

THE INFLUENCES OF Fe(III) ION and Fe(OH)₃ COLLOID ON THE PHOTODEGRADATION of *p*-CHLOROPHENOL CATALYZED BY TiO₂

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ABSTRACT

The influences of ionic Fe(III) and colloidal Fe(OH)₃ on the effectiveness of *p*-chlorophenol photodegradation catalyzed by TiO₂ has been studied. Photodegradation was carried out in a batch system by irradiating a suspension of TiO₂, *p*-chlorophenol, and Fe(III) as ionic or colloidal forms, using UV lamp for a period of time accompanied by magnetic stirring. Concentration of photodegraded *p*-chlorophenol was calculated by subtracting the initial concentration with that of undegraded *p*-chlorophenol. Concentration of undegraded *p*-chlorophenol was determined by gas chromatography. In this study, TiO₂ mass and the photodegradation time were optimized. The influences of concentration of Fe(III) solution, mass of Fe(OH)₃, and pH of the solution have also been systematically studied. The research results showed that the presence of Fe(III) ions improved the effectiveness of photocatalytical degradation of *p*-chlorophenol, which was proportional to the concentrations of Fe(III) ion. In contrast, the increasing mass of Fe(OH)₃ led to a decrease in the degree of *p*-chlorophenol photodegradation. Furthermore, it was observed that increasing pH of the solution resulted in a decrease in the photodegradation of *p*-chlorophenol. This phenomena may be due to the different species of TiO₂ available at the surface of photocatalyst and of ionic Fe(III) and colloidal Fe(OH)₃ in the solution resulted from the pH alteration. The highest photodegradation degree, ca. 80 % was obtained when 20 mg of TiO₂ was applied in the photodegradation of 50 mL of 100 ppm *p*-chlorophenol solution in the presence of 100 ppm Fe³⁺ irradiated by UV-light for 25 hours.

Keywords: *p*-chlorophenol photodegradation, TiO₂, Fe(III) species

INTRODUCTION

p-Chlorophenol is one of persistent hazardous pollutants which may be delivered by several industrial and hospital wastewaters into the environment. This organic pollutant possesses high toxic potentials and carcinogenic at low concentration level. Due to its toxicity, several removal methods have been developed including adsorption [1,2], biodegradation [3,4], and photocatalysis degradation [5-7]. The mentioned methods have both advantages and disadvantages. Among the methods, photocatalysis degradation using TiO₂ semiconductor has received much attention due to its effectiveness for *p*-chlorophenol removal [8-11].

In the environment, *p*-chlorophenol can be found along with metal ions such as iron (Fe) and Fe(OH)₃ colloid which are resulted from electroplating, painting and other industrial wastewater. It has been reported [12] that the presence of Fe(III) ions can significantly improve the effectiveness of the photodegradation of *p*-chlorophenol catalyzed by TiO₂. However, the effect of colloidal Fe(OH)₃ on the photocatalysis degradation of *p*-chlorophenol, so far, has not been explored yet. The aims of the present study is to evaluate the influence of ionic Fe(III) and colloidal Fe(OH)₃ on the photodegradation of *p*-chlorophenol catalyzed by TiO₂.

EXPERIMENTAL SECTION

Materials

p-Chlorophenol, Fe(NO₃)₃, Degusa Type of TiO₂, HCl and NH₄OH in analytical grade were purchased from E.Merck. Distilled water for solution preparation and any dilution was made by Laboratory of Analytical Chemistry, Chemistry Department, Gadjah Mada University. Other solvents were reagent grade and used as received.

Photocatalysis process

Photocatalysis degradation of *p*-chlorophenol was conducted in batch system in a close reactor equipped with UV lamp, as shown by Figure 1. This reaction was carried out by irradiating a solution containing a mixture of *p*-chlorophenol, ionic Fe(III) or colloidal Fe(OH)₃, and TiO₂ powder, using UV light accompanied by magnetical stirring for a certain period of time. In principle, the volume of reaction mixture was 100 ml containing various concentrations of ionic Fe(III) or various mass of colloidal Fe(OH)₃, 100ppm *p*-chlorophenol and various mass of TiO₂. The concentration of undegraded *p*-chlorophenol was determined by Gas Chromatography.

