

INFLUENCE OF CYANIDE ON REMOVAL OF COPPER ION FROM THE SOLUTION BY PHOTOCATALYTIC REDUCTION METHOD WITH TiO₂ SUSPENSION

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ABSTRACT

The removal of Cu(II) by photoreduction method using TiO₂ photocatalyst in the presence of CN⁻ is reported. Photoreduction was carried by batch technique using UV lamp with 290-350 nm of wavelength. The research results indicate that the present of CN⁻ ion gives different effects on the photoreduction effectiveness depends on the mole ratio of both ions. The addition of CN⁻ less than 2 moles for each mole of Cu (II) ion can improve the photoreduction, and the photoreduction sharply goes down into very low degree when the mole number of CN⁻ is increased up to 4, and by further enlarging the mole number into 6, the photoreduction degree remains constant. Furthermore, increasing solution pH generally leads to a decrease in the photoreduction. In the solution with pH 1, the maximal photoreduction degree is reached, while increasing pH from 1 to 9 has declined the photoreduction, and the photoreduction is totally inhibited at pH higher than 9. The effect of the solution pH is related with the speciation of Cu (II), CN⁻ and TiO₂ in the solution.

Keywords: Photoreduction, copper, cyanide, TiO₂ photocatalyst

INTRODUCTION

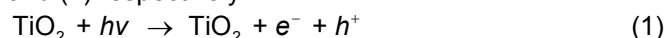
Copper (Cu (II)) ion can be distributed in the environment due to wastewater disposal from some industries including electroplating activities as well as paint, electric equipment, nylon and plastic factories. In such wastewater, the metal ion is frequently present along with cyanide (CN⁻) ion. Since both Cu(II) and CN⁻ ions are hazard for human and environment [1], removal of Cu (II) ion in the present of CN⁻ is urgently required.

Removal of Cu(II) ions has been already studied by conventional adsorption method by using zeolite [2]. Although such method is simple and effective, it can not detoxify the hazardous ion, except only transfer the ion from the solution into solid adsorbent. In addition, when the adsorbent is saturated with the ion metals, they become a solid waste that lead to a further environmental problem. Accordingly, a treatment method that can remove and detoxify Cu(II) ions is required. Such method may be satisfied by photocatalytic reduction.

Photocatalytic reduction is a reduction, or reaction with electrons, induced by photon or UV light and sensitized by photocatalyst such as TiO₂. This oxide 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 [3]. 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 radicals can act as strong oxidizing agent that has been widely tested for removing phenolic pollutant [4]. Meanwhile, the electron is widely used for reducing some metal ions, including Hg(II) [5-6] and Cr(VI) [7-8] as well as for Ag recovering from photography wastewater [9]. It was reported that hazardous Hg(II) and Cr(VI) could be successfully reduced into less or non toxic Hg(0) and Cr(III), respectively. Meanwhile, Ag(I) could be reduced into Ag(0) deposited on the photocatalyst surface, enabling it to be easily taken out as pure and valuable silver metal. Moreover, the study on photocatalytic reduction in the presence of TiO₂ for removing Cu(II) ion from its solution has also been reported [10].

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 photocatalyst 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).

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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 [10-11] from their research of Cu(II) photoreduction catalyzed by TiO₂. The prevention can be carried out by attaching OH radical with oxidizable substances such as organic acids. In the environment, Cu(II) ion is frequently along with oxalic and malonic acids that motivated Wahyuni, et al. [12] to study the influence of both organic acids on Cu(II) photoreduction. It has been concluded that oxalic and malonic acids can effectively prevent OH radical and electron recombination, as indicated by increasing the degree of Cu(II) photoreduction.

In addition with organic acids, Cu(II) in the environment can also be found together with cyanide, that can be oxidized into cyanato as well as react with Cu(II) to form [Cu(CN)₂]²⁻ complex. Such reactions are supposed to influence the photoreduction. In the present paper, the influence of cyanide with varying concentration and solution pH on the photoreduction of Cu(II) ion is reported.

EXPERIMENTAL SECTION

Materials

TiO₂ powder, Cu(NO₃)₂·3H₂O, NaCN, HCl, and NaOH pellet produced by E.Merck, with analytical grade were used without further treatment.

Instrumentation

The instruments used were a photoreduction reactor having dimension of 50x150x 50 cm³, installed with UV Lamp and magnetic stirring plate as illustrated by Fig 1, and Perkin-Elmer atomic absorption spectrophotometer for Cu(II) analysis.

