

**THE INFLUENCE OF OXALIC AND MALONIC ACIDS ON
THE DEGREE OF Cu(II) PHOTOREDUCTION CATALYZED BY TiO₂
(Pengaruh Asam Oksalat dan Malonat terhadap Derajat Fotoreduksi ion Cu(II)
yang Terkatalisis oleh TiO₂)**

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Abstract

The influence of oxalic and malonic acids on the effectiveness of Cu(II) photoreduction catalyzed by TiO₂ has been studied. Photoreduction was carried out by a batch system in a closed reactor equipped by UV lamp. The results of the research show that the addition of TiO₂ photocatalyst can enhance Cu(II) photocatalytic reduction, which may be initiated and/or accompanied by adsorption of Cu(II) ion on the TiO₂ surface. The presence of both oxalic and malonic acids can improve of the Cu(II) photoreduction, and the improvement is observed as the acid concentrations increase. It is also found that the effect of malonic acid in gaining Cu(II) photoreduction is stronger than oxalic is, which are from around 20% into about 55% and that of into around 35%, respectively. The roles of the acids on the enhancement of the photoreduction are OH radical attachment and electron donation.

Keywords : Photoreduction, Cu(II), oxalic and malonic acids, TiO₂, photocatalyst

Abstrak

Dalam penelitian ini telah dipelajari pengaruh asam oksalat dan malonat terhadap hasil fotoreduksi ion Cu(II) yang terkatalisis oleh TiO₂. Proses fotoreduksi dilakukan secara batch dalam reaktor tertutup yang dilengkapi dengan lampu UV. Hasil penelitian menunjukkan bahwa penambahan fotokatalis TiO₂ telah meningkatkan hasil fotoreduksi ion Cu(II) yang cukup nyata, yang reaksinya diawali atau disertai dengan proses adsorpsi ion Cu(II) pada permukaan fotokatalis TiO₂. Adanya asam oksalat dan malonat telah memberikan peningkatan hasil fotoreduksi, yang sejalan dengan kenaikan konsentrasi kedua asam organik tersebut. Asam malonat menghasilkan peningkatan fotoreduksi yang lebih besar daripada asam oksalat, yaitu masing-masing dari sekitar 20% menjadi kira-kira 55% dan menjadi sekitar 35%. Peran kedua asam organik dalam peningkatan fotoreduksi adalah sebagai pengikat radikal OH dan penyedia electron yang mereduksi ion Cu(II).

Kata kunci : Fotoreduksi, Cu(II), asam oksalat, asam malonat, fotokatalis, TiO₂

INTRODUCTION

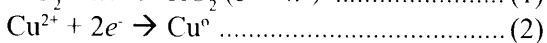
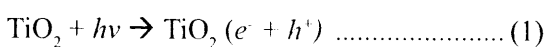
Copper (II) ion categorized as a hazardous heavy metal, is widely distributed in the environment originating from waste wa-

ter disposal of various industries. Due to its toxic properties that can destroy environment and human health, removal the metal ion from the waste water before their discharge is important.

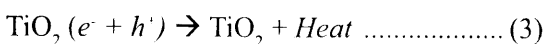
Removal of Cu(II) ions has been carried out by conventional adsorption using natural zeolite as adsorbent (Ouki and Kavannah, 1997). A new and promising method called as photoreductive catalysis for removing Cu(II) ion and other metal ions has been introduced (Chen and Ray, 2001; Yamanaki, *et al*, 2000; Wahyuni *et al*, 2007). Catalytic photoreductive is a reduction induced by UV light and accelerated by TiO₂ photocatalyst.

TiO₂ can be functioned as a photocatalyst due to its semiconductor structured, that is a structure characterized by electron filled valence band and empty conduction band, separated by a gap called as band gap energy as much as 2-3.5 eV. With such a structure, when a semiconductor is irradiated by UV or visible light, one electron in the valence band can be transferred into conduction band by leaving a hole or positive radical forming OH radical. The electron is widely used for reducing some metal ions, while the radical acts a strong oxidation agent (Hoffmann, *et al*, 1995).

The photoreduction of Cu(II) ions takes place by capturing electrons generated by TiO₂ in the aqueous suspension when it is irradiated with UV light. As mentioned previously, that the electron generation at the surface of TiO₂ photocatlyst is always accompanied by hole or positive radical formation. The photogeneration of electron and hole, and photoreduction of Cu(II) ion are written as reaction (1) and (2) respectively.



