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Decomposition of acetic acid by advanced oxidation processes

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Abstract−Decomposition of acetic acid, known as a non-degradable organic compound, was conducted for several advanced oxidation processes such as TiO_2-UV-H_2O_2, Fe^{2+}-H_2O_2-UV, UV-H_2O_2 and TiO_2-UV system. Acetic acid was efficiency decomposed within 120 minutes of UV radiation under the initial concentration of 500 ppm. The initial chemical oxygen demands (COD_{cr}) tended to increase as H_2O_2 was added in most reactions. However, the initial COD_{cr} was not increased as H_2O_2 was consumed for the oxidation of iron salt in the photo-Fenton oxidation process. COD_{cr} and concentration of acetic acid rapidly decreased as the mole ratio of hydrogen peroxide increased owing to rapid decomposition of the reactant at the beginning of reaction. All reactions show first order pseudo reaction rate. The COD_{cr} removal rate and the decomposition efficiency of acetic acid were fastest in the UV-H_2O_2 process.

Key words: Advanced Oxidation Processes, Photocatalysis Reaction, Photo-Fenton Oxidation, Acetic Acid

INTRODUCTION

AOPs (advanced oxidation processes) applied to decompose non-degradable substances. Among chemical oxidation methods to decompose organic compounds, those classified as advanced oxidation processes (AOPs) are Fenton type oxidation, which uses hydrogen peroxide and Fe^{2+} [1,2], ozone [3], photocatalysis [4-6], UV (ultraviolet)-H_2O_2 [5], UV-H_2O_2-Fe(II, III) [7], electro-coagulation, and electro-decomposition. Generally, as UV introduced to the Fenton oxidation, OH radical production rate increases [7,8]. Fenton oxidation process applied for oxidization of organic compounds with high oxidizing power of OH radical produced by reaction between H_2O_2 and Fe^{2+}. Because H_2O_2 and Fe^{2+} react well with non-degradable organic compounds, usually they are used for pre-treatment of non-degradable organic compounds on the biological water treatment [9-11].

When organic compounds exist in waste water, H_2O_2 and ferric ion react to displacement reaction as follows [10,11]:

$$H_2O_2+Fe^{2+}\rightarrow Fe^{3+}+OH^-+\cdot OH \tag{1}$$

$$RH+\cdot OH\rightarrow R\cdot+H_2O \tag{2}$$

$$R\cdot+Fe^{3+}\rightarrow R^++Fe^{2+} \tag{3}$$

$$R^++OH^-\rightarrow R\text{-}OH \tag{4}$$

$$H_2O_2+RH\rightarrow R\text{-}OH+H_2O_2 \tag{5}$$

If a UV wavelength shorter than 300 nm is irradiated to H_2O_2, OH radicals are formed, which are directly used for decomposition of organic compounds [12].

$$H_2O_2+h\nu\rightarrow 2\cdot OH \tag{6}$$

In the photo-Fenton reaction, Fe^{3+}, $Fe(OH)^{2+}$ and $Fe(OH)^{2+}$ are produced by Fenton oxidization, eventually, photo-decomposed by ultraviolet produce Fe^{2+} and OH radicals.

$$Fe(OH)_2^++h\nu\rightarrow Fe^{2+}+\cdot OH \tag{7}$$

Among the oxidizing agents such as O_3, H_2O_2, $KMnO_4$, Cl_2 and HClO, H_2O_2 is the most cost-efficient oxidant [13]. H_2O_2 produces oxonium ion due to reacting with hydrogen ions in acidic solution.

$$H_2O_2+H^+\rightarrow HOOH_2^+ \tag{8}$$

The oxonium ion makes electrophilic H_2O_2 molecules, increasing the stability of H_2O_2. If there are substances more nucleophilic than H_2O_2 such as acid, alcohol and ketone in the solution, protonation occurs in the solution making electrophilic intermediates that react with H_2O_2.

Photo catalytic reaction refers to the reaction in which organic compounds absorbed to the semiconductor surface are decomposed by high oxidizing power of OH radical, and electrons and positive holes produced by light energy having larger than band gap energy. If the absorption rate of the reactant or desorption rate of the product is late, this step might be the rate-determining step for a catalytic reaction. In case of TiO_2 and UV reaction, the absorbing of reactants to TiO_2 surface is the rate-determining step [14].