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. The photoreduction was performed by following optimal condition obtained [11] previously. For that purpose, 50 mL solution containing 10 mg/L Cu(II) with alteration pH as designed, cyanide salt NaCN with various concentrations, and various masses of TiO₂, was irradiated for 24 h. The solution obtained by filtering the mixture was analyzed by Perkin-Elmer AAS to determine the concentration of unreduced Cu(II) ions. By subtracting the initial and unreduced concentrations of

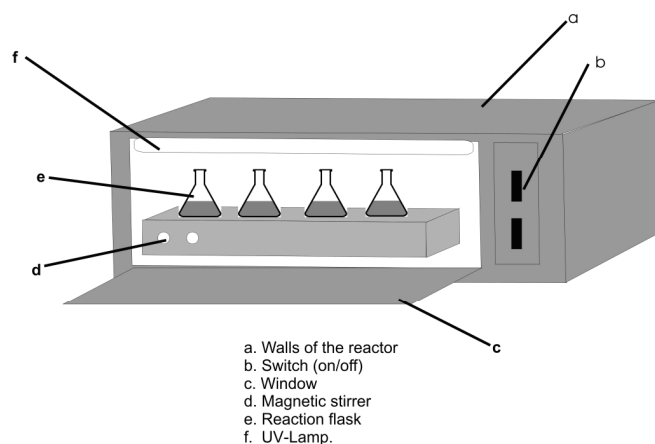


Fig 1. The compartment for photoreduction reaction that was designed by the authors

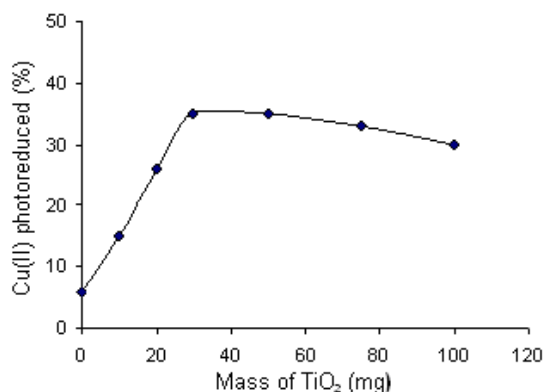


Fig 2. The influence of photocatalyst addition on the Cu(II) photoreduction

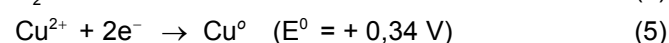
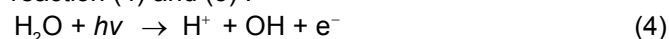
the ions, the degree of Cu(II) photoreduction could be calculated.

RESULT AND DISCUSSION

The influence of photocatalyst addition

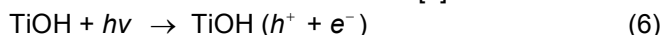
The influence of the addition of TiO₂ photocatalyst on the degree of Cu(II) photoreduction is illustrated by Fig 2. The figure shows that Cu(II) photoreduction is observed both in the absence and presence of TiO₂, and the presence of TiO₂ gives higher degree of Cu(II) photoreduction.

In the absence of photocatalyst, Cu(II) photoreduction is generated by capturing the electrons released via photolysis of water [13], as shown by reaction (4) and (5) :



The water photolysis is very slow leading to a less number of electrons. This explains the low degree of

Cu(II) photoreduction without photocatalyst. The improvement of the degree of photoreduction in the presence of TiO₂ photocatalyst is resulted by more number of electrons provided both by water molecules and TiO₂ when were irradiated by UV light, in which the electron generation in TiO₂ is more effective than that of by water photolysis. The reaction of the electron released by TiO₂ is seen as reaction (6). The stronger ability of TiO₂ in releasing electrons comes from its semiconductor electronic structure [3].



Furthermore, the increase of TiO₂ mass raises the degree of Cu(II) photoreduction, but the degree tends to decline when TiO₂ mass was further enlarged. The higher mass of TiO₂ can release more number of electrons resulting in more effective photoreduction. However, the presence of TiO₂ with very much amount can generate higher turbidity that would inhibit the entered light as source of photon. Consequently, only less number of electrons can be released leading to a decrease in the photoreduction.

The influence of the presence of cyanide

The influence of cyanide with various mole number on the degree of Cu(II) photoreduction with pH 7, has been evaluated, which is depicted as Fig 3. The figure indicates different effects of cyanide depending on the mole number. When 0.25–2 moles of cyanide were added in the solution containing 1 mole Cu(II) with pH 7, in which cyanide was found as HCN and CN⁻ ion, the photoreduction raises. Since the mole number of CN⁻ is lesser than 4, the complex formation of {Cu(CN)₄}²⁻ is not occurred leaving free CN⁻ and Cu²⁺ ions in the solution. This condition enables Cu²⁺ ions to be photoreduced easily.

In addition, CN⁻ is also possible to be oxidized by positive radical *h*⁺ and OH radical provided by TiO₂ photocatalyst to form cyanato [15] as seen in reaction 7 and 8.



The attachment of both *h*⁺ and OH radical acting as strong oxidizing agent can prevent the recombination of *h*⁺ and OH radical with electron in the photoreduction system, resulting an increase in the photoreduction. As a result, the increase of the mole number of CN⁻ can further raise the photoreduction.

