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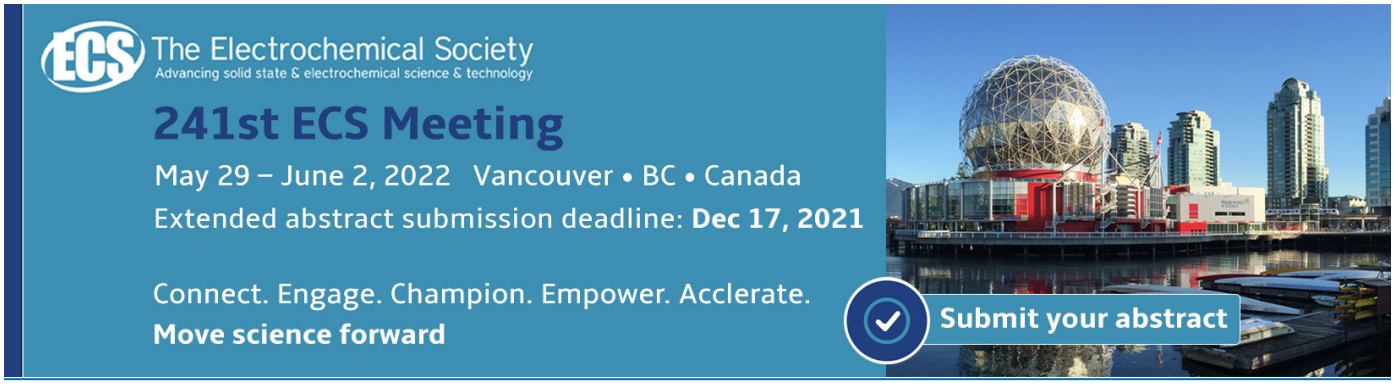

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Chataliytic activity of nano ZnO/Cu for degradation humic acid under ilumination outdoor light

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Abstract. One of the photocatalysts that is being developed for the degradation of humic acid is ZnO, because it is cheap, easy to obtain and the synthesis process is easy, large size ZnO has several disadvantages such as small surface area and energy band gap which are not suitable when applied to visible light. The research developed a method of making zno in nanometer size and composting to reduce bandgap. The maximum degradation of humic acid at nano ZnO doped Cu 7% which is equal to 54.12%. Nano characterization of nano ZnO doped Cu 7% doping using XRD and DRS UV-Vis spectra was found to be 27 nm and bandgap 5.27 eV.

1. Introduction

Photocatalysts are a combination of photochemical processes with catalysts. Light and catalyst, both are needed to accelerate chemical reactions, so the photocatalyst can be defined as photoreaction acceleration by the presence of a catalyst. The addition of catalysts in the photolysis process can increase the decomposition of organic compounds into simpler compounds called photocatalysis[1, 2]. One of the photocatalysts that is being developed for the degradation of humic acid is ZnO, because it is cheap, easy to obtain and the synthesis process is easy[3, 19, 22-23].

Zinc oxide (ZnO) is a semiconductor that has been developed and sought after as a nanomaterial luminisens because it has unique characteristics, which have an energy band gap of 3.37 eV [4], this character provides an opportunity for ZnO to be applied as luminisens. The width of the ZnO energy band gap depends on the particle size when its size is in a nanometer order. The changeable energy band gap makes it possible to adjust the luminisens wavelength emitted by ZnO. Various studies have been developed to produce ZnO in nanometer size [5-7]. In the sol-gel method, according to its name the solution undergoes a phase change into sol (colloid which has suspended solids in the solution) and then becomes a gel (colloid but has a solid fraction larger than the sol) [8].

ZnO particles in large sizes have several disadvantages such as small surface area and energy band gap which are not suitable when applied to visible light. Therefore, to optimize the properties of ZnO, ZnO is needed to have characteristics of 2 types, p-type and n-type. Doping materials for P-type ZnO include potassium, lithium, copper, phosphorus and arsenic [9], whereas doping material for n-type ZnO includes boron, aluminum and fluorine [10]. ZnO that has been doped cu will have a small energy band gap than before, causing an easier excitation of electrons from the valence band to the conduction band [11].

Many modifications and applications were carried out before about photocatalysts and environmental aspects. The role of the catalyst as degrading organic waste, and the application of water separation is also growing rapidly [26-33]. However, the application of catalysts can also be replaced by adsorption techniques, as in non-catalyst metal applications. Metal oxide catalysts can also act as anti-bacterial[34]. The same is true of the role of several algae which have been widely examined as natural anti-bacterial[20, 21, 25]. This research aims to synthesize Cu doped ZnO to degrade humic acid in peat swamp water environments.

