DESIGN OF HUMAT ACID SOLID SOLUTION REACTOR THROUGH PHOTOTRANSFORMATION OF COPPER OXIDE (CuO) SEMICONDUCTOR PLATE

Syanty Rahmadhanty¹⁾Rahadian Zainul^{2*)}

¹⁾Jurusan Kimia, FMIPA, Universitas Negeri Padang

²⁾Jurusan Kimia, FMIPA, Universitas Negeri Padang

³⁾Jurusan Kimia, FMIPA, Universitas Negeri Padang

Jl. Prof. Hamka Air Tawar Padang

Email^{2*)}: rahadianmsiphd1@yahoo.com

ABSTRACT

This research was conducted to make the reactor degrade a solution of humic acid using a copper oxide (CuO) catalyst. The designed reactor consists of 2 types of design, the first reactor consists of 8 copper oxide semiconductors (CuO) as catalyst with a sample volume of 1600 ml and a second reactor consisting of 1 copper oxide (CuO) with a sample volume of 25 ml. The light source used is direct sunlight and light in the room. The catalytic process is carried out through photodegradation of a solution of humic acid using the reactor. Variations in irradiation time are carried out for 2, 4, 6 and 8 hours. Absorbance of humic acid before and after irradiation was measured using spectrophotometer at λ 325 nm. The results showed that direct sunlight irradiation gave better results than light rays in the room. The optimum exposure to sunlight is 4 hours with degradation of 32.80% using a second type of reactor.

Keywords: photocatalyst, photodegradation, copper oxide (CuO), humic acid

INTRODUCTION

Today environmental issues are an important thing for human life. These issues include environmental pollution, especially in waters. Pollutant sources can come from inorganic wastes such as heavy metals, organic wastes such as humic acid, fulvic acid and humin and other particulates distributed in waters.

The problem of peat swamp water is phenomenal in Indonesia. This is because the Indonesian state has a very large peatland. Peatland in Indonesia reaches 20 million Ha, as stated in the National Strategy and Action Plan report (Sustainable Peatland Management, October 2006). More detailed data from the Ministry of Environment and Forestry of the Republic of Indonesia and the Ministry of Agriculture 2016, the extent of peatland on several large islands of Indonesia. Namely, Sumatra Island 5,965,220 Ha, Kalimantan Island 5,036,164 Ha and Papua island 4,931,054 Ha. (Peat Restoration Agency, 2016) This huge potential can be used if peat swamp water can be transformed into mineralized products that support growth agricultural land, such as pH 7, is not acidic and clean. (G. S. Dhillon, et, al., 2013)

In peat swamp water, there are pollutants which cause changes in the color of the swamp water. These substances include humic acid, fulvic acid and humin. Efforts to clear peat swamp water have been carried out using conventional methods, for example through filtering using sand, palm fiber and alum. However, in peat swamp water this cannot work well. Semiconductor photocatalyst

applications for handling industrial and environmental problems are an interesting study. According to Wong et al (1995), this is due to several advantages it has that is relatively inexpensive, non-toxic, can use the sun as an energy source, can be reused and the method of use can be simplified. Various types of compounds, especially organic compounds that have been successfully transformed with these methods as reported by Hoffman et al. (1995), among others, alkanes, aliphatic alcohols, aliphatic carboxylic acids, alkene, phenol compounds, aromatic carboxylic acids, dyestuffs, simple aromatic compounds, halogenated alkanes and alkenes, surfactants and pesticides.

Catalyst design using copper oxide semiconductors has been developed as a good photocatalyst. Copper Oxide (CuO) has the advantage of being non-toxic, has a low band gap of 1.2 eV which is able to work in visible light or direct sunlight, low production costs, good electrical properties so that copper oxide has been widely used for various applications in various fields such as solar cells, electronic coatings and catalytic applications (Al-Kuhaili. MF, 2007).

Based on the above, researchers want to examine how the activity and efficiency of copper oxide semiconductors in the phototransformation of humic acid. In this study, the researcher proposes research that is "What are the specifications of the design of the Humid Acid Solution Integration Reactor using a copper oxide (CuO) semiconductor catalyst? Based on the above, researchers want to examine how the activity and efficiency of copper oxide semiconductors in the phototransformation of

humic acid. In this study, the researcher proposes research that is "What are the specifications of the design of the Humic Acid Solution Integration Reactor using a copper oxide (CuO) semiconductor catalyst?"

A. Time and Place

The study was conducted at the FMIPA UNP Chemical Research Laboratory starting from March-June 2018.