In addition to the photoreduction, the pair of electron and hole can recombine easily by liberating heat, that is written as reaction (3).

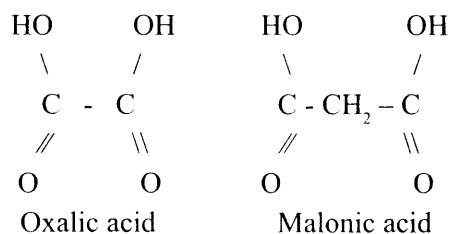


Such recombination leads to a decrease in the effectiveness of photoreduction that is expressed by low degree of photoreduction. The low degree of Cu(II) photoreduction has

also been found by Yamanaki, *et al*, (2000) and Wahyuni, *et al* (2007) from their research of Cu(II) photoreduction catalyzed by TiO₂. It is reasonable therefore, that for improving photoreduction, the pair recombination has to be prevented.

The prevention can be carried out by attaching OH radical with oxydizable substances such as organic acids. In addition, since in the environment, the heavy metal can be found along with organic acids including oxalic and malonic acids produced from biodegradation of organic garbage or materials, it is interesting to investigate the influence of the presence of organic acids on Cu(II) photoreduction.

In the present paper, the influence of the concentrations of oxalic and malonic acids on the degree of Cu(II) photoreduction catalyzed by TiO₂ as a suspension in the aqueous solution is evaluated. Oxalic acid is selected in this study to represent of organic acids widely found in the waters, while the selection of malonic acid is considered on the similarity of its structure as oxalic's. The molecular structure of oxalic and malonic acids are presented below:



EXPERIMENTAL

Materials and apparatus

TiO₂ powder, Cu(NO₃)₂·3H₂O, oxalic acid, malonic acid, HCl, and NaOH pellet produced by Merck, that are analytical grade and were used without further treatment. The apparatus used were a closed photoreactor equipped with UV lamp and magnetic stirring plate, as shown by figure 1, and a Perkin-Elmer AAS for Cu analysis.

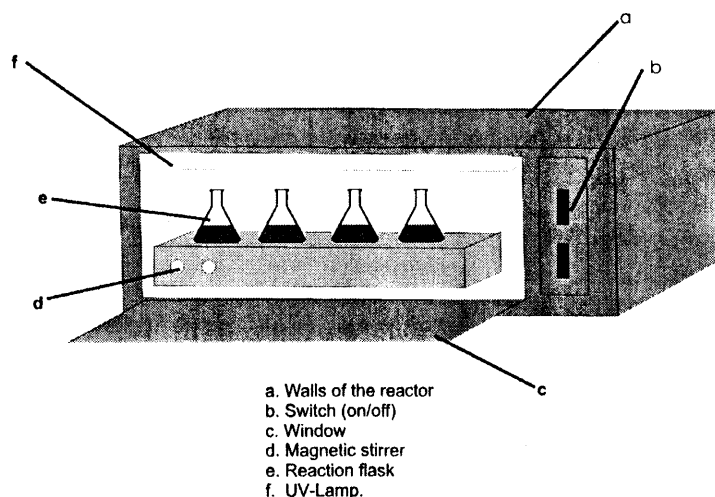


Figure 1. A self-designed photoreactor equipped with a 40 Watt UV lamp and magnetic stirring plate

Procedure :

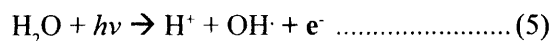
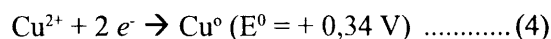
Photocatalytic reduction of Cu(II) solution was carried out in a closed reactor equipped with a 40 watt UV lamp having λ in the range of 290-390 nm, as illustrated by figure 1. Photocatalytic reduction was performed by following optimal condition obtained by Wahyuni, *et al* (2007), that was by irradiating 50 ml solution containing a mixture of Cu(II) ions 10 ppm at pH 3, 20 mg TiO₂ powder, and oxalic or malonic acids in various concentrations, with UV light accompanied by magnetic stirring for 24 h. The solution obtained by filtering the mixture was analyzed by AAS to determine the concentration of unreduced Cu(II) ions. By subtracting the initial and unreduced concentrations of the ions, the degree of Cu(II) photoreduction could be calculated.

