Degradation Kinetics of Recalcitrant Organic Compounds in a Decontamination Process with UV/H$_2$O$_2$ and UV/H$_2$O$_2$/TiO$_2$ Processes

Hong-Joo Lee[†], Duk-Won Kang, Junhwa Chi and Dong Hun Lee

Nuclear Power Laboratory, Korea Electric Power Research Institute (KEPRI),
103-16 Moonji-dong, Yuseong-gu, Daejeon 305-380, Republic of Korea

Abstract−In this study, degradation aspects and kinetics of organics in a decontamination process were considered in the degradation experiments of advanced oxidation processes (AOP), *i.e.*, UV, UV/H$_2$O$_2$ and UV/H$_2$O$_2$/TiO$_2$ systems. In the oxalic acid degradation with different H$_2$O$_2$ concentrations, it was found that oxalic acid was degraded with the first order reaction and the highest degradation rate was observed at 0.1 M of hydrogen peroxide. Degradation rate of oxalic acid was much higher than that of citric acid, irrespective of degradation methods, assuming that degradation aspects are related to chemical structures. Of methods, the TiO$_2$ mediated photocatalysis showed the highest rate constant for oxalic acid and citric acid degradation. It was clearly showed that advanced oxidation processes were effective means to degrade recalcitrant organic compounds existing in a decontamination process.

Key words: Advanced Oxidation Process (AOP), Hydrogen Peroxide, Organic Compounds, Degradation, Degradation Kinetics

INTRODUCTION

Conventional methods to remove recalcitrant organic compounds in industrial effluents such as air stripping or adsorption by activated carbon are not good alternatives for contaminants having low volatility or poor adsorption properties. Additionally, these methods only change the pollutants from one phase to the other leaving the problem only partially solved. Meanwhile, effective oxidative treatments lead to the complete mineralization (or degradation) of a great variety of organic substances. Some of these mineralization methods employ strong oxidants such as hydrogen peroxide or ozone combined with an activation step initiated by UV radiation. They are recognized as some of the alternatives offered by the so-called advanced oxidation processes (AOP). Essentially, the degradation of organic compounds is the result of the strong oxidative properties of radicals generated by strong oxidants. AOP is considered as a promising treatment owing to its ability to degrade a large variety of organic pollutants, including recalcitrant chemical species [Wu et al., 2002]. It is based on oxidative degradation reactions by hydroxyl radical and other radicals in solutions generated by various methods, *i.e.*, O$_3$/UV, H$_2$O$_2$/UV, and O$_3$/H$_2$O$_2$/UV, and H$_2$O$_2$/UV photocatalysis and TiO$_2$ mediated photocatalysis in an aqueous solution or photo-assisted Fenton process [Kiwi et al., 2000; Blake et al., 1999; Beltrán et al., 1997; Alfano et al., 2001].

Of methods, the UV/H$_2$O$_2$ process has some advantages with respect to the UV/O$_3$ systems. Ozone is not a stable gas and should be generated in situ. Even though it has difficulty in analyzing hydrogen peroxide concentration due to low absorption coefficient at 254 nm [Buxton et al., 1988], hydrogen peroxide can be transported and stored safely and its oxidative properties are equivalent to those of ozone. Also, advanced oxidation process of hydrogen peroxide

has advantages due to infinitely high solubility in water, low installation, capital and operation cost, and non-production of halogen or metals [Ince and Apikyan, 2000]. In the UV/H$_2$O$_2$ process, a radiation having wavelength shorter than 300 nm (mainly 254 nm) transforms hydrogen peroxide into OH$^\bullet$, but very often radiation of these wavelengths acts directly and simultaneously on the organic compounds. Since the oxidative potential of the OH$^\bullet$ is very high (2.7 V) among oxidants in acidic solution, activation of the organic molecules may produce from direct dissociation to form organic radicals or other intermediate compounds [Buxton et al., 1988; Getoff et al., 1971]. The majority of organic compounds may be transformed into CO$_2$ and H$_2$O when excess H$_2$O$_2$ concentration is usually provided over the stoichiometric demand during sufficient reaction time [Höfl et al., 1997].