B. Tools and materials

The tools used in this research are: glassware, analytical balance, a set of glassware, furnaces, pH meters. Then the tools for characterization, XRD analysis function to see the crystal structure, SEM to determine morphology

The materials used in this study are: humic acid, aquades, 3mm thick clear glass of various sizes, copper oxide plate (CuO), paralon pipes.

C. Research procedure

1. Synthesis of Copper oxide plates

Cu metal in the form of sheets (36.5 cm x 120 cm) is cut into pieces 4 cm wide and 12 cm long according to the designed reactor container. Then the Cu metal plate is calcined in the furnace at 4000C for 1 hour, then cool for 5 hours. The copper oxide plate is then tested with XRD and SEM after it will be installed into the reactor that is designed.

2. Making Reactor Design

The reactor design made consists of 2 types, namely: Design 1, which is clear glass with a thickness of 3 mm which is made of beams and paired with a copper oxide plate with a size of 4 x 12 cm as many as 6 pieces. Design 2, which is transparent glass with a thickness of 3 mm, cut to a size of 2 cm x 12 cm by 4 pieces. There is one copper oxide plate in all four reactors.

3. Test of Humic Acid Photocatalyst Degradation

1. First Reactor

A total of 3100 ml of 20 ppm humic acid solution into the first reactor with the help of sunlight (light entering the room) with a time of 2 to 6 hours. Then, sort the absorbance by UV-Vis spectrophotometer.

2. Second Reactor

A total of 25 ml of 20 ppm humic acid program put in the first reactor by illuminating sunlight in the room and outdoors with a time of 2 to 6 hours. Then the absorbance was measured by UV-Vis spectrophotometer. Calculate the Decrease of Humic Acid Aggregation with the formula:
$$\frac{(\text{Initial Absorban}-\text{Final Absorban})}{(\text{Initial Absorban})} \times 100\%$$

Characterization using Ray Diffraction XRD This test is carried out in the Physics laboratory, FMIPA, UNP. XRD or X-Ray Diffraction is used to determine the characteristics in terms of the structure and size of the crystal in a sample. The three basic components of X-Ray diffraction are X-rays, sample sites, and detectors located in a circle parallel to the focus circle.

Characterization using Scanning Electron Microscopy (SEM)

This test aims to see the surface structure of material or material in micro size. SEM uses scattering electrons to form shadows so that SEM has a higher resolution than optical microscopes. This is due to the de Broglie wavelength that is owned by electrons shorter than optical waves. The smaller the wavelength used, the higher the resolution of the microscope. The point is that at very close distances can still produce maximum magnification without solving images (Irvan, 2008)

RESULTS AND DISCUSSION

The results of the study consisted of identification of the structure and size of crystals in copper oxide (CuO) from the results of XRD testing, surface morphology of copper oxide (CuO) using SEM. Measurement of the absorbance of a solution of humic acid which is before and after degraded using a UV-Vis spectrophotometer, measuring changes in pH of the solution of humic acid, and determining the percent degradation of the solution of humic acid. Characteristics of copper oxide (CuO) X-Ray Diffraction (XRD) XRD analysis was carried out to identify the compounds contained in the sample. In the graph below, it can be observed that the XRD measurements that have been made on copper form two oxides, namely CuO and Cu₂O, each of which form a peak. It is known that the CuO compound formed is 80.42 and Cu₂O compounds are 77.36 percent.

1. Scanning Electron Microscope (SEM) Characterization of copper oxide is used to determine the morphology and particle size on the surface of the copper pipe. In this study the results of characterization will be observed using SEM from copper pipes before and after calcination. calcination was carried out at 400°C for 1 hour. The combustion temperature used is the optimum temperature for the formation of oxides (Cu₂O) and CuO). SEM results in copper oxide before and after calcination with 5000x magnification can be seen in the figure below:

The results of SEM measurements on the surface of copper oxide (a) before calcination with 5000x magnification (b) after calcination with 5000x magnification.

In the picture it can be seen that there has been a change in the surface of the copper plate (Cu) after calcination at a temperature of 400 ° C. Burning for 1 hour at 400 ° C gives optimum results, the formation of copper oxide in the pipe, as a sign that the copper pipe has changed its nature from conductor to semiconductor and is catalyst. and can be used as a photocatalyst in a reactor that is designed.

1. Effect of Light on Humic Acid Photodegradation
The test of the effect of light on the degradation of humic acid aims to find out the most effective light for photocatalysts in producing ·OH.

Picture. Relationship diagram between indoor and outdoor light variations

In the picture shows that the value of degradation with light outside the room is higher than in the room, because the intensity of sunlight outside the room is greater than in the room so that the energy of the photons absorbed is greater to produce OH radicals.

