. Light Flux 2 layer TiO$_2$ temperature 400°C neon light

| Time   | Lamp 1 | Lamp 2 | Lamp 3 | Lamp 4 |
|--------|--------|--------|--------|--------|
| 2 hours| 3255.0 | 4436.0 | 4184.0 | 5256.0 |
| 4 hours| 3255.0 | 4056.0 | 4284.0 | 3464.0 |
| 6 hours| 3961.0 | 3898.0 | 4226.0 | 5151.0 |
| 8 hours| 3462.0 | 2458.0 | 2441.0 | 2330.0 |
| 24 hours| 3255.0 | 4436.0 | 4148.0 | 5256.0 |

Figure 4. The decrease in humic acid activity with 4 layers of TiO$_2$ 400°C neon light
**Table 2.** Light Flux 4 layer TiO$_2$ temperature 400°C neon light

| Time   | lamp 1 | lamp 2 | lamp 3 | lamp 4 |
|--------|--------|--------|--------|--------|
| 2 hours| 4079.0 | 3786.0 | 4622.0 | 5820.0 |
| 4 hours| 4238.0 | 4044.0 | 4687.0 | 5717.0 |
| 6 hours| 3303.0 | 3609.0 | 4489.0 | 6046.0 |
| 8 hours| 1992.0 | 3073.0 | 4606.0 | 5913.0 |
| 24 hours| 3797.0 | 3858.0 | 4508.0 | 5433.0 |

**Figure 5.** The decrease in humic acid activity with 2 layers of TiO$_2$ 400°C UV light

**Table 3.** Light Flux 2 layer TiO$_2$ temperature 400°C UV light

| Time   | lamp 1 | lamp 2 | lamp 3 | lamp 4 |
|--------|--------|--------|--------|--------|
| 2 hours| 39.0   | 13.0   | 39.0   | 13.0   |
| 4 hours| 30.0   | 13.0   | 27.0   | 25.0   |
| 6 hours| 30.0   | 16.0   | 34.0   | 27.0   |
| 8 hours| 30.0   | 13.0   | 30.0   | 20.0   |
| 24 hours| 25.0   | 11.0   | 27.0   | 18.0   |

**Figure 6.** The decrease in humic acid activity with 4 layers of TiO$_2$ 400°C UV light
Table 4. Light Flux 4 layer TiO\textsubscript{2} temperature 400\degree C UV light

| Time   | Lamp 1 | Lamp 2 | Lamp 3 | Lamp 4 |
|--------|--------|--------|--------|--------|
| 2 hours| 41.0   | 37.0   | 34.0   | 39.0   |
| 4 hours| 32.0   | 39.0   | 32.0   | 30.0   |
| 6 hours| 32.0   | 32.0   | 32.0   | 32.0   |
| 8 hours| 30.0   | 30.0   | 30.0   | 32.0   |
| 24 hours| 30.0 | 30.0   | 30.0   | 30.0   |

The above results indicate the highest presentation level of the decrease in humic acid with 0.5 M TiO\textsubscript{2}, that is 59.94\% for 24 hours using 8 watt fluorescent lamps with 4 TiO\textsubscript{2} coatings on ceramic. When using fluorescent light sources, the results of % D are higher than those of UV lamps, but the results with UV light irradiation produce humic acid water that is clearer than neon lights, because UV lamps serve to kill bacteria and purify water, in addition to UV lamps can minimize the growth of the population against viruses, bacteria, fungi, protozoa and algae. Decrease in degradation of humic acid as a result of tests with UV spectrophotometry, there is a floating object in a solution of humic acid and therefore a decrease in %D decreases. During the degradation process when the photocatalyst is exposed to light or light, a certain amount of energy in the form of photons will be absorbed. The absorption of photon energy results in electron excitation in the valence band to the conduction band. so leaves behind a positive charge called a hole. Most of these electron-hole pairs will survive on the surface of the semiconductor, so the hole can act by initiating an oxidation reaction and electrons initiate a reduction reaction of the chemical compounds that surround the surface of TiO\textsubscript{2}. The photon source for activating a photocatalyst may come from lights or natural light sources such as sunlight. [11]. As a comparison (blank) of irradiation of peat marsh water with glass plates that are not coated with titania, the purification percentage is 3.76\%. These results showed that the nature of the titanium oxide photocatalysts made in the form of thin layers can accelerate the degradation process of organic compounds in peat bog water.

5. Conclusion

Based on the research that has been done, it can be concluded that the highest presentation of degradation of humic acid with 0.5 M TiO\textsubscript{2} for 24 hours is 59.94\% using 8 watt fluorescent lamps with 4 layers TiO\textsubscript{2} coatings on ceramic. Factors influencing the degradation of humic acid are light, catalyst properties and irradiation time, the longer the degradation time, the more energy photons are absorbed by the photocatalyst, there by increasing the effectiveness of humic acid photo degradation.

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