RESULTS AND DISCUSSION

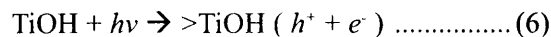
The influence of photocatalyst addition

The influence of the addition of TiO₂ photocatalyst on the degree of Cu(II) photoreduction is illustrated by figure 2. The figure shows that Cu(II) photoreduction is observed both in the absence and presence

of TiO₂, and the presence of TiO₂ gives higher degree of Cu(II) photoreduction. In the absence of photocatalyst, Cu(II) photoreduction is generated by capturing the electrons released via photolysis of water (Brezova, *et al*, 1998), as shown by reaction (4) and (5) :



The improvement of the degree of photoreduction in the presence of TiO₂ photocatalyst is resulted by more number of electrons which is provided both by water molecules and TiO₂ after being irradiated by UV light. The reaction of the electron released by TiO₂ is shown by reaction (6).



The electron generation in TiO₂ is more effective than that of by water photolysis. The stronger ability of TiO₂ in releasing electrons comes from its semiconductor electronic structure (Linzebigler *et al*, 1995; Hoffmann, *et al*, 1995).

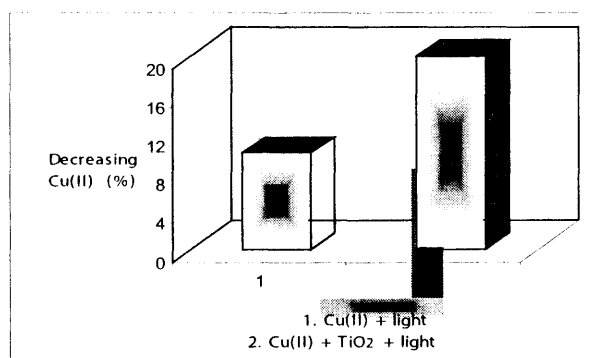


Figure 2. The influence of photocatalyst addition on the Cu(II) photoreduction

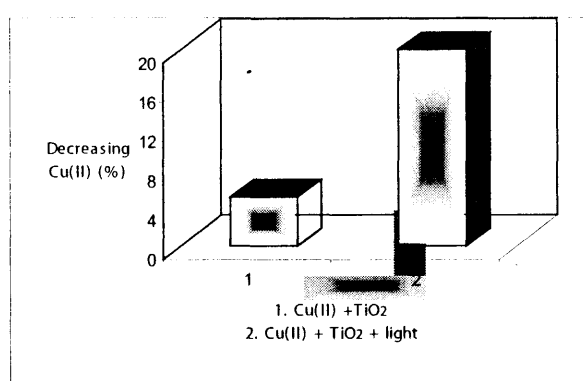


Figure 3. The influence of the UV light on the Cu(II) photoreduction

The influence of UV light

The decrease of Cu(II) concentration seen in figure 2, can be caused by adsorption of Cu(II) on TiO₂ surface alone, or photoreduction alone, or simultaneous adsorption and photoreduction. In order to confirm the processes involved in the decreasing Cu(II) concentration, the effect of UV light irradiation was observed and compared to the same reaction system taking place in the dark system. The result is presented as figure 3.

It is seen in the figure that, although in the dark system, a slight decrease in the concentration of Cu(II) is observed, due to the adsorption of Cu(II) ions on TiO₂ surface. Contrary, by irradiating with UV light, a high decrease of Cu(II) concentration is seen, indicating the involvement of photoreduction process. It is clear

therefore that both adsorption and photoreduction are involved. In the heterogeneous catalysis reaction, the adsorption of the substrate on the catalyst surface is required enabling them to contact with electrons effectively (Hoffmann, *et al*, 1995).

The influence of Oxalic and Malonic Acids

From data presented above, though the presence of TiO₂ photocatalyst can improve the degree of photoreduction, the effectiveness remains relatively low, that is about 20% from 10 ppm of the initial Cu(II) concentration. This may be caused by recombination of electron and hole pair, that can reduce the number of electrons available in the reaction system. In order to prevent such recombination, a hole capture agent, such as oxalic and malonic

acid have been added. The effect is shown by figure 4.

Figure 4 indicates that the presence of both malonic and oxalic acids can improve significantly the degree of Cu(II) photoreduction catalyzed by TiO_2 . Both malonic and oxalic acids can react with OH radicals *via* hydrogen atom at carboxylic group forming water that release from the structure, and leaves an unstable molecule radical. Such molecule radical is readily degraded into smaller molecules. The reaction with OH radical can prevent the electron and hole pair recombination, resulting in more effective photoreduction as represented by higher degree

of Cu(II) photoreduction. This is supported by enhancement of Cu(II) photoreduction when the concentrations of the organic acids are increased, as larger number of OH radicals are attached.