When photocatalysts are irradiated with energy greater than the band gap energy, a strong oxidizing hole will be produced to form OH radicals and radicals

degrade humic acid into simpler compounds. From the data of the effect of the light, direct sunlight is more effective as a potential source of light for photocatalysts in degrading humic acid.

1. Effect of time on degradation of humic acid
The length of the irradiation time in the degradation process describes the length of interaction (contact) between photocatalyst and light (hv) in producing OH radicals and contact between OH radicals and humic acid substrate in the degradation process.

In the figure shows that the degradation of humic acid increases with the increase in the duration of sunlight exposure (indoors and outdoors). In the irradiation for 2-4 hours there was a significant increase in degradation, while on the 4th to 8th hour the degradation obtained was constant due to the longer the irradiation of the color of the solution faded, so that to reach the photocatalyst became easier. In addition to the addition of irradiation time, the photon energy

more and more absorbed by CuO photocatalysts on the surface, making it easier to degrade humic acid. Another factor that causes the results of the hearing to be constant is due to differences in the intensity of the sun's rays during the degradation process, so that the number of OH radicals produced is not the same for each use. The difference in the intensity of sunlight that reaches the earth is influenced by the season, geographical location and presence of clouds. However, this study shows that CuO photocatalysts are less effective for use in the photodegradation of humic acid because it produces% degradation of less than 50%
CONCLUSION

Based on the results of the research that has been done, it can be concluded as follows:

1. Research has been conducted on the degradation of humic acid using a designed reactor
2. The reactor that has been made consists of two designs, namely the first design using 8 CuO and the second design using 1 CuO
3. The irradiation time greatly affects the phototransformation process of humic acid
4. The highest percentage of degradation produced is 32.80% using design reactor 2

SUGGESTION

Based on the research that has been done, it is recommended to use other semiconductors to produce a greater percentage of degradation.

BIBLIOGRAPHY

- [1] Abdullah, Mikrajuddin. 2008. *Review Sintesis Nanomaterial*. ITB: Bandung
- [2] Agus, F dan I.G.M. Subakti.(2008). *Lahan Gambut : Potensi untuk Pertanian dan Aspek Lingkungan*. Balai Penelitian Tanah dan ICRAF. Bogor. 36 hal.
- [3] Al-Kuhaili. M.F. 2007. *Characterization of copper oxide thin films deposited by the thermal evaporation of cuprous oxide (Cu₂O)*. Physics Department, King Fahd University of Petroleum and Minerals, Saudi Arabia. 623-629
- [4] Anam, Choirul. Sirojudin dkk.(2007). Analisis Gugus Fungsi Pada Sampel Uji, Bensin Dan Spiritus Menggunakan Metode Spektroskopi FT-IR. *Berkala Fisika*. Vol 10 no.1. 79 – 85
- [5] Atkins. P.w. 1989. *Kimia Fisika jilid 2 Edisi keempat*. Erlangga, ISBN 22-00-032-4, hal: 308-313.
- [6] Aziz, H., Alif, A., Ariani, R., Trisna, L., Wahyuni, A., Munaf, E., Biomaterials supported with titania as photocatalyst in peat water purification, *J. Chem.Pharm. Res.*, 2015, 7(6): 192-197
- [7] Badan Restorasi Gambut, (2016). 'Rencana Strategis Badan Restorasi Gambut Tahun 2016-2020', *Badan Restorasi Gambut*, November 2016
- [8] Cullity. 1956. *Element of X-Ray Diffraction*. Addison-Wesly pub,co.inc. Massachusetts
- [9] Dadan Suherman & Nyoman Sumawijaya .(2013). Removing Colour and Organic Content of Peat Water Using Coagulation and Flocculation Method In Basaltic Condition *Ris.Geo.Tam*. Vol. 23, No.2, 127-139
- [10] Dauglas A. Skoog, et al.1998. *Principle Of Instrument Analysis 5th Edition*. Harcourt Brace College Publisher: USA
- [11] Fiolida, Intan Agnes Singyu (2016) *Preparasi dan Karakterisasi Komposit CuO-Zeolit Alam Untuk Fotodegradasi Zat Warna Rhodamin B dengan Sinar Ultraviolet*. S2 thesis, Fakultas Matematika dan Ilmu Pengetahuan Alam UNY
- [12] G. S. Dhillon, S. K. Brar, S. Kaur, and M. Verma,(2013) 'Screening of Agro-Industrial Wastes for Citric Acid Bioproduction by *Aspergillus Niger* 2001 through Solid