2. Experimental Section

2.1 Synthesis of Nano Cu-doped ZnO with Sol-Gel Method

2,743 grams of $Zn(CH_3COO)_2.2H_2O$ dissolved with 50 mL of isopropanol in 100 mL beaker, and covered with aluminum foil. Stir it using a magnetic stirrer for 40 minutes. Added $CH_3COO)2.H_2O$ as doping material, again covered with aluminum foil and stirred using a magnetic stirrer for 40 minutes. After that, MEA (Monoethanolamin) 1.4 mL and stirring was continued for 90 minutes resulting in soles. The soles were left for one night, after which they were put into a vaporizer cup, dried in an oven at 110 ℃ for 1 hour. The gel formed is put into the furnace, heated at a temperature of 500 °C for 2 hours. The formed product is stored in the desiccator, and crushed [12]. After that it was tested with XRD (X-ray diffraction) and DRS UV-Vis spectra (UV-Vis Diffuse Reflectance Spectrocopy).

2.2 Reactor Design

The making of the reactor begins by providing transparent glass with a thickness of 3 mm then cutting the glass in a square shape with 11 cm side for the bottom and top of the reactor, for the top of the reactor to be perforated with a diameter of 1 cm to place humic acid. In the part between the glass the cutting board is arranged in the shape of a bracelet that is crossed with rubber sil.

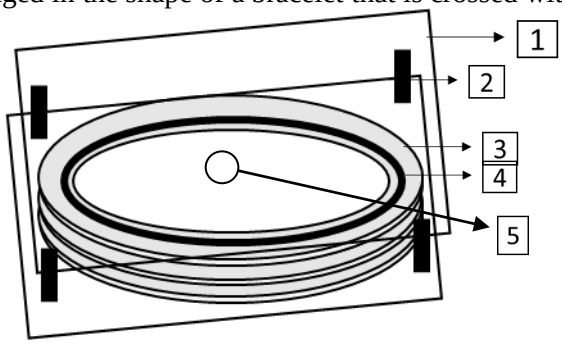

Figure 1. Static photoreactor. 1. Glass 3 mm; 2. Bolts; 3. Cutting board; 4. Rubber sil; 5. Reactor hole

2.3 Photocatalyst Activities for Humid 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 first stage of the process begins by taking 100 mL of 20 ppm humic acid solution into the reactor and then entering ZnO / Cu, the time variation used in the degradation process is 1 to 5 hours and using cu doping variations 3%, 5% and 7%, after the degradation process then measured the adsorption with a UV-Vis spectrophotometer and calculated the percent degradation (% D).

3. Results and Discussion

3.1. Synthesis of Nano Cu-doped ZnO with Sol-Gel Method

Nano ZnO/Cu produced is dark blue, the blue color produced comes from Cu which is distributed in ZnO. In the results of this synthesis, it can be observed that the greater the percent Cu in nano ZnO, the more concentrated the color of the product.

(a) (b) (c)

Figure 2. Nano ZnO doped Cu (a) 3% (b) 5% (c) 7%

After the product was produced, it was then crushed and produced powdered nano ZnO doped Cu, then characterized using XRD and DRS UV-Vis spectro. XRD testing obtained nano size ZnO doped Cu 7% is 27 nm. Nanomaterial is a material that has a scale in the nano meter scale which ranges from 1nm-100nm [13], this will optimize the work of the catalyst because it is in nano-size that can enlarge the surface area of the catalyst in contact with the sample [14]. Testing of the DRS UV-Vis spectroscope to determine the material bandgap number, bandgap ZnO doped Cu 7% is 2.57 eV.

3.2. Photocatalytic Reactors

Reactor, which is made up of a stastic reactor, is a reactor without a rotary device. In this study, the photocatalytic process was carried out outdoors with the help of direct sunlight and sunlight fluxes measured which entered into a reactor from the upper and lower sides of the reactor with a Light Sensor tool. Humic acid is inserted in the reactor through a hole above the reactor, then the hole is closed with glass so that the sample does not evaporate outside the reactor.

3.3. Photocatalyst Activity for Humic Acid Degradation

Absorbance measurements can be carried out by UV-Vis spectrophotometry. On the method, first determined the maximum wavelength of humic acid 20 ppm. Determination of the maximum wavelength can be seen in figure 3 which is at 265 nm.

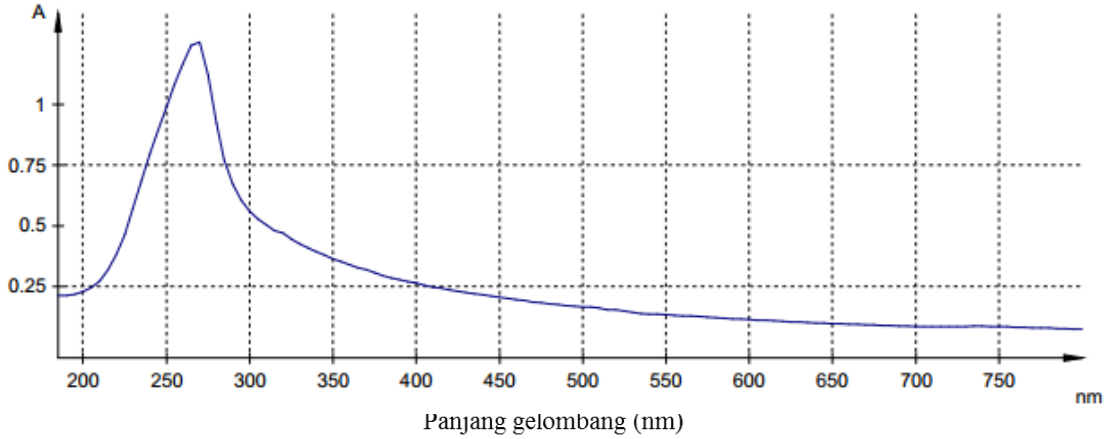

Figure 3. Humic acid 20 ppm spectrum

The process of degradation of humic acid with nano ZnO doped Cu, time variation which is 1 hour- 5 hours. The test results showed a decrease in the concentration of humic acid, according to the following figure 4.