Furthermore, the effect of malonic acid on the enhancement of the photoreduction is stronger than that of oxalic acid. The stronger effect of malonic acid can be explained based on their structure regarding the affinity toward OH radicals. As presented above that hydrogen atom at carboxylic group can be easily attacked by OH radical (positive radical) forming water and release from the structure. In malonic acid structure, the two carboxylic groups are sepa

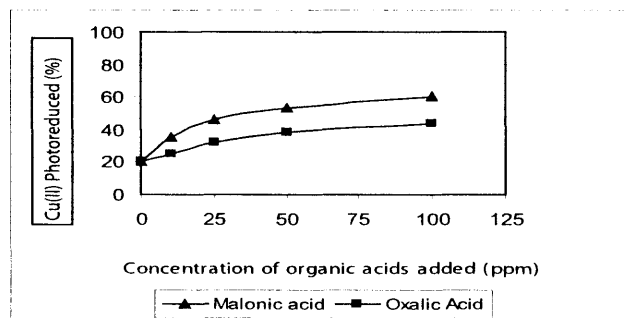


Figure 4. The influence of oxalic and malonic acids

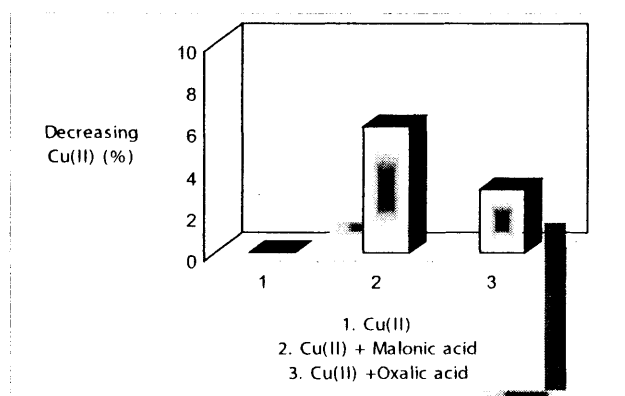


Figure 5. The role of the organic acids on the decreasing Cu(II) concentration

rated by methylene group (CH_2) enabling them to react with OH radical easily. As a result, the pair recombination can be prevented effectively giving higher degree of photoreduction.

Meanwhile, in oxalic acid, the two carboxylic groups are closer as they are not separated by methylene group (CH_2) generating a sterical hindrance. Such hindrance can decline the attacking of OH radical, and so the photoreduction. In addition, the results are in a good agreement with the value of rate reaction constant (k) of both acids with OH radicals, as reported by Stumm (1988). It was found that k of malonic acid-OH radical reaction is $2.4 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ while k of the reaction of oxalic acid-OH radical is $1.4 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$.

The role of the Organic acids

To further evaluate the role of both organic acids on the enhancement of Cu(II) photoreduction, the reactions of Cu(II) with malonic and oxalic acids were carried out separately in the dark condition and the results are seen as figure 5.

The figure indicates that, in the condition with no light and TiO_2 photocatalyst, the Cu(II) content in the solution with the presence of the organic acids is decreased. The most possible reason of decreasing Cu(II) concentration is due to conventional reduction. As known that carboxylic groups in the structure of both oxalic and malonic acids are electron rich, enabling them to donate their electrons, that can generate Cu(II) reduction. In addition, the same trend for oxalic and malonic acids effect are also observed, that is malonic acids shows stronger effect than oxalic acid does. Since the distance of the two carboxylic groups in malonic acid structure is farther, it is easier for the acid to release its electron, compared to malonic acid. It is clear therefore that the roles of the organic acids on the Cu(II) photoreduction are not only by attaching OH radicals, but also by donating their electrons that can reduce Cu(II) ions conventionally.

CONCLUSIONS

The addition of TiO_2 photocatalyst can increase Cu(II) photocatalytic reduction, that is initiated and/or accompanied by adsorption of Cu(II) ion on the TiO_2 surface.

The presence of both oxalic and malonic acids gives rise of Cu(II) photoreduction, and it is observed as the acid concentrations was increased.

Malonic acid shows stronger effect on the improvement of Cu(II) photoreduction than oxalic acid does, which are 20 % into 55% and into 35 % respectively

The roles of the acids on the enhancement of the photoreduction are by attaching OH radical as well as by donating electron.

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