The degree of *p*-chlorophenol photodegradation was calculated by the difference between the initial and

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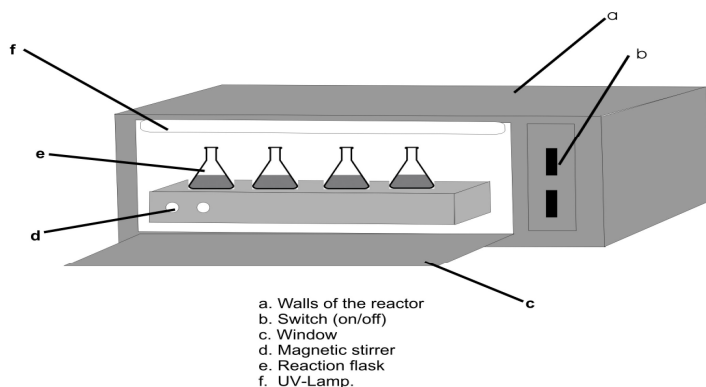


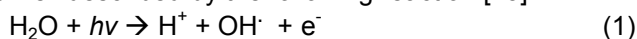
Fig 1. Photocatalysis reactor

the residual concentrations. Hence, in this study, TiO_2 mass and the photodegradation time were optimized and the influences of concentration of Fe(III) solution, mass of Fe(OH)_3 , and pH of the reaction solution was also systematically studied.

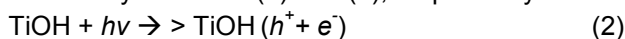
RESULT AND DISCUSSION

The effect of the presence of TiO_2 photocatalyst

The effect of the TiO_2 photocatalyst addition on the photodegradation of p-chlorophenol is shown in Fig 2. From Fig 2, it is clearly observed that without addition of TiO_2 p-chlorophenol was able to be degraded by light/photon but the portion of degraded p-chlorophenol reaches only around 20 % relative to initial concentration. Interestingly, as can be seen from Fig 2, the degree of photodegradation can be improved significantly by the addition of TiO_2 semiconductor due to the photo-catalytical effect. Photodegradation of p-chlorophenol could occur in the UV-irradiated solution because of the production of OH radicals from water molecules as the solution is irradiated. This mechanism is well described by the following reaction [13]:



In the suspension reaction, TiO_2 photocatalyst normally exists in the form of TiOH and it would produce OH radicals when the species is irradiated with UV light, as presented by reactions (2) and (3), respectively.



Therefore, two sources of OH radical generation are available in the solution when the solution is irradiated by UV-light, i.e.: water molecules and TiO_2 photocatalyst. As a result, a larger number of OH radicals can be obtained in the solution during UV-irradiation, resulting in the higher effectiveness for the photodegradation of p-chlorophenol in the presence of TiO_2 catalyst.

The influence of the mass of TiO_2 photocatalyst

It has been demonstrated in the previous section that the presence of TiO_2 photocatalyst in the reaction

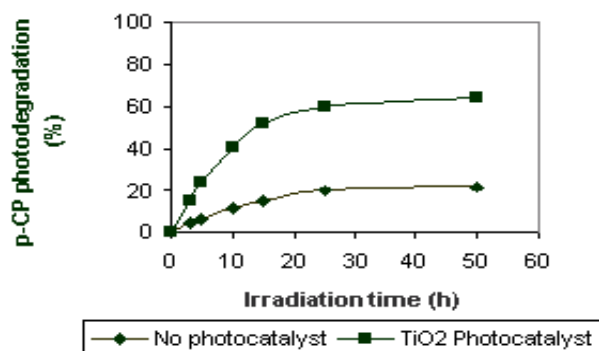


Fig 2. The effect of TiO_2 photocatalyst on the photodegradation of p-chlorophenol

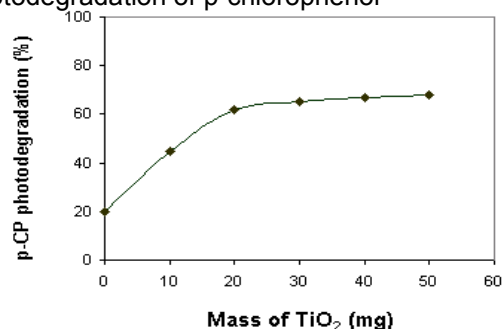


Fig 3. The influence of TiO_2 mass on the photodegradation

mixture enhances photodegradation of p-chlorophenol by providing OH radicals. In order to optimize the photodegradation process, the influence of TiO_2 mass on the photodegradation process has also been evaluated and the results are presented in Fig 3.

