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Design of rotary photoreactor using nano Cu/TiO₂ for degradation humic acid in outdoor visible light

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Abstract. Doping agents that can increase the activity of TiO₂ photocatalysts, namely copper (II) or Cu²⁺ ions because copper is one of the abundant transition metal elements on earth and has Cu²⁺ (0,68 Å) ion radius which is close to the radius Ti⁴⁺ that is (0,74 Å) so that it can be incorporated in TiO₂ crystals. Coping is done using the sol-gel method. The Cu concentration used for drying was 5% and calcined at 4000C. the results obtained were then characterized by XRD and obtained by the structure namely anatase, then the crystals were used to degrade humic acid in external light and by using variations in rotation speed and length of time of irradiation. The best reduction in absorbance was found at a rotation speed of 1500 rpm, which was 69,18 % degraded humic acids.

1. Introduction

TiO₂ is the most commonly used semiconductor material in photocatalyst applications because of its low cost, simple but reliable in the method of synthesis and photo-corrosion resistance. Photocatalyst is a material that can accelerate chemical reactions with the help of light as activation. Photocatalysts belong to semiconductor materials with band gaps ranging from 1-3 eV [1, 12-15].

Some method were used in purification of water, such as adsorption using microorganism [23]. The others method, water can purified by inorganic material, ie catalyst from oxide. Metal oxide can be used for anti bacterial, i.e. microalgae can be used as anti-bacterial and anti oxidant[24-26]. According to Lysandra (2017) titanium dioxide is a type of photocatalyst that is often used for wastewater treatment. Some properties of TiO₂ is high oxidation properties, super hydrophilicity and chemical stability[2], using photocatalyst methods of metal oxide semiconductor materials such as titanium oxide (TiO₂) so that it can degrade humic acid and decrease humic acid in peat water at 89.4%, but the TiO₂ band gap is large (3.2 eV nm) so TiO₂ requires UV light activity (<387 nm) which means that only a small portion of the solar spectrum can be used for photocatalytic applications [3, 16-20]. TiO₂ has three main crystal structures, namely anatase, rutile, and brookite with band gaps ranging from 3.0 - 3.2 eV [4].

Physics and chemistry modification is done one of them to reduce the band gap of TiO₂ in order to work in the wavelength range of visible light [5, 21-22]. This study used modifications to the chemical properties of TiO₂ using copper (II) or Cu²⁺ ions as doping agents to improve photocatalytic activity of TiO₂ [6]. Doping agents that are known to increase optical and photocatalytic properties of TiO₂ are copper ions (Cu²⁺) because copper is one of the abundant transition metal elements on earth and has a radius of Cu²⁺ (0.68 Å) which is close to the finger- finger Ti⁴⁺ that is (0.74 Å) so that it can be



incorporated in TiO_2 crystals [7]. Coping is done using the sol-gel method to simplify the preparation in synthesizing small-sized material, besides that the sol-gel method is also easy to control chemical composition, has good heat stability, can be carried out at low temperatures and relatively low costs [8].

2. Tools and Materials

Tools for the preparation of Cu-doped TiO_2 photocatalyst materials using the sol-gel method are: glass beaker (pyrex), measuring cup, magnetic stirrer, porcelain cup, volume pipette and spatula. Then the tool for making reactor design reactors, glass, cable, dynamo, tachometer, propeller and wire. The tool for characterizing TiO_2 photocatalysts doped with Cu is scanning electron microscopy (SEM), UV-Vis spectrophotometer and mass spectroscopy. the ingredients used in this study are: humic acid, Titanium (IV) tetra isopropoxide ($\text{Ti}(\text{OCH}(\text{CH}_3)_2\text{CHOH})_4$), Copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), Aquades (H_2O), HNO_3 p.a

3. Experiment

3.1. Making Reactor Design

The making of the reactor begins with providing a transparent glass with a thickness of 3mm and then cutting the glass with a height of 15 cm and a width of 7 cm then the glass is glued to form a hexagon. The glass that has been formed is then in the upper part of the hole as the entry point of the stirrer, the stirrer is connected to the dynamo so that the stirrer can rotate.

