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The Influence of Cu(II) on Methyl Orange and Methylene Blue Photodegradation Catalyzed by TiO_2 – Chitosan Nanocomposites

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Abstract**—**The influence of Cu(II) on the catalytic photodegradation of methyl orange (MO-cationic dye) dan methylene blue (MB-anionic dye) using TiO_2 – chitosan nanocomposite had been studied. The photodegradation process was carried out using a batch system in a closed reactor equipped with a UV lamp. The experimental results show that the presence of Cu(II) ion was able to increase the photodegradation of MO and MB, from 41% to 81% for MO, and from 30% to 64% for MB. The mechanism by which Cu(II) ion increase the photodegradation of MO and MB was by capturing the electrons released by the photocatalyst, thus preventing the recombination of electron and holes. The decrease in recombination of electrons and holes will then increase the number of OH radicals needed for the initiation of the reaction, thus resulting in the increase of the photodegradation.

Keywords**—**Photodegradation, Methyl Orange, Methylene Blue, Methyl orange, TiO_2 – chitosan Nanocomposite

I. INTRODUCTION

ENVIRONMENTAL pollutions have become a serious problem due to the danger it poses to human lives. One of the important sources of pollution is industrial activities, such as textile and dye industries. About 15% of total dyes from textile industries all over the world was estimated to pollute water bodies during coloring or dyeing processes. There are almost 400 tons dyes are released to the environment, both as solubles and precipitates [1,2]. This waste is difficult to treat due to the use of more persistent dyes that are more difficult to degrade naturally [3].

Methyl orange (MO) and Methylene blue (MB) are two of the dyes that have been widely used. MO is an azo (-N=N-) group compound with a diethylamine group in one of the aromatic rings. When ionized in water, a negatively charged chromophore is produced, so that MO is also known as an anionic dye, or acidic dye. MB however, is a tiazine dye, with a chromophore attached to the positively charged sulphonic group (usually as an amine salt or ionized imine), so that it also known as cationic dye, or basic dye [4]. The molecular structure of MO and MB can be seen in Figure 1.

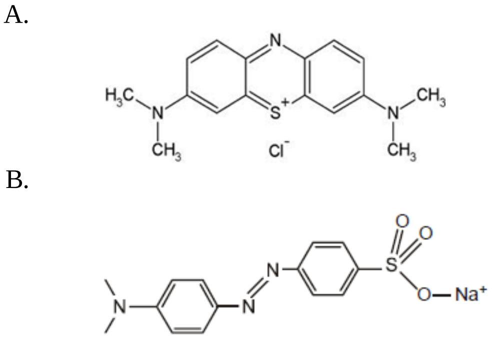

Fig. 1 The structure of (A) Methylene Blue and (B) Methyl orange

Cu(II) is one of the heavy metals which is toxic to both human and animals. The presence of Cu(II) in water bodies is increasing due to its more widespread use for textile industries, metallurgy and electroplating [5]. Cu(II) in liquid waste comes primarily from dyeing process in textile industries using the blue coloured $CuSO_4.5H_2O$. When released, the Cu(II) containing waste was then able to go into water system and mixed with organic waste [6]. Therefore, the likelihood for Cu(II) ions to co-exist with organic dyes such as MO and MB in the water system is very high. When this happens, the water system will become toxic and very dangerous not only to human, but also plants and other living things.

One of the techniques for handling dye liquid waste is the degradation techniques using TiO_2 as photocatalyst. Titanium dioxide (TiO_2) is one of semiconductor materials with a band gap energy (Eg) as high as 2-3 eV. When irradiated with sufficient energy associated to the band gap energy, electron transfer may occur. The ability for electron transfer in TiO_2 makes it possible to be used as a trigger to initiate reduction and oxidation reactions to a substrate. Such redox reaction can initiate photodegradation of organic compounds, including dye molecules, and convert them into simple compounds such as CO_2, H_2O and other mineral acids [7], as well as reduce heavy metal ions and change them into less toxic metal ions [8].

