Semiconductor-Based Photocatalysts Degradation of Methyl Orange Using CuO-Fe$_2$O$_3$ Nanocomposites

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Abstract - Indonesia is a country rich in natural resources. One of the resources is natural material including minerals and the metals such as iron ore, copper, silica, bauxite, tin, nickel, etc. However, Indonesia only has been using the raw materials for exportation. The low utilization of hematite (Fe$_2$O$_3$) in iron ore and tenorite (CuO) in copper motivated the researcher to improve the use value of the two materials. The effort made by the researcher was developing hematite (Fe$_2$O$_3$) and tenorite (CuO) into a semiconductor nanocomposite photocatalyst CuO-Fe$_2$O$_3$ that had the degradation ability of methyl orange.

It was an experimental research. The research was the development of nanocomposite photocatalyst materials of CuO-Fe$_2$O$_3$. These materials were used for observe degradation ability of methyl orange under the sunlight. Then, the thin layer formed from it was characterized by using UV-Vis.

The result from this research showed that the long solar radiation duration of the materials affected the degradation ability of Methyl Orange. The percentage of degradation also increased when they were heated up from 2 hours (0.2377%) to 4 hours (2.2043%) and continuously increased when 6 hours radiated (5.1866%). The longer the sample was radiated, the higher the percentage was. The optimal Methyl Orange degradation ability was obtained when it was radiated for 6 hours (5.1866%).

Keywords - Nanocomposite, Photocatalyst, Percentage of Degradation, Methyl Orange.

I. INTRODUCTION

As one of rich areas in natural resources, Indonesia possesses various natural materials such as iron ore, copper, silica, bauxite, tin, nickel and others. These materials have been only used until its raw level for export. The low utilization of hematite (Fe$_2$O$_3$) in iron ore and tenorite (CuO) in copper encouraged the researcher to increase the use value of both materials. Hematite can be found in natural materials such as iron ore. It is one of excessive minerals that can be easily found in nature. About 5% of the earth crust is formed by the ore [1]. The ore is classified into several types of iron oxide. They are hematite (α-Fe$_2$O$_3$), maghemite (γ-Fe$_2$O$_3$), magnetite (Fe$_3$O$_4$), goethite (FeOOH), limonite (FeOOH$_n$H$_2$O) and siderite (FeCO$_3$) [2]. The ore that has been through calcination process up to the temperature of 800°C has become hematite in all phases [3]. Since Indonesia has been only using the raw material, it does not get optimal benefit.

In fact, hematite is a type of iron oxide that is very beneficial to society or industry. Hematite is a major component for photoelectrochemical solar cells [4], acetone gas sensors [5], as a catalyst in oil production [6], pigments in industries such as the dye industry in paint, ceramic, glass, textile, plastics and coatings [7].

Not only hematite can be found in natural materials, but tenorite (CuO) can also be found in natural materials. Tenorite can be found in copper material. In Tembaga Nagari Pinti Kayu Kec. Koto Parik Gadang Diately Sokol Selatan District, West Sumatra, all of its phases are tenorite (CuO) when they are calcinated at a temperature of 1000°C [8]. Tenorite particle size is 67.85 nm at 20 hours milling time [9]. CuO is applied as a catalyst, sensor, supercapacitor, lithium ion battery, adsorbent, self-cleaning, anti-corrosion, etc. [10].

The low utilization of hematite (Fe2O3) derived from iron ore and tenorite (CuO) from copper raises the desire of...
researchers to increase the use value of these two materials. Efforts carried out by the researchers were developing hematite (Fe2O3) and tenorite (CuO) into CuO-Fe2O3 nanocomposite. The incorporation of Fe2O3 and CuO into a composite, is due to the catalytic activity of Fe2O3 / CuO better than CuO and Fe2O3 only [11]. The efforts of the researchers were to develop hematite (Fe2O3) and tenorite (CuO) into a CuO-Fe2O3 nanocomposite photocatalyst semiconductor which has the ability to degrade methyl orange.

II. REVIEW OF RELATED LITERATURE

1. Iron Ore

Iron ore is one of the abundant types of minerals found in nature. About 5% of the earth’s crust is composed of iron ore [1]. The presence of iron ore in nature can be in the form of rocks, very hard corals, small grains and can be loose soil with a variety of colors from black to red [12]. Available color differences in iron ore depend on iron oxide and iron ore constituent compounds. The most dominant constituent of iron ore is iron (Fe) in addition to other constituent elements such as Mn, Si and Al [13]. Iron oxide found in iron ore can be magnetite (Fe3O4), hematite (α-Fe2O3), maghemite (hem-Fe2O3), [14], wustit (FeO) [15], goethite (FeOOH), limonite (FeOOH₃·nH₂O), and siderite (FeCO3) [2].