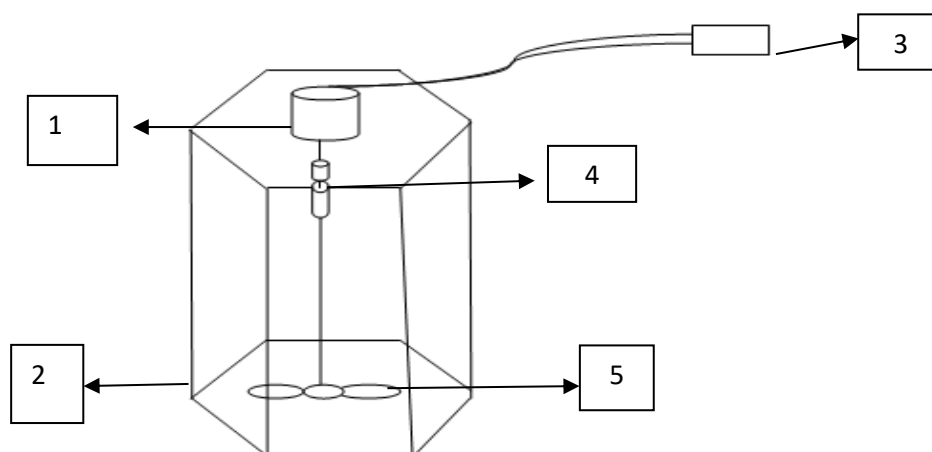


Figure 1. Photocatalyst Reactor Design

Information :

1. Dinamo
2. Transparent glass
3. Voltmeter
4. The connection between the dynamo and the stirrer
5. Propellers

3.2. Photocatalyst preparation of TiO_2 was doped with 5% Cu using the Sol-Gel Method

8,4 ml of titanium (IV) tetra isopropoxide (TTIP) mixed with 8 ml of isopropanol then homogenized using a magnetic stirrer with a speed of 3000 rpm for 30 minutes (solution A). then add ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) which has been dissolved in 2 ml of isopropanol into ocean A and homogenize at a constant speed of 10 minutes. Solution B was prepared by mixing 10 ml of isopropanol with 1 ml of aquabies and homogeneous for 15 minutes, then solution B gradually added in solution A. Both solutions were homogenized until the sol then formed sol formed in the furnace at 4000C for 2 hours, then carried out test with XRD [9].

3.3. Photocatalyst Activity Test for Humic Acid Degradation

In conducting this catalyst test humic acid is used as a pollutant or material to be decomposed (degradation). This degradation process involves light to accelerate the reaction, commonly called photodegradation. Humic acid was first made with a concentration of 20 ppm. This solution is obtained by weighing 0.02 grams of humic acid and then dissolving it in 1000 ml of distilled water.

The process of the first stage begins by taking 200 ml of 20 ppm humic acid solution put into the reactor then put the insoles formed from the synthesis of Cu doped TiO₂, before inserting the sol first calcined at 400 °C for 2 hours, the time variation used is 1 to 5 hours and by using a variation of the rotation speed of 500, 1000, 1500 rpm then measuring the adsorption with a UV-Vis spectrophotometer

4. Result and Discussion

Preparation of Cu doping TiO₂ using the sol-Gel method and characterized using XRD to provide information about structure, phase, texture, crystallinity, and crystal size. XRD analysis carried out on 5% Cu doping catalyst TiO₂ and calcined at 4000C showed the appearance of Crystal peaks, where theoretically TiO₂ has three forms of structure namely anatase, brookite and rutile [10]. Anatase has the highest 2θ 25.280 (101) and 48.040 (200), Rutile has the highest 2θ 27.440 (110) and 39.8 (200) (JCPDS cards No. 12-1272 and 29-1360). based on the analysis that has been done, the crystal structure is anatase because it has a value of 2θ which is the same as the anatase structure theoretically 25.35°, 38.11°, 48.12°, 54.77°. Anatase is a stable phase and is formed at low temperatures). Generally anatase displays photocatalytic activity which is much higher than rutile and brookite because it has more surface area so that the active side is also large and results in the ability to degrade a compound (humic acid) also getting better.