OH radical formation in the reaction where H_2O_2 is applied to photo catalytic reaction can be explained in two ways. One explanation is that the electrons of the conduction band produced when UV is irradiated to TiO_2 surface react with H_2O_2 to produce OH radicals, and the other is that the holes in the valence band react with OH group to produce OH radicals. Its reaction mechanism is as follows [8].

$$H_2O_2+h\nu\rightarrow 2\cdot OH \tag{11}$$

$$H_2O_2+e^-_{CB}\rightarrow \cdot OH+OH^- \tag{12}$$

$$2OH^-+h^+_{VB}\rightarrow \cdot OH+OH^- \tag{13}$$

$$\cdot OH+H_2O_2\rightarrow H_2O_2+HO_2\cdot \tag{14}$$

$$H_2O+H_2O_2\rightarrow O_2+H_2O+\cdot OH \tag{15}$$

In case of acetic acid decomposition, the role of H_2O_2, TiO_2, UV and Fe ions is important in the reaction rate; however are has not been

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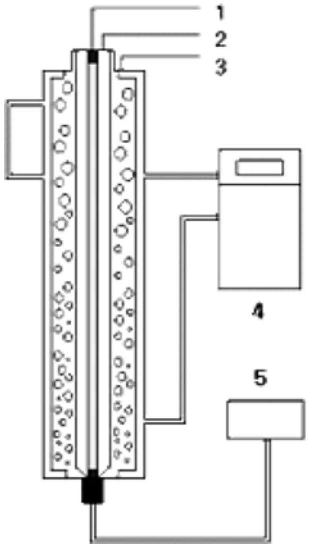


Fig. 1. Schematic diagram of experimental apparatus.
1. UV lamp
2. Quartz tube
3. Cooling apparatus
4. Thermostat
5. Air pump

studied yet. We compare the decomposition rates based on the chemical oxidation demand (COD_{cr}) by introducing H_2O_2, TiO_2-UV-H_2O_2 (photo catalysis), UV-H_2O_2 and Fe^{2+}-H_2O_2-UV (photo-Fenton) with acetic acid as non-degradable organic compounds. We also select a reaction system having the fastest decomposition of acetic acid utilized for high-concentration acetic acid decomposition process.

MATERIALS AND METHODS

1. Experimental Equipment

A schematic diagram of the reactor system is illustrated in Fig. 1. For the reactor, 960 mm-long and 70 mm-diameter cylindrical pyrex pipe was used. At the top center of the reactor, a 39 W mercury low-pressure single lamp (Philips, USA) was installed inside a cylindrical quartz tube (1,000 mm in length, 1.7 mm in thickness, 20.7 mm in internal diameter, and 25.0 mm in outer diameter) to prevent the light source body from being in contact with the reaction sample. To keep the temperature constant at 20 °C, a thermostat was connected to the reactor. For agitation, compressed air was introduced to the reactor. In the middle of the reactor, a cock valve was installed to collect the sample.

2. Analysis Method

Chemical oxidation demand by dichromate (COD_{Cr}) was measured by using the colorimetric method (HACH, DR 4000), and pH by using Corning 320. For HPLC, C18(M) 25CM column and Shimadzu LC 10A with UV detector were used. At this time, for the eluent, $NH_4H_2PO_4$ 0.1 M (pH 2.5 H_3PO_4) was applied at the rate of 1.0 mL/min.

3. Experimental Method

The initial concentration of the acetic acid (Junsei GR) was 500 ppm. UV lamp was 39 W mercury low pressure lamp (Philips, USA). 35% H_2O_2 (Merck. GR), $FeSO_4 \cdot 7H_2O$ (Junsei, GR) and TiO_2 (Sigma, GR, anatase) were prepared according to the stoichiometric mole ratio based on the concentration of acetic acid. As the initial pH of acetic acid 500 ppm was 3.34, all reaction was performed without pH control. The sample was collected every 10 min or 30 min, for 120 min of total reaction time. The collected samples were immediately measured for COD_{cr} and pH. In case of the photo-Fenton reaction and the TiO_2-added reaction, COD_{cr} was measured after the samples were filtered with 0.45 μl in order to remove iron salt and TiO_2.