Fig 3 shows that improvement of the effectiveness of the photodegradation is observed when the mass of TiO_2 is increased up to 20 mg, but further increase in the mass of photocatalyst gives no significant effect on the photodegradation effectiveness. The increasing amount of TiO_2 in the solution provides much more OH radical supplies, resulting in the higher effectiveness of photodegradation. However, at higher mass of TiO_2 , the turbidity of the solution also increases. This gives rise to the reduction in UV-light absorption by substrate and/or photocatalyst, resulting in the decrease in OH radical production and thus also decreases the photodegradation effectiveness.

The influence of Fe(III) concentration in the solution

The effect of Fe(III) concentration in the solution on the photodegradation effectiveness of p-chlorophenol is presented in Fig 4. It is clearly shown that the effectiveness of the photodegradation increases with the increasing concentration of Fe(III) ion in the solution. This tendency may be explained with respect to the ability of Fe(III) ions to form

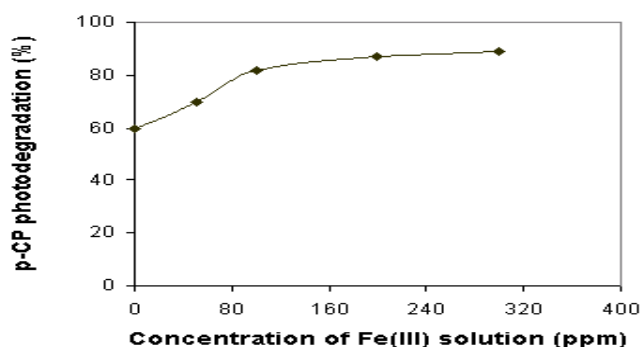


Fig 4. The influence of Fe(III) concentration in the solution on the effectiveness of p-chlorophenol photodegradation

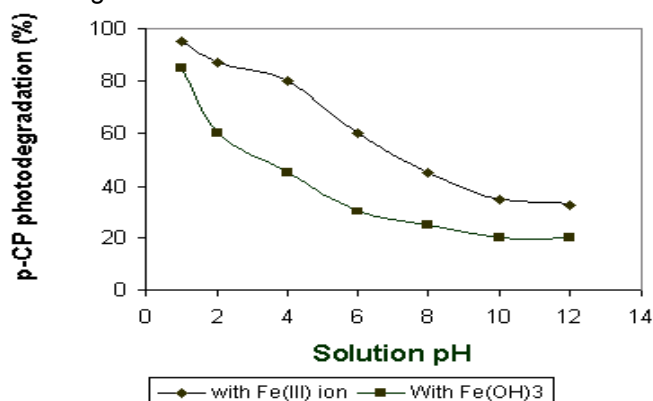
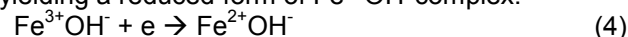


Fig 6. The influence of solution pH on the photodegradation

$\text{Fe}^{3+}\text{OH}^-$ complex in the solution which in turn will release OH radicals in to the solution as the species absorbs the light of suitable energy when it is irradiated [14]. Moreover, $\text{Fe}^{3+}\text{OH}^-$ complex is also able to capture photogenerated electrons (represented by Equation 4), yielding a reduced form of $\text{Fe}^{2+}\text{OH}^-$ complex.



This capturing electron can prevent the recombination process of OH radicals with free electron, e.g.: $\text{OH}^\cdot + e^-$ [15], leading to the enhancement of the effectiveness of the photodegradation. Such ability of Fe(III) ions to do so is termed as a sensitizing effect [15]. Increasing the concentration of Fe(III) ions in the solution gives rise to the increase in sensitizing effect and therefore enhancing the photodegradation process.

The influence of the mass of $\text{Fe}(\text{OH})_3$ colloid

Fig 5 exhibits the influence of the mass of $\text{Fe}(\text{OH})_3$ colloid on the photodegradation of p-chlorophenol. The figure shows a decrease in the p-chlorophenol photodegradation when $\text{Fe}(\text{OH})_3$ colloid was present, and the photodegradation further reduced as the increasing mass of $\text{Fe}(\text{OH})_3$ colloid. It is implied that sensitizing effect was not shown by $\text{Fe}(\text{OH})_3$ colloid or event the colloid may hindrance or block the entering light into the solution. The higher mass of $\text{Fe}(\text{OH})_3$ colloid led to an increase in the light blocking due to higher turbidity.