- State Fermentation', *J Sci Food Agric*, 93, 1560-7
- [13] Jayadi, S. F., Destiarti, L., Sitorus, B., Pembuatan Reaktor Fotokatalis dan Aplikasinya untuk Degradasi Bahan Organik Air Gambut Menggunakan Katalis TiO_2 , *Jkk*, 2014, 3(3): 55-58
- [14] Kusnaedi. (2006). *Mengolah Air Gambut Dan Air Kotor Untuk Air Minum*. Penebar Swadaya : Jakarta
- [15] Linsebigler, A. L., Lu, G., & Yates, J. T. (1995). Photocatalysis on TiO_2 Surfaces: Principles, Mechanisms, and Selected Results. *Chemical Reviews*, 95(3), 735-758.
- [16] John R. Swierk and Thomas E. Mallouk. 2013. *Design and Development of -Photoanodes for Water Splitting Dye -Sensitized Photoelectrochemical Cells*. Chem. Soc. Rev. 42: 2357-2387
- [17] Kriswarini, Rosika dkk, 2010. *Validasi Metode XRF (X- Ray Fluoresence) Secara Tunggal Dan Simultan Untuk Analisis Unsur Mg, Mn Dan Fe Dalam Paduan Auminium*. Seminar Nasional VI. Banten: PTBN BATAN
- [18] K. M. Carlson, R. Heilmayr, H. K. Gibbs, P. Noojipady, D. N. Burns, D. C. Morton, N. F. Walker, G. D. Paoli, and C. Kremen, (2018). 'Effect of Oil Palm Sustainability Certification on Deforestation and Fire in Indonesia', *Proc Natl Acad Sci U S A*, 115, 121-26.
- [19] Mohd rafie johan, et al. 2011. *Annealing Effects on the Properties of Copper Oxide Thin Films Prepared by Chemical Deposition*. Int. J. Electrochem. Sci., Vol. 6 (6094 – 6104)
- [20] Novita, E. (2008). *Penurunan Intensitas Warna Air Gambut Menggunakan Cangkang Telur*. Tesis Pasca Sarjana, Teknik Lingkungan, Institut Teknologi Bandung: Bandung.
- [21] Papadimitropoulos, G.; Vourdas, N.; Vamvakas, V.; Davazoglou, D. Publication: *Thin Solid Films*, vol. 515, issue 4, pp. 2428-2432.
- [22] Rahadian Zainul, Admin Alif, Hermansyah Aziz, Syukri Arief and Syukri. 2015. Photoelectrospilting water for hydrogen production using illumuniati of indoor light. *jurnal of chemical and pharma ceutical reasearch (JOCPR)*, 7(95) : 246-256
- [23] Rahadian Zainul. 2016. Effect of Themperature and Particle Motion Against the Ability of ZnO Semiconductor Photocatalyst in Humic Acid. *Der Pharma Lettre*, 8(15): 120-124
- [24] Rahadian Zainul. 2016. Determination of the Half -Li and the Quantum Yield of ZnO Semiconductor Photocatalyst in Humic Acid. *Der Pharmation Lettre* ,8(15), 176-179.
- [25] Rahadian Zainul. 2016. *Determination of the Half -Li and the Quantum Yield of ZnO Semiconductor Photocatalyst in Humic Acid*. Der Pharmation Lettre 8(15), 176-179.
- [26] Rahadian, dkk. 2015. *Disain Geometri Reaktor Fotosel Cahaya Ruang*. ISSN : 1978-628X / eISSN : 2476-8960. Hal 131-142
- [27] Rahadian Zainul. 2016. *Design and Modification of Copper Oxida Elektrodes for Improving Conversional Coefficient Indoor Light (PV-Cell) Photocells*. Der Pharmation Chemica 8(19), 388-395.
- [28] Rahadian, et.al.2015. *Design of Photovoltaic Cell with Copper Oxide Electrode by Using Indoor Lights*. ISSN: 0975-8585. Hal: 353-354
- [29] Salimin, M.I., Gandaseca, S., Ahmed, O.H., & Majid, N. M.A. (2010). Comparison of selected chemical of peat swamp soil before and after timber harvesting. *American Journal of Environmental Sciences* 6(2): 164-167.
- [30] Sharpless, C. M., Aeschbacher, M., Page, S. E., Wenk, J., Sander, M., & McNeill, K. (2014). Photooxidation-induced changes in optical, electrochemical, and photochemical properties of humic substances. *Environ Sci Technol*, 48(5), 2688-2696.
- [31] Sibilia, p .1996. *A Guide To Materials Characterization And Chemical Analysis* 1, 2nd ed. USA: Wiley-VCH