RESULTS AND DISCUSSION

1. Effect of H_2O_2 at TiO_2-UV Process

TiO_2 was used in the form of suspension for the reaction. Fig. 2 shows the change of COD_{cr} in the acetic acid by the amount of H_2O_2 at the mole ratio (TiO_2/acetic acid) of 1. The amount of H_2O_2 addition was determined by the mole ratio with the acetic acid as 1 : 1, 1 : 5 and 1 : 10. Even though UV radiation time increased, COD_{cr} degradation ratio was very low during TiO_2-UV process. However,

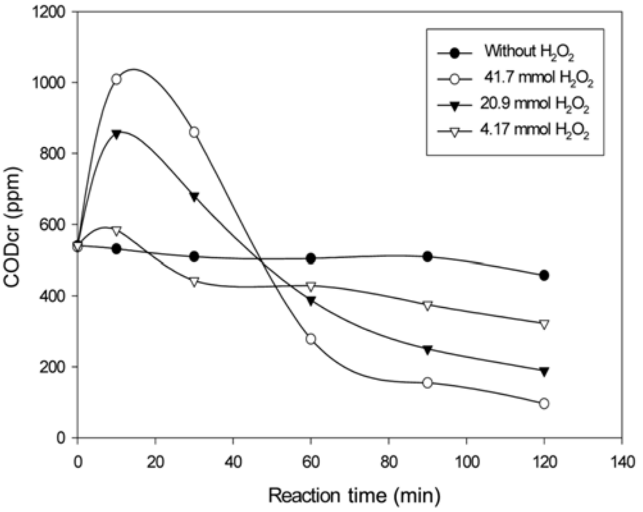


Fig. 2. COD_{cr} change of aqueous acetic acid solution with various H_2O_2 concentrations in TiO_2-UV process (acetic acid 4.17 mmol, TiO_2 4.17 mmol).

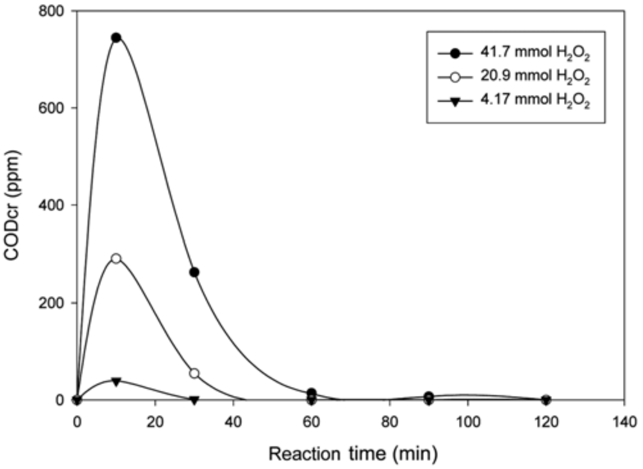


Fig. 3. COD_{cr} changes in distilled water with various hydrogen peroxide addition rates.

when H_2O_2 was added, removal rate of the acetic acid and initial COD_{cr} increased as the amount of H_2O_2 increased. It would be probably because it takes time for H_2O_2 to produce OH radical as it is very stable in the acidic solution. In other words, when H_2O_2 reacts over the stoichiometric mole ratio with the sample, the existing H_2O_2 rather increases COD_{cr} at the early stage of reaction. Fig. 3 confirms that the existing H_2O_2 increased the initial COD_{cr}; all reactions show that H_2O_2 completely decomposed in about 60 min.

2. Photo-Fenton Oxidation Process

Because acetic acid is one of the organic compounds having a low diffusing rate for radicals, it is known that it is hard to decompose by Fenton oxidation process. The result of applying Fenton oxidation for the synthetic wastewater containing 700 mg/L of acetic acid, COD_{cr} removal rate was 26% when H_2O_2 3,600 mg/L and ferric sulfate (II) were added. The ratio of H_2O_2 to remove COD_{cr} was 0.55-0.77. This result proves that the efficiency of Fenton oxidation reaction is very low [15].