Hematite (α-Fe2O3) is one of the iron oxides found in iron ore. Hematite (α-Fe2O3) is a stable iron oxide in ambient conditions at a price that is cheap, non-toxic, and environmentally friendly [16]. Hematite is an n-type semiconductor that has a 2.2 eV band gap [17]. Hexagonal granular shape, round stone appearance. In general, the shape is massive, the mass contains granules, the surface is colorful, the color of the mineral rocks is brownish red [18], the hematite has a reddish color after it is isolated [16]. Synthesis of nanoparticles using a top down method such as the HEM method. This HEM method has been used by Putri to obtain nano-sized hematites. The optimal time needed to make hematite into nanoparticles is at 5 hours milling time [18].

2. Copper

Copper ore is a mineral that can be found in nature. In the realm of existence this is not in the form of elements but in the form of compounds. The oxide content in copper is in the form of tenorite (CuO) [19], chalcocite (Cu2S), bornite (Cu5FeS4), chalcopyrite (CuS), enargite (Cu3AsS4). The main minerals are malachite (Cu2 (CO3) (OH) 2) and Azurit (Cu3 (OH2) (CO3) 2) copper oxide [20]. Phases found in copper ore can be deposition changes in calcination temperature [21].

Tenorite is one of the phases found in copper ore. Tenorite is a misnomer of copper oxide. Tenorite can be found in nature in copper material. Tenorite is a member of copper oxide prepared by Cu and O. Tenorite has a monoclinic crystal system with cell dimensions a = 4.6853 Å, b = 3.4257Å and c = 5.1303 Å, (a = 90 Å, b = 99 Å, c = 90 groups the space is C2 / c [8] Tenorite has a density of 6.5 g cm-3. CuO is a p-type semiconductor with a band gap of about 1.2 eV [16]. Tenorite grain size is finer or in the form of nanoparticles with a variation of 10 hours milling time, 20 hours, 30 hours and 40 hours. The optimum tenorite grain size at milling time of 20 hours is 30.27 nm. The grain size obtained is relevant to the particle size of the SEM results at 20 hours ie 67.85 nm [9].

3. Photocatalyst

Photocatalyst is a catalyst that works with the help of light (photons). Photocatalysts are defined as chemical transformation processes in the presence of catalysts and the aid of light [22]. In this process light acts as a trigger and catalyst as an accelerator of the chemical transformation process. In photocatalysts, the catalyst must have the ability to absorb photon energy. The absorption of the catalyst utilized in the photocatalyst process is owned by semiconductor materials. Some semiconductor materials are reported to have photocatalyst capabilities such as TiO2, CuO, ZnO and Fe2O3 [23].

The use of semiconductor material as a catalyst in the photocatalyst process has several benefits. As reported the advantages of using photocatalyst semiconductors include being able to carry out total mineralization of organic pollutants, the cheap cost, the relatively fast process, non-toxic and has the ability to use long-term [24]. The use of semiconductors is able to degrade a number of pollutants [25].

In semiconductor materials there are terms of conduction bands and valence bands. The conduction band and valence band have an important role in the semiconductor photocatalyst process. The distance between the conduction band and the valence band is called a bandgap. The energy band gap is the energy needed by an electron to be excited from the valence band to the conduction band. Good semiconductor band gap energy is in the range of 1 eV [25]. If the band gap of a compound or element increases the photocatalyst effect decreases and the electrons will be more difficult to be excited. The difficulty of electrons to be excited is due to the greater energy needed to excite the electron [22].