The degradation reaction of organic compounds catalyzed by TiO_2 can be generally described as follow [9]:

$$TiO_2 + h\nu \rightarrow TiO_2\ (e^- + h^+) \qquad (1)$$

h or hole will react with water molecule to form hydroxyl

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radicals.

$$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+ \quad (2)$$

Hydroxyl radical is a very strong non-selective oxidizing agent ($E0 = +3.06$ V) capable of initiating chain reactions of organic compounds and convert them into smaller and simpler compounds. The reaction of TiO_2 with the organic compounds can be generally written as follow [10]:

$$C_cH_hO_o+[(h-2_o)/4 + n]\ O_2 \rightarrow TiO_2, h\nu \rightarrow cCO_2 + h/2H_2O \quad (3)$$

Some of the electron and holes pairs (e^- dan h^+) will recombine, either on the surface or in the bulk particles by releasing thermal energy. The recombination will then reduce the photodegradation level by decreasing of the number of holes. Thus, to prevent the recombination of electrons and holes, an electron capturing agent may be added to the system.

The use of powdered TiO_2 could reduce the effectiveness as well efficiency of the photocatalytic activity, since once dispersed, the powdered TiO_2 is difficult to recover [10]. In addition, the dispersed powder may increase the turbidity of the solution, making it difficult for the UV radiation to activate the dispersed photocatalyst particles. Therefore, new methods need to be developed for the synthesis and development of the TiO_2 photocatalyst. One of the methods used is by *in-situ* synthesis of TiO_2 in a host material made of polymer with typical reology structure such as chitosan, which can also interact with the photocatalyst to form nanocomposite [11].

This study was conducted to determine the photodegradation activity of MO and MB – catalyzed by chitosan in the presence of Cu(II) ions. The influence of Cu(II) ions needs to be studied as it might coexist with dyes in the water system. Cu(II) ion is also capable of capturing electrons and therefore can act as an oxidizing agent. This will in turn affect the recombination process between electrons and holes. The influence of Cu(II) was studied by comparing the the photodegradation of MO and MB catalyzed by TiO_2 – chitosan nanocomposite with and without the presence of Cu(II) ions.

II. PROCEDURE

A. Materials and Apparatus

TiO_2 bulk photocatalyst and TiO_2 – chitosan nanocomposite photocatalyst have been prepared using a methods discribed previous research [11]. Metil Orange ($C_{14}H_{14}O_3N_3SNa$) and Methylene Blue ($C_{16}H_{18}ClN_3S.2H_2O$) purchased from Merck. Aqua Bidestilata and deionized Water was taken from Pharmaceutical Laboratories Jakarta. All chemicals were of reagent grade and were used without further treatment.

All reactions were conducted with stirring using magnetic stirrer (Cimarec Barnstead Thermolyne) at 600 rpm and centrifugation was carried out using Boeco C-28 Centrifuge (Model BOE 1205-13, Boeckel & Co, Hamburg, Germany). The reaction simulation was carried out using a closed photoreactor equipped with UV lamp with magnetic stirring plate, black light blue (BLB) (40 watt, 220 Volt), with wavelength ranging between 290 – 390 nm.

B. Methods

Photodegradation process of dyes were carried out in a closed photoreactor equipped with a 40 watt UV lamp having λ in the range of 290 – 390 nm, as illistrated by figure 2. A mixture solution containing 20 mL of MO 20 ppm or MB 5 ppm, 20 mg TiO_2 – chitosan nanocomposite and 2 mL of Cu(II) ions in various concetrations: 1,0; 2,0; 4,0; 6,0; 8,0 dan 10,0 ppm, with UV light accompanied by magnetic srirring for 5 h for MO treatment and for 6 h for MB treatment. The solution was obtained by centrifuge with 5000 rpm for 5 min for phase separation and the dyes concentration of the supernatant was analyzed using Spectronic 20D. All measurements were made at the wavelengths corresponding to maximum absorption (MO at 464 nm and MB at 664 nm). As a reference, no added of Cu(II) ions in the dyes solution for photocatalytic process using the same condition. By subtracting the initial and undegradated concetrations of the dyes solution, the degree of dyes photodegradation could be calculated

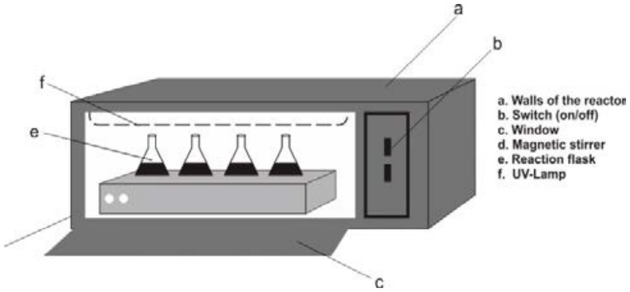

Fig. 2 Photoreactor equipped with a 40 Watt UV lamp and a series of magnetic stirrers [12]

III. RESULT AND DISCUSSION

A. The Activity of TiO_2 – Chitosan Nanocomposite as Photocatalyst

The activity of TiO_2 – chitosan as a photocatalyst was studied by comparing the photodegradation of MO and MB dyes in systems with TiO_2 bulk photocatalyst and TiO_2 – chitosan nanocomposite. The experimental results is shown in Figure 3, and it can be seen that the photodegradation percentage for the two dyes in the system with TiO_2 – chitosan nanocomposite photocatalyst is higher than that of TiO2 bulk.