The combination of Fenton reaction in UV light, which is the photo-Fenton reaction enhanced the efficiency of the Fenton process. Based on these results, we tried to evaluate the acetic acid decomposition rate using the photo-Fenton oxidation process, which combines UV to the Fenton oxidation process, in order to increase the production of radicals. The result of the photo-Fenton process is shown in Fig. 4. During the reactions, the mole ratio of Fe^{2+}/acetic acid maintained equivalent ratio and the added amounts of H_2O_2 for reacting acetic acid were 1 : 1, 1 : 5, and 1 : 10, respectively.

Unlike the TiO_2-UV-H_2O_2 reaction, the initial COD_{cr} was not increased in the photo-Fenton oxidation process. It refers to the fact that OH radicals were consumed more efficiently. Because H_2O_2 and ferric ion react stoichiometrically, an equivalent amount of iron salt is needed to produce enough OH radicals for oxidation of organic compounds; thus excessive iron salt acts as a scavenger for OH radicals. It means that H_2O_2 is consumed only for the iron oxidation [16,17].

When the mole ratio of acetic acid and H_2O_2 is 1 : 1 and 1 : 10, the removal of COD_{cr} occurs mostly during the initial reaction process. COD_{cr} removal rate decreased over 30 min later. For the photo-Fenton oxidation process, COD_{cr} is reduced not only by OH radicals, but also by the absorption rate of acetic acid on the iron salt.

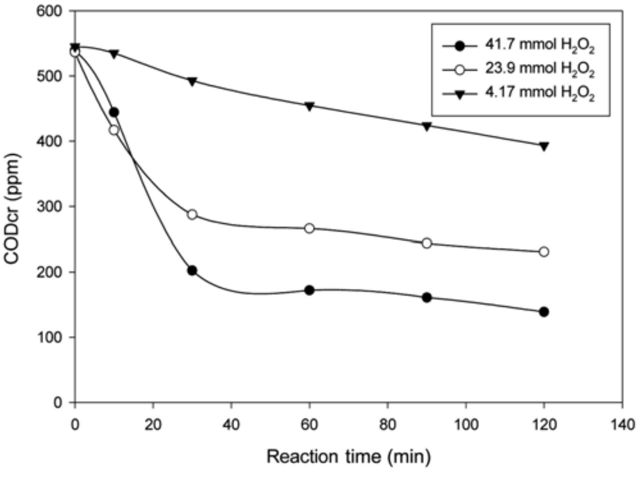


Fig. 4. Effect of hydrogen peroxide for acetic acid (4.17 mmol) oxidation as a function of reaction time under photo Fenton (Fe^{2+}-H_2O_2-UV) system.

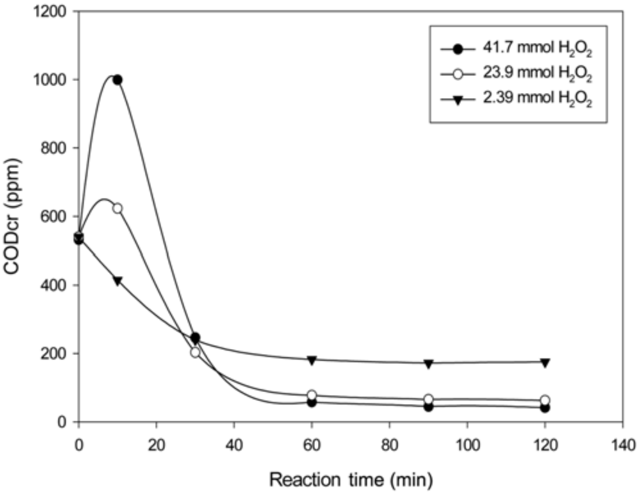


Fig. 5. Effect of hydrogen peroxide for acetic acid (4.17 mmol) oxidation as a function of reaction time under UV-system.

3. UV-H_2O_2 Process

Fig. 5 shows the rate of COD_{cr} removal by UV-H_2O_2 process. For the UV-H_2O_2 process, as the injection amount of H_2O_2 increased, the initial COD_{cr} increased due to the remaining H_2O_2. These phenomena disappeared when UV was irradiated over 60 min. In the case of H_2O_2/acetic acid (mole ratio) varying from 10, 5 and 1, the COD_{cr} removal rate decreased 91%, 88% and 68%, respectively, for 120 min reaction. From these results, it was confirmed that photo catalytic removal rate of COD_{cr} was more efficient than other photo-Fenton oxidation reaction.