Furthermore, the photoreduction sharply goes down into very low degree when the mole number of CN⁻ is increased up to 4, and further enlargement of the mole number into 6 gives no different effect in the photoreduction degree. This is caused by unreduced {Cu(CN)₄}²⁻ complex formation, which may be formed

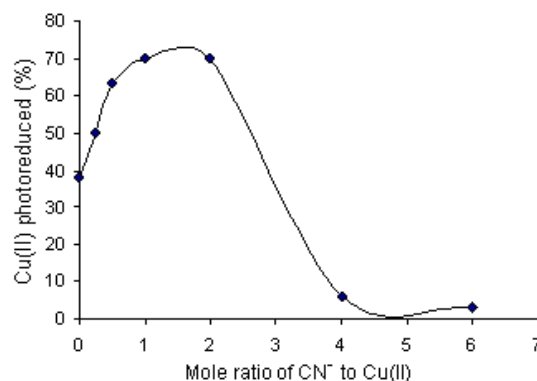


Fig 3. The influence of mole ratio of cyanide to Cu(II) on the degree of photoreduction

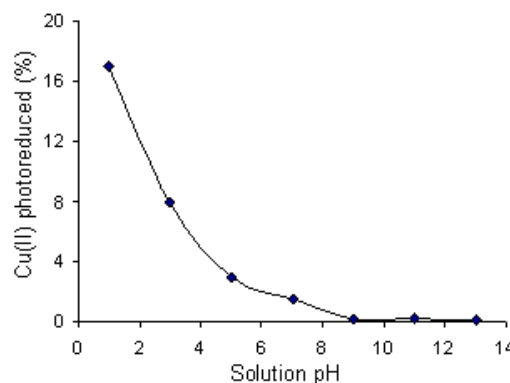


Fig 4. The influence of solution pH the degree of Cu(II) photoreduction

maximally as the mole of CN⁻ is present in exes. With such ratio, it is supposed that photoreduction is quitted, but low degree of the photoreduction is still observed. The low photoreduction of Cu(II) is taken place, because not all of the cyanide forms as CN⁻ ion, but some is found as HCN. Consequently, not all of Cu²⁺ reacts with CN⁻ to form complex compound, leaving small part of Cu²⁺ in the solution that can be photoreduced.

The influence of solution pH

The degree of Cu(II) photoreduction in the presence of cyanide with mole of Cu/CN is 1:4 at various solution pH is presented in Fig 4. It is seen in the figure a decline in the photodegradation when the solution pH was increased. At pH 1, the highest degree of photoreduction, though it is only low, is reached. At such pH, all of Cu(II) is found as reducible Cu²⁺, and all of cyanide form HCN preventing Cu(CN)₄²⁻ complex formation, that can induce the effective photoreduction.

However, because most of TiO₂ exist as TiOH₂⁺ as well as adsorb HCN, inhibiting them in releasing

electrons, the only low degree of photoreduction is obtained.

The next, a sharp decline in the photoreduction is seen when the pH was increased from 1 to 5. In such condition, the number of reducible Cu^{2+} is getting lesser due to the formation of CuOH^+ that is more difficult to be reduced, whereas all cyanide is found as HCN that can prevent the recombination, and most of TiO_2 is still found as TiOH^+ releasing only few electrons. It is clear that increasing number of CuOH^+ and the small number of electrons are the causes of a sharp decline in the photoreduction.

The increase of pH from 5-9 can suppress the photoreduction. In the range pH 5-9, Cu^{2+} and CuOH^+ disappear from the solution instead by $\text{Cu}(\text{OH})_2$ precipitation, meanwhile all of TiO_2 exists as TiOH that can provide more number of electrons, and cyanide is found as HCN and CN^- with same fraction. The presence of CN^- can dissolve the precipitate to form unreducible complex $\text{Cu}(\text{CN})_4^{2-}$, while HCN can be adsorbed by TiOH that inhibits the releasing electron. Accordingly, the photoreduction becomes much less effective.

The photoreduction is totally inhibited at pH higher than 9. In the solution with such high pH, all cyanide exists as CN^- resulting in maximal number of unreducible $\text{Cu}(\text{CN})_4^{2-}$ and all of TiO_2 is deprotonated into TiO^- leading to a very few electron available. This condition explains the inhibition of the photoreduction.

CONCLUSION

It is concluded that the present of CN^- ion gives different effect on the photoreduction effectiveness, depending on the mole ratio of both ions. The low mole number of CN^- can enhance $\text{Cu}(\text{II})$ photoreduction, and the photoreduction sharply drops into very low degree when the mole number of CN^- is increased. Furthermore, increasing solution pH generally leads to a decrease in the photoreduction. The effect of the solution pH is related with the speciation of $\text{Cu}(\text{II})$, CN^- and TiO_2 in the solution. It is recommended that for removing $\text{Cu}(\text{II})$ in the presence of cyanide effectively, the photoreduction should be carried out at low to moderate pH.

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