The table and graph below shows a process of degradation of humic acid using Cu doping TiO₂ catalysts and using clock variations and rotational speed.

Table 1. Degradation of humic acid at 500 rpm with a 5% TiO₂-Cu catalyst at 400°C calcination temperature

Time(Hours)	ABS	%D	Front luks (LX)	Rear luks (LX)
1	0.44	55.82%	9809.5	2413
2	0.428	57.03%	10106	2489.3
3	0.421	57.73%	12139.75	2608.75
4	0.399	59.94%	13840.6	2860
5	0.39	60.84%	15284	2977.17

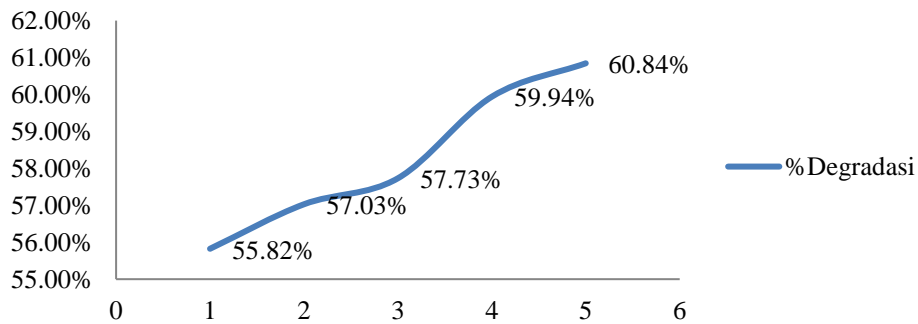
Table 2. Degradation of humic acid at 1000 rpm with a 5% TiO₂-Cu catalyst at 4000C calcination temperature

Time	ABS	%D	Front luks (LX)	Rear luks (LX)
1 hours	0.466	53.21%	8753.125	1620.65
2 hours	0.476	52.21%	8489	1579.67
3 hours	0.438	56.02%	10030.5	2337
4 hours	0.397	60.14%	15156	2839
5 hours	0.409	58.94%	13835	2834.5

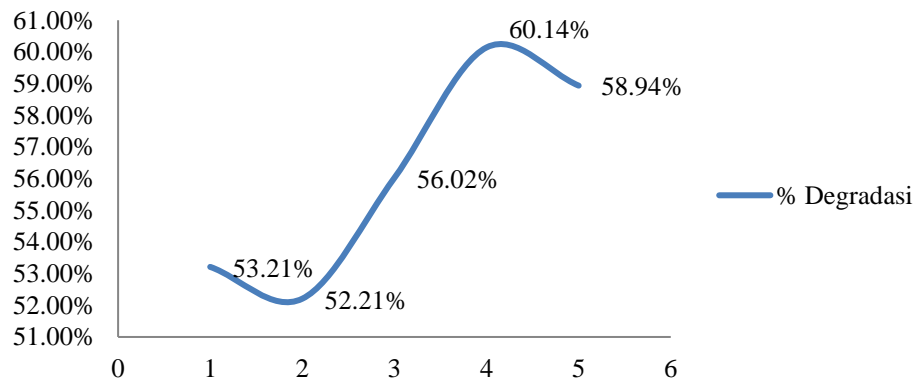
Table 3. Degradation of humic acid at a rotation of 1500 rpm with a 5% TiO₂-Cu catalyst at 4000C calcination temperature