4. Comparison of Advanced Oxidation Process with H_2O_2 Concentrations

Fig. 6 shows the comparison of the reaction rate for several advanced oxidation processes under the concentration of 20.9 mmol and 4.17 mmol of H_2O_2 to fixed acetic acid concentration at 4.17 mmol. The COD_{cr} changes were almost flat after 60 min of reaction regardless of the amount of H_2O_2. It was shown that COD_{cr} decreased after 60 min of reaction in the order of UV-H_2O_2>Fe^{2+}-H_2O_2-UV>TiO_2-UV-H_2O_2>TiO_2-UV. The removal ratio of COD_{cr} after 90 min of reaction was in the order of UV-H_2O_2>TiO_2-UV-H_2O_2>Fe^{2+}-H_2O_2-UV>TiO_2-UV-H_2O_2>TiO_2-UV. The reason that the rate of COD_{cr} removal by photo-Fenton oxidation process decreased after 90 min of reaction is because the H_2O_2 was consumed for the oxidation of iron and thus no more OH radicals were produced.

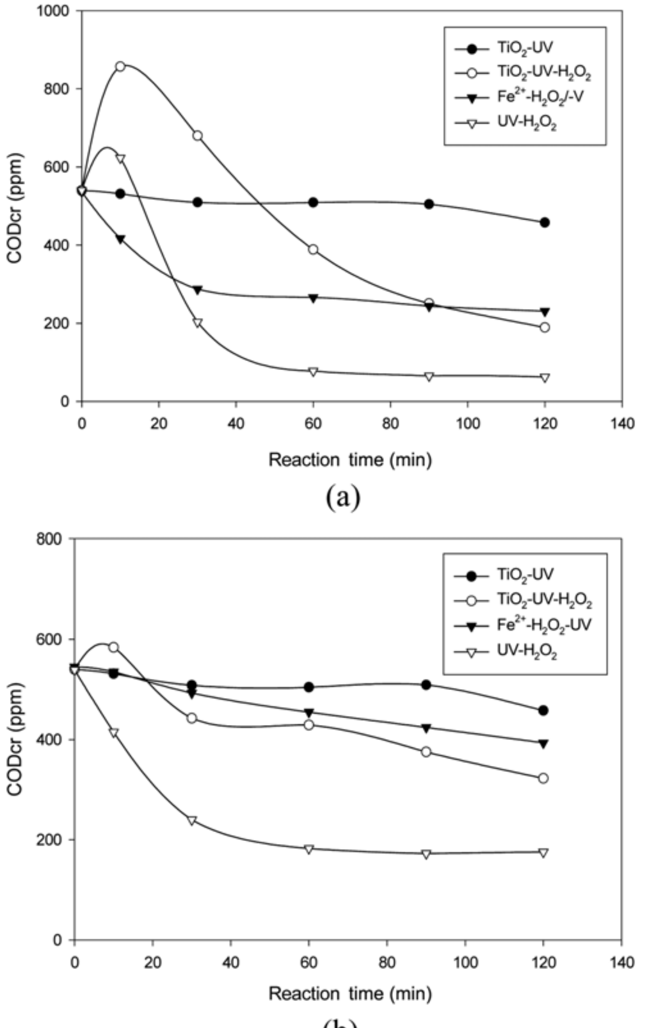
5. Degradation Kinetics of Acetic Acid

Degradation kinetic studies were performed in terms of rate constants in order to find the optimum concentration of hydrogen peroxide. The equation of the kinetic model for the batch system is as follows:

$$\frac{dC}{dT} = -kC$$

$$\ln\frac{C}{Co} = -kt$$

where, C, Co are the concentration of acetic acid, initial concentra-



(a)

(b)

Fig. 6. Comparison of oxidation rates of acetic acid (4.17 mmol) for various reaction methods at various H_2O_2 41.7 mmol concentration; (a) 20.9 mmol, (b) 4.17 mmol.