The higher photodegradation of the dyes in the system catalyzed by TiO_2 – chitosan nanocomposite might be caused by the smaller size of TiO_2 particles in the chitosan matrices as compared to that of the TiO_2 bulk [11]. The smaller size of TiO_2 particles will increase the band gap energy (Eg). The higher the Eg, the more effective the photodegradation. Hence, the use of TiO_2 – chitosan nanocomposite as a photocatalyst will be able to increase the degree of photodegradation of both MO and MB.

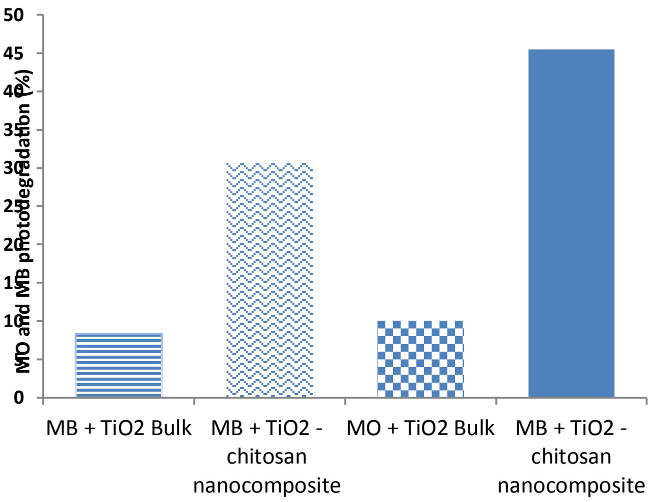

Fig. 3 The influence of the addition of 0.02 g TiO_2 bulk and 0.02 g TiO_2 – chitosan nanocomposite on the photodegradation of MO and MB

The higher photodegradation of the dyes in the system catalyzed by TiO_2 – chitosan nanocomposite might be caused by the smaller size of TiO_2 particles in the chitosan matrices as compared to that of the TiO_2 bulk [11]. The smaller size of TiO_2 particles will increase the band gap energy (Eg). The higher the Eg, the more effective the photodegradation. Hence, the use of TiO_2 – chitosan nanocomposite as a photocatalyst will be able to increase the degree of photodegradation of both MO and MB.

Catalyzed photodegradation generally occurs via initiation reaction by hydroxyl radicals (${}^\bullet OH$). The source of the hydroxyl radicals is either the dissosiation of water molecules by light or photolysis, or the oxidation of holes in the photocatalyst by water molecules or organic molecules. The holes h^+ originating from bands with higher Eg is more effective in reacting with substrate molecules to produce OH radicals [13]. OH radicals will then initiate the degradation reaction of organic compounds, or in this case the dye molecules, as depicted by the following reaction equations [14]:

$$H_2O + h\nu \rightarrow H^+ + {}^\bullet OH + e^- \quad (4)$$

$$TiO_2/\ Ti + h\nu \rightarrow TiO_2/\ Ti + e^- + h^+ \quad (5)$$

$$h^+ + OH^- \rightarrow {}^\bullet OH \quad (6)$$

the reactive OH radical will attack the dye molecules to produce smaller organic compounds and mineral acid.

$$R + {}^\bullet OH \rightarrow R^{\bullet`} + H_2O \quad (7)$$

The reaction was followed by photocatalytic degradation of the dye molecule

$${}^\bullet OH + \text{dye} \rightarrow \text{products*}$$

$$TiO_2/\ Ti + h^+ + \text{dye} \rightarrow TiO_2/\ Ti + \text{products*} \quad (8)$$

Product*: CO_2, H_2O, mineral acid and non toxic inorganic compounds.

Fig. 3 shows that the photodegradation percentage of MO is higher than MB. The difference is partly caused by the charge difference in MO and MB, with MB having a negative charge and MB having positive charge. The ionic charge will influence the affinity and the adsorption of the dye molecules by the photocatalyst. This is because in a heterogeneous catalytic reaction, photocatalysis is always preceded by the adsorption of the substrate molecules on the surface of the catalyst so that effective contact with the electrons may occur [9].

