Degradation of methyl orange by photo assisted fenton reaction using Indonesian bauxite as catalyst

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Abstract. Photo fenton catalyst is an effective and environmentally friendly catalyst for degrade organic pollutants. Novel photo fenton catalyst was successfully prepared from Indonesia bauxite was used as a catalyst for degradation of methyl orange solution. This catalyst is more cheaper than Nafion-based catalyst and more greener than other synthesized catalysts. It is easily prepared from Indonesian natural resources. X-ray diffraction measurements provide structure and mineral composition of bauxite, while XRF provides information on the composition of Fe by 18% by weight of bauxite mass. The presence of large amounts of Fe in bauxite acts as a catalyst in the decomposition of methyl orange. Testing of photo fenton activity to decompose methyl orange showed that Indonesian bauxite had high catalytic activity, was able to decompose 99.4% methyl orange within 40 minutes on irradiation using a 9Watt UVC radiation source.

1. Introduction
The declines of environmental quality due to the increase of pollutants entering the environment outside its capacity causes deteriorating environmental conditions. The poorness of a water reservoir, such as the sea, rivers, lakes, ponds, and land caused by human activities is called water pollution. All major pollutants are sourced from chemical residues which are disposed of into the environment. Six indicators that environmental water has been polluted, namely: (1) The change in water temperature; (2) changes in pH or hydrogen ion concentration; (3) changes in colour, smell and taste of water; (4) The existence of micro-organisms; (5) The generation of deposits, colloidal, and dissolved materials; and (6) Increased radioactivity of environmental water. This can result in a decrease in the number of COD (Chemical Oxidation Demand), so that the equilibrium of the aquatic ecosystem will be disrupted [1].

Several attempts have been made, some of which are using homogeneous catalysts and conventional methods [2]. The method using homogeneous catalysts is considered ineffective because the operational costs are relatively expensive and incomplete steps to protect & regenerate these catalysts, such as the deposition process and recovery of iron catalysts. The waste model used in this study is methylene orange, because this waste is easily obtained and has a negative impact on the biotic component when interactions occur. Although it is considered not as a toxic dye, but methylene orange can also cause symptoms of side effects in the human body, such as vomiting, shock, cyanosis, necrosis, and increase heart rate to cause death [3].
The conventional method is also not able to completely eliminate high levels of toxic organic pollutants, because of the limited testing equipment and some non-biodegradable components. In the last decade, various methods emerged using redox techniques as an alternative to conventional methods and homogeneous catalysts which were considered to have many weaknesses [4]. The method that is considered the most promising and environmentally friendly in dealing with the problem of liquid waste is the Advanced Oxidation Process. Using a simpler technique, metal oxides can be included in a variety of solid supports, such as bauxite from Tanjung Pinang which has an 18% weight Fe$_2$O$_3$ content that needs to be utilized as an advanced catalyst. The use of heterogeneous catalysts is very effective because it is able to mineralize organic waste to be harmless, together with the easy separation of catalyst from treated wastewater and does not produce secondary metal ion pollution. Specifically, the reaction involved in the AOP system is the fenton reaction [5]. The involvement of polar and nonpolar particles increases sorption of reactant on the surface of the catalyst which can be degraded to carbon dioxide and water.

2. Methods
In a 250 mL volumetric flask methylene orange powder is dissolved using deionized water and the concentration is 0.0002 M. Into another 250 mL volumetric diluent 30% hydrogen peroxide using deionized water also to obtain a concentration of 0.02 M, and into an inserted container 1 gram of zeolite synthesized. Then mix the whole gradually into the reactor and homogenize it for 5 minutes using a magnetic stirrer at 500 rpm, then also adjust the best pH (pH 3) by adding concentrated hydrochloric acid reagent drops. After 5 minutes, the 9-watt UV-C lamp dipped before touching the stirrer rod. Photocatalytic tests were carried out for 120 minutes and absorbance measurements were carried out at intervals of 10 minutes from the 10th minute to the 120th minute.

3. Results and discussion
Bauxite is a multi-component ore with more than 100 different mineral forms that can be identified, depending on where the ore originates. The main components of aluminum present in bauxite in the form of hydrated oxide: hydragilite (gibbsite; Al$_2$O$_3$.3H$_2$O), boehmite and diaspore(Al$_2$O$_3$.H$_2$O). Hydragilite (gibbsite) Al$_2$O$_3$.3H$_2$O is crystallized in a monoclinic system with limited hexagonal ion dislocation. The base cell consists of 8 aluminum (III) ions and 24 hydroxyl ions, which form 8 molecules Al(OH)$_3$. Gibbsite has a complex structure. It consists of an alumohidroxyl layer constructed from a double layer of hydroxyl groups, including a distributed aluminum (III) ion field. The hydroxyl alumo layer is interrelated by hydrogen bonds [6].