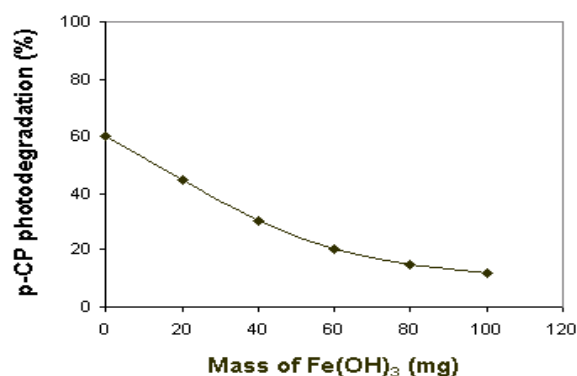
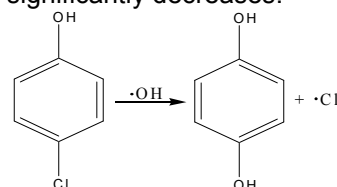


Fig 5. The influence of the mass of $\text{Fe}(\text{OH})_3$ colloid on the photodegradation

The influence of solution pH on the photodegradation

The influence of solution pH on the photodegradation of p-chlorophenol in the presence of Fe^{3+} ions together with that in the presence of $\text{Fe}(\text{OH})_3$ colloid is presented in Fig 6. Both curves exhibits the same trend and the most effective photodegradation was obtained at pH 1. Increasing the pH the solution results in the decrease in the photodegradation. This phenomena is readily understood from the viewpoint of the speciation of p-chlorophenol, TiO_2 surface, as well as ionic Fe(III).

During the course of the photodegradation, when p-chlorophenol is attacked by OH radical, Cl substituent in p-chlorophenol is replaced by OH radical to yield hydroquinone radical and which subsequently degraded into more simple species and Cl^- ion. This leaving group of Cl^- then easily combines with H^+ ions to form HCl [13], as described by Equation (5). This is the reason why at low pH (higher concentration of H^+) the effectiveness of the photodegradation is enhanced. In contrast when the pH of the solution is increased (lower concentration of H^+ ions), as would be expected, the effectiveness of the photodegradation of p-chlorophenol significantly decreases.



It is important to note that at a very low pH of the solution, a mixture of $>\text{TiOH}_2^+$ and $>\text{TiOH}$ were formed at the surface of photocatalyst in which the portion of the former species is dominant as compared to the latter one [15]. Since $>\text{TiOH}_2^+$ species is less effective in providing OH^\cdot ion, consequently there is fewer radicals available in the solution. Nevertheless, at low pH (ca.1.0) OH radical is a strong oxidizing agent [10]. Therefore, although the number of OH radicals available in the solution is fewer, its effectiveness in initiating degradation is not significantly affected. On

the other hand, in the pH range of 2-8, TiOH^+ at the surface of photocatalyst which easily release OH radical would be the major species. In this range of pH, the large number of photogenerated charge carriers, such as OH radical could be generated, but their ability as oxidizing agent is much lower. This brings about to the decrease in the photodegradation. At pH higher than 8, TiO^- is the predominant species at the surface of photocatalyst. This species is considered to be difficult to release OH radical and electron into the solution thus producing only a small number of the charge carriers, as a result, much lower photodegradation is obtained. From this results, it is obvious that the speciation of TiO_2 resulted from pH alteration determine the effectiveness of photodegradation as can be shown in Fig 6.

Furthermore, it has been discussed in succeeding section that the role of Fe^{3+} ion in the enhancement of p-chlorophenol degradation is by taking part in supplying OH radicals and preventing recombination of electron and OH radicals simultaneously. The ionic Fe^{3+} can be found only at very low pH and it will completely precipitate in the form of $\text{Fe}(\text{OH})_3$ colloid as the pH of the solution rises in the range of 4-8. when the pH of the solution is continuously increased to reach the level of 8-14, Fe^{3+} would partially dissolve again to form anionic complexes of $\text{Fe}(\text{OH})_4^-$ and $\text{Fe}(\text{OH})_5^-$ [16]. The formed colloids of iron could reduce the light absorption by the species involved in reaction system, leading to less effective photodegradation. In addition, the dissolved $\text{Fe}(\text{OH})_4^-$ and $\text{Fe}(\text{OH})_5^-$ species are unlikely to release OH radicals, therefore it is not surprising to observe low photodegradation at high pH. In the case of p-chlorophenol photodegradation in the presence of $\text{Fe}(\text{OH})_3$, the similar explanation may be applied because, more or less, the speciation of $\text{Fe}(\text{OH})_3$ is same as that of Fe^{3+} described above. As a conclusion, it has been proved that the changes in speciation form of p-chlorophenol, TiO_2 and $\text{Fe}(\text{III})$ (as cation and colloid) due to pH alteration control the effectiveness of the photodegradation process and explain clearly why the effective photodegradation is reached at relatively low pH of the solution.