Hypothetically, the Ti species will interact with the chitosan matrices through either a Lewis acid-base interaction [15] or hydrogen bonding [16,17]. Such interaction will cause the Ti in the chitosan matrices to have a positive charge or neutral [14,18], allowing the positively charge surface of the catalyst to have a higher affinity toward electrostatic interaction with anionic MO compared to cationic MB. This will in turn lead to a higher level of photodegradation of MO.

B. The Influence of Cu(II) on The Photodegradation of MO and MB Catalyzed by TiO_2 – Chitosan Nanocomposite

To study the influence of Cu(II) ion on the photodegradation of MO and MB dyes, experiments were carried out using different Cu(II) concentration (2.0, 4.0, 6.0, 8.0, and 10.0 ppm). The experimental results can be seen in Figure 5.

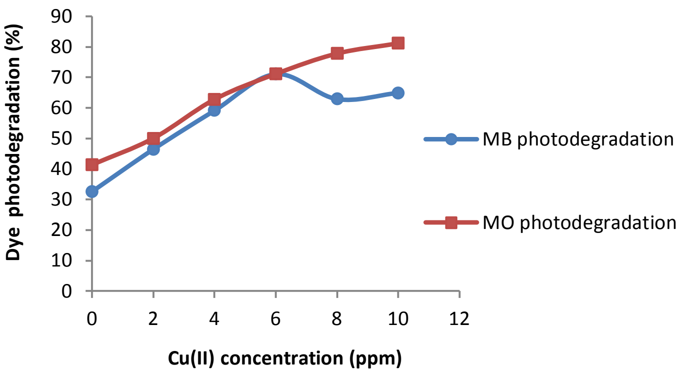

Fig. 4 The influence of different concentrations of Cu(II) on the degradation of MO 20 ppm and MB 5 ppm.

From Fig. 4, it can be seen that in the presence of Cu(II) in the solution, catalytic photodegradation of MO and MB dyes using TiO_2 – chitosan increased from 41% to 81% for MO and from 30% to 64% for MB. This increase is in line with the increase of Cu(II) concentration in the solution, which suggest that the presence of Cu(II) in water system together with dye compounds will be able to increase the degradation of the dyes.

Basically, photodegradation of dye molecules can be increased as long as the recombination between electrons and holes is prevented, leaving more holes available in the system to react to produce hydroxyl radicals. The recombination can be prevented by adding a species capable of capturing the electrons released by TiO_2. Any species having a standard reduction potential (E_o) more positive than the standard reduction potential (E_0) of conduction band (E_o = +0,30) should be able to capture the electron or be reduced [8].

Cu(II) has an E_0 value which is more positive than the E_0 value of the conduction band. With $E_o = +0,34$, Cu(II) can capture electron via the following reduction reaction [12]:

$$H_2O + h\nu \rightarrow H^+ + {}^\bullet OH + e^- \qquad (9)$$

$$Cu^{2+} + 2e^- \rightarrow Cu^0 \qquad (10)$$

The above mechanism is responsible for the prevention of electrons and holes in the photocatalyst leading to more OH radicals being produced. Thus, the presence of Cu(II) was able to increase the photodegradation reaction of dye molecules catalyzed by TiO_2 – chitosan nanocomposite.

The increase of dye degradation is in proportion to the increase of Cu(II) concentration in the solution. The higher the concentration of Cu(II), the more electrons can be captured, which means more holes will be able to react to produce OH radicals, and eventually increase the photodegradation of the dye molecules.

IV. CONCLUSION

The use of TiO_2 – chitosan nanocomposite as photocatalyst had been examined, and experimental results indicate that the photodegradation of dye molecules catalyzed by the nanocomposite shows higher activity than that of TiO_2 bulk photocatalyst. As photocatalysis reactions are always preceded by the adsorption of the dye molecules on the surface of the catalyst, dye molecules which are easier to be adsorbed should be able to be degraded more. Due to the positive charge of the photocatalyst surface, the anionic MO was be able to be adsorbed easier than the cationic MB, and hence easier to be degraded.

The presence of Cu(II) in the solution was also able to increase the photodegradation percentage of both dyes due to the synergic effect of Cu(II) with the photocatalyst. The increase of the photodegradation percentage with the presence of Cu(II) for MO and MB is from 41% to 81% and from 30% to 64%, respectively.

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