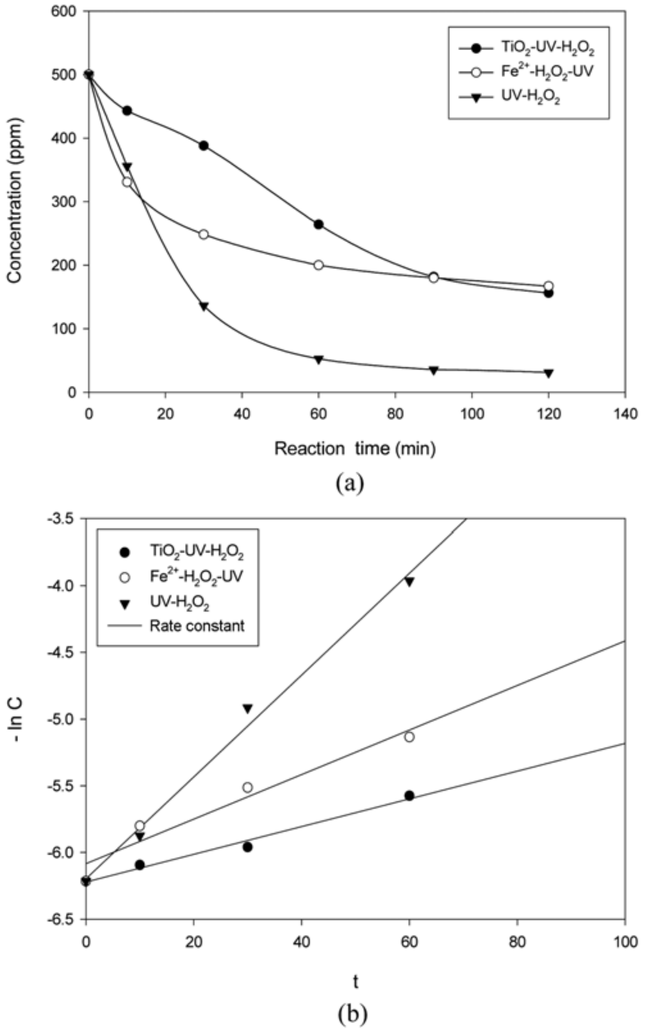
tion, respectively; k, rate constant; t, reaction time.

The plots of the logarithm of acetic acid concentrations versus reaction time gave the reaction order of acetic acid as shown in Fig. 7. The degradation rate of acetic acid was the first pseudo order reaction, giving linear slope as the degradation rate constant, k (L/min). The reaction constants for acetic acid were compared in three experimental conditions: (1) the TiO_2-mediated photo catalysis (UV-H_2O_2-TiO_2 system), (2) photon-Fenton (Fe^{2+}-H_2O_2 system) by addition of UV, and (3) the photo catalysis by addition of hydrogen peroxide (UV-H_2O_2 system). The results show that the rate constants were 2.87×10^{-3}, 4.64×10^{-3} and 1.06×10^{-2} respectively.

CONCLUSION

From the results of the acetic acid decomposition in the advanced oxidation methods, we reached the following conclusions.

1. Acetic acid was efficiently decomposed with TiO_2-UV-H_2O_2, Fe^{2+}-H_2O_2-UV and UV-H_2O_2 except TiO_2-UV system. UV-H_2O_2 reaction was the most efficient oxidation method.



(a)

(b)

Fig. 7. Comparison of oxidation rates and plot pseudo first order rate constant for decomposition in aqueous acetic acid solution under various systems (acetic acid: 4.17 mmol, TiO_2 4.17 mmol, Fe^{2+} 4.17 mmol, H_2O_2 41.7 mmol, T=293.15 K, 39 W low pressure mercury lamp).

2. Acetic acid was completely decomposed within 120 minutes of UV irradiation under the initial concentration of 500 ppm.

3. In the UV-H_2O_2 system, as H_2O_2 was added, the initial COD_{cr} increased owing to the residual H_2O_2. However, in the photo-Fenton oxidation process, the initial COD_{cr} was not changed because H_2O_2 was consumed for the oxidation of iron salt.

4. All advanced oxidation processes show the pseudo first order reaction.

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