CONCLUSION

The effectiveness of p-chlorophenol photocatalytical degradation is enhanced in the presence of increasing concentration of Fe^{3+} . On the other hand, increasing mass of $\text{Fe}(\text{OH})_3$ colloid leads to a decrease in the effectiveness of p-chlorophenol photodegradation. The decline in p-chlorophenol photodegradation is observed as the pH of the solution is increased. However, at pH = 6, i.e.: the most applicable pH in real waste water treatment, an adequate effectiveness of photodegradation is still obtained. The highest photodegradation degree, ca. 80 % is achieved when 20 mg of TiO_2 is applied for the

degradation of 50 ml of 100 ppm p-chlorophenol in the presence of 100 ppm Fe^{3+} in the solution with irradiation time of 25 h.

REFERENCES

1. Hu, Z., Srinivasant, M.P., and Ni, Y., 2000, Adsorption and Desorption of Phenol and Dyes on Microporous and Mesoporous Activated Carbon, *Proceeding of The 2nd Pacific Basin Conference on Adsorption Science and Technology*, Brisbane.
2. Wahyuni, E.T dan Mudasir, 2005, *Selektivitas Adsorpsi Zeolit Alam terhadap p-Nitrofenol dan p-Klorofenol*, Prosiding Seminar Nasional Kimia XVI FMIPA-UGM Jogjakarta 14 April 2005.
3. Abd-El-Halem, D., Beshay, U., Abdelhamid, A.U., Moaward, H. and Zaki, S., 2003, *Afr. J. Biotech.*, 2, 8-12.
4. Ruiz-Ordaz, N., Ruiz-Langunez, J.C., Castanon-Gonzalez, J.H., Hernandez-Manzano, E., Christiani-Urbina, E., and Galindez-Mayer, J., 2001, *Revista Latinoamericana de Microbiologia*, 43, 19-25.
5. Wahyuni, E.T., Lestari, A.D., and Mudasir, 2004, Preparation, Characterization, and Photocatalytic Test of ZnO-zeolite, *The Regional Conference for Young Chemist*, Penang Malaysia.
6. Sabhi, S. and Kiwi, J., 2000, *Wat. Res.* 35 (8), 1994-2002.
7. Wahyuni, E.T., Trisunaryanti, W., and Sugiharto, E., 2006, Photocatalytic Activity of FeO-Zeolite for p-Chlorophenol Degradation, *Penang International Conference for Young Chemist USM*, Penang, Malaysia.
9. Alemany, L.J., Banares, M.A., Pardo, E., Martin, F., Galan-Fereres, M., and Blasco, M.J., 1997, *Appl. Catal. B : Envir.* 13, 289-297.
10. Peiro, A.M., Ayllon, A., Peral, J., and Domenech, X., 2001, *Appl. Catal. B : Envir.* 30, 359-373.
11. Linsebigler, A., Lu, G.Q, and Yates, J, Jr., 1995, *Chem. Rev.* 95, 735-758.
12. Wahyuni, E.T. and Mudasir, 2006, Synergic removal of p-chlorophenol and Cr(VI) ion using photoreaction method catalyzed by TiO_2 , *Penang International Conference for Young Chemist USM*, Penang, Malaysia.
13. Brezova, V., Blazkova, A., Borosova, E., Ceppan, M., and Fiala, R., 1995, *J. Molec. Catal. A : Chem.* 98, 106-116.
14. Burrows, H.D., Ernestova, L., Kemp, T.J., Skurlatov Y.I., Purmal, A.P., and Yermekov, A.N., 1998, *Progress in Reaction Kinetics.* 23, 145-207.
15. Herrera, F., Lopez, A., Mascolo, G., Albers, P., and Kiwi, J., 2001, *Appl. Catal. B : Envir.* 29, 147-162.
16. Hoffmann, M.R., Martin, S.T., Choi, W., and Bahnemann, D.W., 1995, *Chem. Rev.* 95, 69-96.