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Determination of the half-life and the quantum yield of ZnO semiconductor photocatalyst in humic acid

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ABSTRACT

This research aim to investigate kinetics of humic acid photo-transformation. This study was done under some optimum conditions: lighting time of 2 hours, using Hg lamp of low pressure (λ = 254 nm), humic acid of 100 ppm and pH=9.2. it was disclosed that 97.51 % of humic acid transformed into minerals product which involved the first orde reaction, 38.4 minute half-life, the constant rate of reaction is 0.02 minutes^{-1} and the quantum rendement of 0.115 molecules per photons.

Key words : Humic Acid, Photo-transformation, Zinc Oxide, Half-life, Quantum yield

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INTRODUCTION

Semiconductor photocatalyst is a prospective research, both activity and efficiency in the process of photo-transformations. One of them is the humic acid is a major component of peat swamp water causes reddish to brown, in addition to other components that fulvic acid and humin [1]. As a result of the peat water has a less pleasant smell and taste sour [2] so it does not meet the requirements of clean water set by Department of Health, Indonesia. Peat swamp water polluted water classified because it contains both organic and inorganic material [in this case organic material] which causes the water unfit for use [3]. In addition, peatlands and swamps in Indonesia are very spacious, the amount is not less than 32 million Ha [4].

In another study, Nasr and Vinodgopal (1996) have examined the mechanism of photo-transformations NBB (Nephtol Blue Black) on the surface of the semiconductor ZnO (also contained TiO_2) are exposed. The initial process of transformation began with his NBB activated after receiving photons. NBB activated submit a electrons in ZnO to form a radical NBB. This is the beginning of a chain reaction that transformed its molecular NBB[5].

$$\mathrm{NBB} \xrightarrow{hv} \mathrm{NBB}^{+} \xrightarrow{\mathrm{ZnO}} \mathrm{ZnO}^{-} + \mathrm{NBB}^{*}$$

ZnO semiconductor research has been growing rapidly. ZnO more efficient, such as resistant to corrosion, has a are relatively low light energy (Eg = 3.40 eV), and is much cheaper than TiO_2(6) Research photocatalyst ZnO has been made include studies in nano material of ZnO [7-15]. The commercial ZnO powder was used economically and directly for application on water purification.

In this research, conducted investigations on reaction kinetics photo humic acid transformation with the aid of semiconductor ZnO. Among others; the half-life of photo-transformation ($t_{1/2}$), the reaction rate constant photo-transformation (k) and quantum yield of photo-transformation (Ø) of humic acid.

MATERIALS AND METHODS

Samples are peat water that was in the location of PT Mutiara Agam, Tiku, Pariaman. The tools used are Spectronic 20 B & L, balance of electric fan, mercury-vapor lamp low pressure (λ = 254 nm), oven Gallenkamp, burette 25 mL, stopwatch, centrifuges, shakers, stirrers automatically, thermometer, desiccator, tube lighting, tweezers, glass plates, an electric cooker and tools commonly used glassware.

Materials used in the form of commercial ZnO powder, concentrated sulfuric acid, uranyl acetate 0:02 M, oxalic acid 12:02 M, potassium permanganate 0:02 M, HCL 0.1N NaOH 0.2 N, NaCl, fenolptalein, ethyl acetate, hexane, methanol, plate TLC and distilled water

Isolation Humic Acid

Humic Acid will be isolated by simple method. Into a glass beaker with a capacity of 30± L filled 25 L of water peat 0.1 N HCl is added until a pH less than 2. After settling for 4 days, the precipitate separated by centrifuge. The precipitate was washed with 95% alcohol and then dried in the desiccator. Structure of Humic Acid can be modeled and showed in figure 1.

Identification and Purification Humic Acid

To test whether the isolated form brownish powder is humic acid or not done tests with a solution of NaCl. When the positive test solution precipitates a brown and grayish. Humic acid purification is done by washing the blackish brown powder with 95% alcohol many times until got 2 staining on Thin Layer Chromatography (TLC).

Determination of Effective Condition

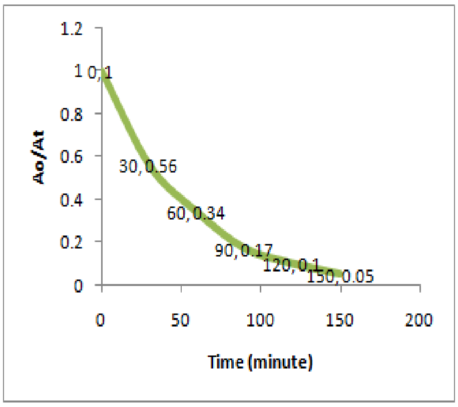
Determination of the effective conditions include determining the distance of irradiation effectively done actinometry of uranyl oxalate, determining the effective concentration of ZnO, the determination of the effective exposure time and the determination of the effective pH.

RESULTS AND DISCUSSION

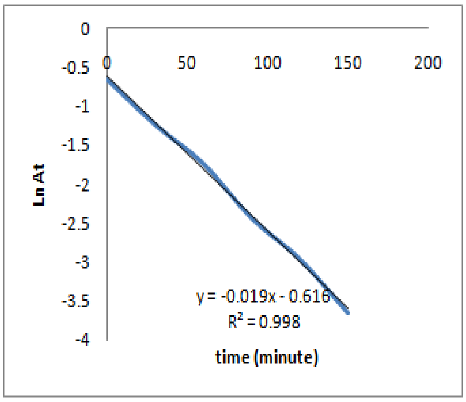
Photo-transformation Kinetics Humic Acid

Against a suspension consisting of 10 mg of ZnO and 20 mL of 100 ppm humic acid at pH 9.2 to vary irradiation time. The goal is to get the relationship between the irradiation time to the ratio At/Ao (absorbance after time t divided by absorbance at first). Data and calculation results are displayed in Figure 2.