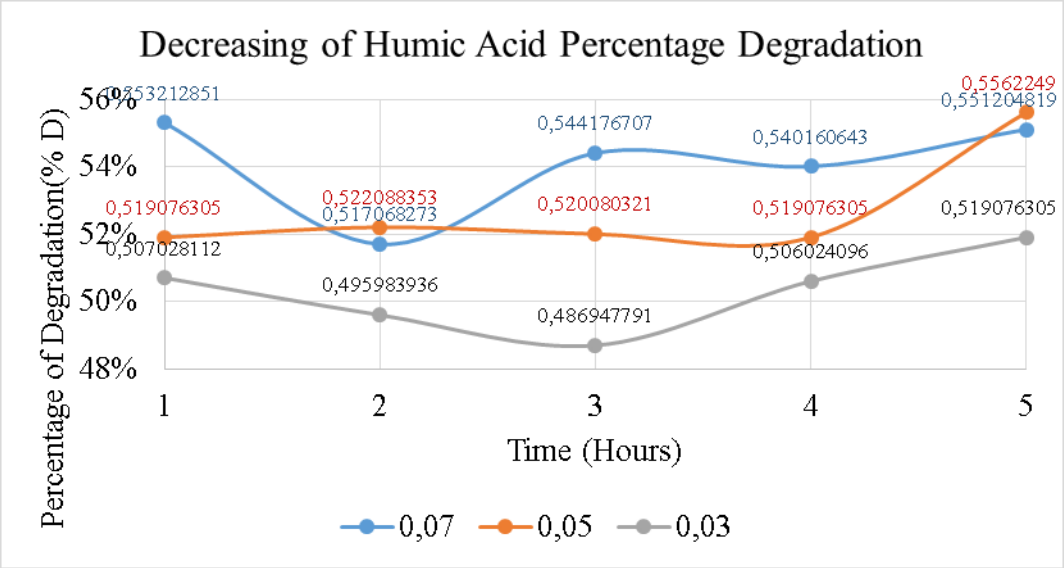

Figure 4. Percentage of decreasing in humic acid

In Figure 4, we can see the optimal time of degradation of humic acid with nano ZnO doped Cu 7% is at 3 hours. Degradation of humic acid is influenced by several factors, degradation time, sunlight, catalyst surface area and catalyst characteristics [15].

The decrease in average humic acid by using nano ZnO doped 3% Cu is 50.30%, nano ZnO doped 5% Cu is 52.73% and nano ZnO doped 7% Cu is 54.12%. This proves the effect of Cu composting on nano ZnO, the greater the composting, the band gap will decrease, causing easy excitation of electrons from the valence band to the conduction band.

Radiation with sunlight causes interactions with photocatalysts to form radicals • OH, •OH radicals interact with organic matter in the degradation process. When a photocatalyst is subjected to energy, the photon will experience electron excitation to form electrons and holes. The conduction band electrons in the catalyst react with O_2 to form superoxide radical anions. The anion reacts with water molecules which are adsorbed to produce hydroxide ions. While valence band holes on the surface of the catalyst react with water and can also react with hydroxide ions (OH-) to form radicals • OH which is a strong oxidizing agent. This OH radical will degrade organic matter [16, 17]. Hydroxy radicals are active so they play a role in oxidizing target organic compounds and converting them to simpler compounds such as carbon dioxide and water [18].

The degradation of organic matter is also influenced by the time of direct sunlight, the longer the degradation time the more photons are absorbed by the photocatalyst, the more • OH radicals that form on the photocatalyst surface and the interaction between the photocatalyst and organic matter will increase effectiveness of photodegradation of organic matter [16]. However, at a longer irradiation time in this study there was no increase in the effectiveness of humic acid photodegradation caused by reduced sunlight causing radicals • OH formed less and also because the active side of the catalyst had a recombinant reaction that caused acid molecules humic will queue for contact with the active side of the catalyst.

4. Conclusion

Based on the results of the research that has been done, it can be concluded that the maximum degradation of humic acid using nano ZnO doped Cu 7% which is characterized by XRD to determine its size is 27 nm, and uses the DRS UV-Vis Spectroscope to determine the bandgap number which is 2.57 eV . The maximum degradation of humic acid is using nano ZnO doped Cu 7% which is equal to 54.12%. Factors that affect the degradation process are degradation time, sunlight, catalyst surface area and catalyst properties.

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