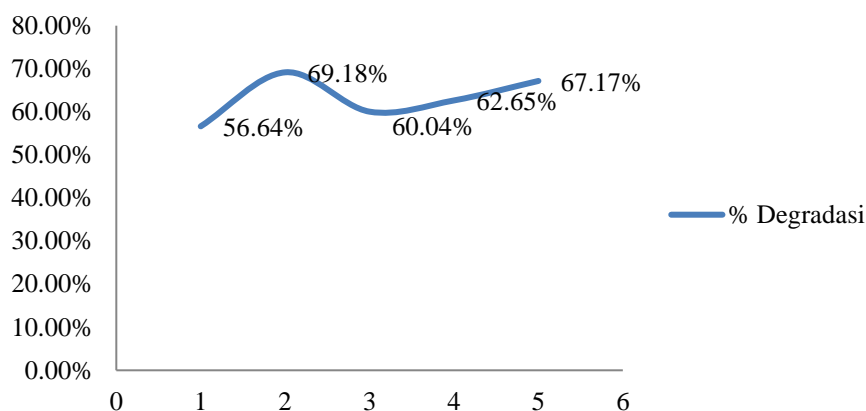
Time	ABS	%D	Front luks (LX)	Rear luks (LX)
1 hours	0.428	56.64%	10701.5	2569.5
2 hours	0.307	69.18%	25188.5	3307.33
3 hours	0.398	60.04%	13569	2875
4 hours	0.372	62.65%	18233	2945.2
5 hours	0.327	67.17%	20283.8	3054.83

(a) **Degradation of Humic Acid at a speed of 500 rpm**



(b) **Degradation of Humic Acid at a speed of 1000 rpm**



(c) **Degradation of Humic Acid at a speed of 1500 rpm****Figure 2.** The degradation graph of humic acid using rotation speed of (a). 500, (b). 1000 and (c). 1500 rpm

The photodegradation process requires a photocatalyst to accelerate the reaction rate. The principle of photodegradation is the jump of electrons from the valence band to the conduction band in the photocatalyst which is subject to photon energy. These electron jumps cause holes (electron holes) that can interact to form radicals. radicals are active and can continue to decompose the target compound. The photocatalyst used in this study was Cu doping TiO₂ and using photon energy from direct sunlight, while the variables used were the influence of the length of irradiation time and the effect of rotational acceleration. The purpose of determining the time of sunlight irradiation and acceleration of rotation is to determine the effectiveness of Cu doping TiO₂ photocatalyst in degrading humic acid. The time of sunlight irradiation is carried out with variations of hours which are 1 to 5 hours and the velocity of rotation is 500, 1000 and 1500 rpm.

The test results in the graph above show that in grain 1 using a rotation speed of 500 rpm and with a variation of time 1 to 5 hours resulting in a decrease in absorbance of humic acid, the results of the test showed a decrease in absorbance of humic acid at a maximum of 5 hours with a decrease in absorbance of 60.84%. this is because the longer a Cu doping semiconductor absorbs photon energy, namely UV light, the more OH radicals are formed on the surface of the semiconductor (OH radicals are used for the degradation of humic acid) and the interaction between humic acid and OH radicals will be longer so can increase the photodegradation efficiency of the humic acid. Graphs 2 and 3 absorbance of humic acid produced does not match the length of time of irradiation. This is because the formation of a recombinant reaction between electrons and holes on the active side of the catalyst. If the active side of the catalyst has been used to degrade humic acid molecules, then the degradation process for other humic acid molecules will stop (saturate), so that stirring is used to reactivate the part of the active side of the catalyst that has been closed. The active side of the catalyst must be maintained to provide a place for the catalytic process to occur from a reaction.

Based on the graph above the high decrease in absorbance occurs at a rotation of 1500 rpm which is equal to 69.18%, this is because the faster the rotation, the absorbance of humic acid produced is also higher.

5. Conclusion

The decrease in absorbance of humic acid is influenced by light flux, the higher the light lux received, the lower the absorbance of humic acid produced is also higher. Rotational speed also affects the decrease in absorbance of humic acid, the greater the rotation, the higher the decrease in absorption of the humic acid

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