The mathematical equations for curves At/Ao versus t results of this research and transformed to Ln At/Ao=-kt, were obtained Y=1.0343 -0,0199x, and is therefore determined the value of the half-life ($t_{1/2}$) is 0.64 hours or 2313 seconds (38.4 minutes).



(a)



(b)

Figure 2. Graph of At/Ao versus t (a) and lnAt versus t (b)

According to Raquel and Nogueira (1993) semiconductor photocatalyst process is followed first-order kinetics(16). This was evident in this study in which after being tested for a few points, then for the equation of first order constant values obtained in this study can be found by a simple equation as described by Bird (1987)(17) as follows:

Ln At/Ao = -kt

Where :
Ao = Initial Absorbance
At = Absorbance after irradiation

From the calculation [k = ln (Ao/At)/t] at three points above where the same k values obtained, ie 0.02 min^{-1} so that the kinetics of photo-transformation test humic acid with the using of ZnO semiconductor photocatalyst is following first order reaction rate as showed in Figure 2. Another way to determine reaction order photo-transformation is to create a graph logarithm Ao/At versus t, where the straight line will be obtained as evidence of a reaction of order one.

Quantum Yield of Photo-transformation Humic Acid

To see the light efficiency of the mercury vapor lamp (λ = 254 nm) is used it is necessary to determine the quantum yield, as confirmed by Levine (1978)(18).

The data obtained are as follows
C = $6{,}67\times10^{-6}$M, lo = $5{,}112\times10^{15}$ photon mL^{-1} $second^{-1}$ t = 2 hours = 7.200 seconds
D = 1,17, Ao = 0,56, At = 0,01.

Thus, with the formulation :

$$\emptyset = \frac{\left[\frac{\mathrm{Ao} - \mathrm{At}}{\mathrm{Ao}}\right] \mathrm{C.No}}{\mathrm{Io.t.}(1 - 10^{-\mathrm{D}})}$$

The yield of the quantum (ϕ) obtained are 0,115 molecules/photon. From the calculation results, obtained quantum yield for photo-transformation of 20 mL, 100 ppm of humic acid at pH 9.2 with the using of 10mg ZnO irradiation under low pressure mercury vapor lamp (λ= 254nm) of 0.1115 molecule/photon.

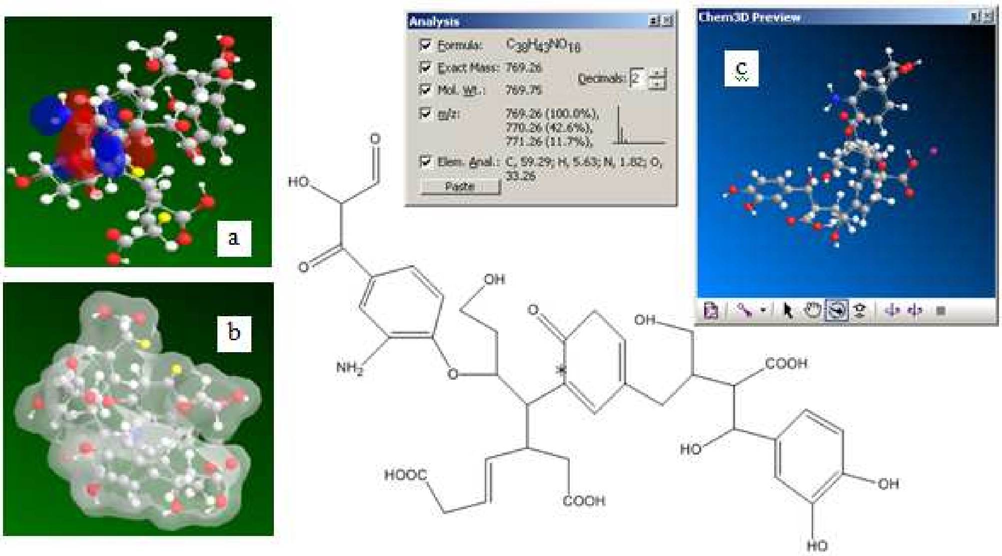


Figure 1. Structure, surface and analysis modeling of Humic Acid using ChemBio3D computerizing with software Cambridgesoft Ultra 11.0 (a-b) modeling surface HA of Connoly Molecular with Tranclucent display mode, (c) analysis of Humic Acid monomer structure according Steelink Model using Chemoffice 2008 (19)

Value also means that the quantum yield for changing one molecule of humic acid required 9.09 photons or rounded to 9 photons. It can also be said is that the efficiency of light mercury-vapor lamp low pressure (λ=254nm) to the process of photo-transformation that is about 11% or from 5.112 x 10^{15} photons/mL^4.$seconds^{-1}$ that touch system (suspension), there are about 0.562 x 10^{15} photons/mL.seconds can change humic acid to form its transformation products.

CONCLUSION

Based on this result, we conclude that the kinetics of photo-transformation of 20 mL of humic acid at pH 9.2 under irradiation mercury-vapor lamp low pressure (λ=254 nm) with the help of 10 mg ZnO obtained value of the half-life ($t_{1/2}$) is 38.4 minutes and a constant rate of reaction (k) is 0.02 $minutes^{-1}$. Irradiation with a low-pressure mercury vapor lamp (λ=254 nm) provides an efficiency of 0115 molecules/photon against photo-transformation process of humic acid assisted ZnO semiconductor photocatalysts.

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