![Figure 1. Photomicrograph SEM-EDX of Bauxite from Tanjung pinang magnification and its composition.](image-url)
surface using FTIR, shows the existence of organic molecules on the bauxite surface. This is indicated by the typical absorption of aliphatic compounds at 1400 cm\(^{-1}\) and 2800 cm\(^{-1}\) in figure 2. This fact provides information that bauxite originating from Tanjung Pinang has another functional group other than metal oxide; organic compound.

**Figure 2.** FTIR of bauxite from Tanjung Pinang.

**Table 1.** Chemical composition of bauxite obtained from XRF.

| Components | Mass percentage |
|------------|-----------------|
| SiO\(_2\)   | 19.45           |
| Al\(_2\)O\(_3\) | 42.67           |
| K\(_2\)O     | 0.30            |
| FeO\(_2\)   | 18.52           |
| TiO\(_2\)   | 1.03            |

**Figure 3.** XRD powder diffractogram of bauxite from Tanjung pinang.

The results of XRD analysis for mineralogical composition of bauxite from Tanjung pinang inform that silica minerals are exist in bauxite. The most common are hydrated kaolinite aluminosilicate Al\(_2\)Si\(_2\)O\(_5\)(OH)\(_4\) and quartz (SiO\(_2\)), as observed in the analysis of chemical composition in table 1 and X-ray diffraction in Figure 3. Bauxite also contains TiO\(_2\) rutile and anatase mineralogy modifications, whose content varies between 1 and 3%. Iron is found in bauxite in the form of different minerals, the most common of which are hematite water oxide, Fe\(_2\)O\(_3\), and goethite oxide, (HFeO\(_2\)), which is very different in color, crystal structure, and behavior during processing. Magnetite and limonite are found in smaller amounts.
3.1. Degradation of methyl orange by bauxite

The effect of the time on photo fenton reaction of orange methyl is given in Figure 4. Bauxite is able to degrade methyl orange from the first minute of interaction and shows high performance. Within ten minutes, the concentration of orange methyl was degraded by more than 95%. And in forty-minute methyl orange degraded 99.4%. Meanwhile, if not given a UV lamp, the ability to remove orange methyl is only about 60%, this is a contribution of the decomposition of dyes by H2O2 and adsorption performance of bauxite itself.

![Figure 4](image)

**Figure 4.** Bauxite photo fenton performance to degrade methyl orange aqueous solutions.

The high ability to degrade orange methyl due to the release of Fe to the solvent which then acts as a catalyst in the reaction of photofenton. The longer the photo fenton reaction, more of Fe released as seen at Figure 5. This is due to the location of Fe metal oxides is on the bauxite surface and is only physically absorbed, so that the Fe ion is easily released into solution environment at a relatively low pH reaction, which is pH 3. The highest fenton photo activity for immobilized Fe in bentonite also showed the highest activity at pH 3 as reported by Gao et al. [7].

![Figure 5](image)

**Figure 5.** Fe Contents in solution after photo fenton reaction of methyl orange and bauxite as catalyst.

3.2. Kinetics of methyl orange degradation by bauxite as photo fenton catalyst

To determine the kinetics model of the degradation of orange methyle reaction with bauxite as a catalyst for photo fenton, it was done using the order 1, order 2 and pseudo-order 2 equation models. The first order kinetics model as shown in Figure 6 gives the value $r^2$ of 0.4636, while for the second order kinetics gives the value $r^2$ of 0.8936, and for pseudo order 2 gives the value $r^2$ equal to 1. According to this correlation coefficient, it can be concluded that the kinetics model is selected for degradation of orange methyle is pseudo order 2. This model suggests that the greater the concentration of the dye, the value of the speed constant will be proportional to the increase in the concentration of the dyes. This kind of reaction kinetics was also found for the decomposition of dye by bearing iron on zeolite done by McDonald et al. [8].
Figure 6. Kinetics curve of photo fenton reaction of methyl orange and bauxite as catalyst.

4. Conclusion
Bauxite from Tanjung pinang shows the composition of gibbsite, quarsa and kaolinite minerals with high hematite levels. Hematite minerals in bauxite is a source of Fe which can be used as a catalyst for photo fenton reaction. Bauxite from tanjung pinang shows high performance to degrade methyl orange with pseudo order 2 reaction kinetics.

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