A semiconductor can undergo a photo-excitatatory process when it absorbs energy that is suitable or greater than the band gap energy. When the excitation process takes place an electron transfer occurs from the valence band to the conduction band. A positive hole will be formed in the valence band left by the electron. So that in the photokation process electrons are generated in the conduction band and hole in the valence band. The electron-hole pair will mostly recombine; others will survive to the surface of the semiconductor and experience a redox reaction to the molecules adsorbed on the photocatalyst surface. Hole can initiate oxidation reactions and electrons will initiate chemical reduction reactions around the semiconductor surface, has been displayed in Picture 1.
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In the picture, a hole in the valence band interacts with nucleophilic molecules, forming radicals (oxidation processes). While electrons in the conduction band when interacting with molecules that are electrophilic produce radicals (the reduction process). If this process continues it is called the photocatalytic process. The oxidation reaction will take place when excited electrons diffuse onto the surface of the catalyst. Specifically, (h +) can react with the surface H$_2$O or OH- to produce hydroxyl radicals (* OH) and reduction occurs when (e-) reacts with oxygen (O$_2$) to produce superoxide radical anions (* O$_2$-). The hydroxyl radical has strong oxidizing properties and has a large redox potential of 2.8 V. The potential possessed by hydroxyl radicals is strong enough to oxidize most organic substances. The total degradation of organic pollutants will produce CO$_2$ (carbon dioxide), H$_2$O (water), and mineral acids [25].

Semiconductor photocatalytic activity is influenced by several factors. The factors determining the photocatalyst activity are surface morphology, surface area, crystalline phase, crystallinity [26] and crystal size especially on the nanoscale [27]. Not only dry sample impurities can be degraded by semiconductor particles, but the degradation process of pollutants (impurities) on aqueous media can also be degraded by semiconductor particles. The process of degradation of orange methyl is shown in picture 2.

In picture 2 the mechanism of methyl orange degradation ability is shown. At first the electrons in the conduction band react to oxygen then form OH radicals as well as the holes react with H$_2$O also forming OH radics. The resulting OH radicals cut the bonds of Methyl Orange (C$_{14}$H$_{14}$N$_3$NaO$_3$S) to (NaO$_3$C$_6$SH$_6$N and C$_{8}$H$_{10}$N$_2$O$_2$). OH radicals break the bonds (NaO$_3$C$_6$SH$_6$N and C$_{8}$H$_{10}$N$_2$O$_2$) to Aliphatic acid. OH radicals break Aliphatic acid bonds into CO$_2$ and H$_2$O.

Semiconductor materials generally have the ability as photocatalyst materials. In a single semiconductor state the photocatalyst activity is rather slow, due to the recombination of electron pairs and fast holes. Many approaches can be taken to improve photocatalyst activities such as the selection of the synthesis method, semiconductor composites, and coupling [29]. The photocatalyst activity of semiconductor material is increasing when the material is combined as a semiconductor composite. In general, the mechanism of photocatalytic degradation through semiconductor-based nanocomposite can be shown in Picture 3.

In Figure 3 when a semiconductor photocatalyst is subjected to its light energy equal to or greater than the semiconductor bandgap, an electron-hole pair is formed due to the absorption of the energy of the photon (hv). Composite CuO / Fe$_2$O$_3$ has Eg (2.05 eV) [31], if the composite of CuO / Fe$_2$O$_3$ is subjected to light with such energy, there will be electron displacement which will later function in degrading impurities.

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Determining the ability of CuO-Fe$_2$O$_3$ nanocomposite to degrade impurities was carried out by placing CuO-Fe$_2$O$_3$ nanocomposite in the impurities solution of Methyl orange. The results of the percentage of MO degradation by CuO-Fe$_2$O$_3$ nanocomposite catalyst are shown in table 1.
At first the electrons in the conduction band react with oxygen then form OH radicals as well as the holes react with H2O, forming OH radicals [28]. The OH radicals cut the bonds of Methyl Orange (C14H14N3NaO3S) to (NaO3C6SH6N and C8H10N2O2). OH radicals break the bonds (NaO3C6SH6N and C8H10N2O2) to Aliphatic acid. OH radicals break Aliphatic acid bonds into CO2 and H2O. The longer the irradiation, the longer the contact time between photons and catalysts, the more electrons and holes are generated as a result [32]. The more electrons and holes that are regenerated, the more pollutants (MO) that can be degraded.

VI. CONCLUSION

The duration of solar radiation on nanocomposites CuO-Fe2O3 affected the dirt degradation (Methyl Orange). The optimum percentage of the degradation (Methyl Orange) was obtained when the nanocomposites were solar radiated for 6 hours (5.1866%).

REFERENCES


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[21] Ratmawan, Ahmad Fauzi, and Sukma Hayati AE. 2017. Effect of calcination temperature on phase transformation and crystallite size of copperoxide (CuO) powders. Citation: AIP Conference Proceedings 1868, 06009 (2017); View online: https://doi.org/10.1063/1.4995173 View Table of Contents: http://aip.scitation.org/toc/apc/1868/1 Published by the American Institute of Physics