Recalcitrant organic compounds are found in many streams including industrial effluents, wastewater, chemical process and others. This study focuses on the degradation of organic compounds in decontamination processes for nuclear power plants. Generally, decontamination means the removal of contaminated oxide films, or oxide deposits from the surfaces of pipes, pumps, valves, heat exchangers etc., located in the various systems of water-cooled reactors such as PWR (Pressurized water reactor) and BWR (Boiled water reactor). In general, decontamination methods are classified with three major types: electrical, chemical, or mechanical. Of methods, chemical decontamination involves dissolution of the radioactive contaminants themselves, or the matrix (oxide film or deposit), which are trapped by chelating agents [Ocken, 1999; Ayres, 1970]. In the chemical decontamination methods, EDTA (Ethylenediamine tetraacetic acid), citric acid, and oxalic acid are mainly used as chelating agents to remove metal oxides such as magnetite (Fe$_3$O$_4$), nickel ferrite (NiFeO$_4$), hematite (Fe$_2$O$_3$) and chromium oxides. The metal species are recovered from an ion exchange process by using chelating agents in the decontamination process. However, the chelating agents are not easily degradable under mild conditions. Now, degra-

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[†]To whom correspondence should be addressed.
E-mail: hjlee95@kepri.re.kr

dation of recalcitrant organic compounds (EDTA, citric acid, and oxalic acid) existing in the decontamination process has been of interest using AOP [Zuo and Deng, 1997; Kolthoff et al., 1972]. This work mainly addresses degradation of citric acid and oxalic acid by H_2O_2/UV or TiO_2 mediated photocatalysis and their kinetic rate constants are considered.

EXPERIMENTAL

The experimental tests were performed in a lab-size continuous photocatalytic reactor. It has four rectangular configurations having four lamps (total power of 0.272 Kwh and characteristic wavelength of 254 nm), each effective volume of 0.348 L. Samples of the liquid were taken along the reactor in order to investigate the conversion of the reactants at different residence times. And, concentrations of oxalic acid with two moles of water (MW 126.07, Sigma, USA) and citric acid (MW 192.12, Sigma, USA) in the solution were analytically determined by total organic carbon (TOC) using a total organic analyzer, DC-180 (Dohrman, USA) and by COD_{Mn}. Also, the concentration of hydrogen peroxide was analyzed at 454 nm by a spectrometric method using copper (II) ion and 2,9-dimethyl-1,10-phenanthroline (DMP) [Kosaka et al., 1998].

In a typical degradation experiment of H_2O_2/UV system, the influence of the hydrogen peroxide concentration on degradation of organic compounds was investigated by changing the initial molar concentrations from 0 to 1.0 M. Then, the degradation rates of oxalic acid and citric acid (both 1.0%) were compared after the optimum concentration of hydrogen peroxide was determined. For H_2O_2/UV/ TiO_2 system, P-25 TiO_2 (a 20/80 mixture of rutile and anatase) was obtained from DeGussa Corp [Hoffman et al., 1995; Beltrán et al., 1999; Park et al., 2001].

RESULTS AND DISCUSSION

1. Degradation of Oxalic Acid in the Presence of Hydrogen Peroxide

In order to evaluate process performance in the degradation experiments, the residence time was mainly considered instead of operating time. Fig. 1 shows the experimental results of oxalic acid degradation when the initial concentration of hydrogen was 0.1 M. It is interesting that the solution pH was not changed up to 16.7 min
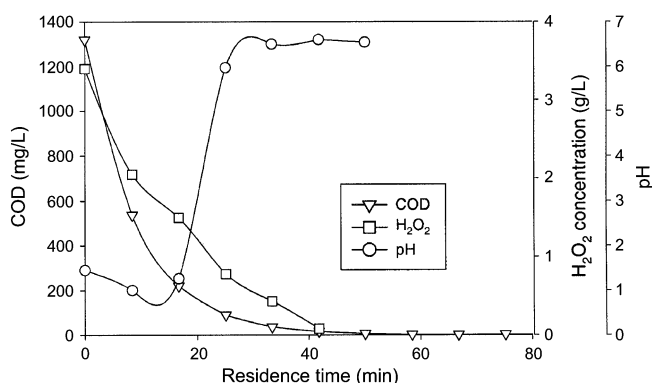

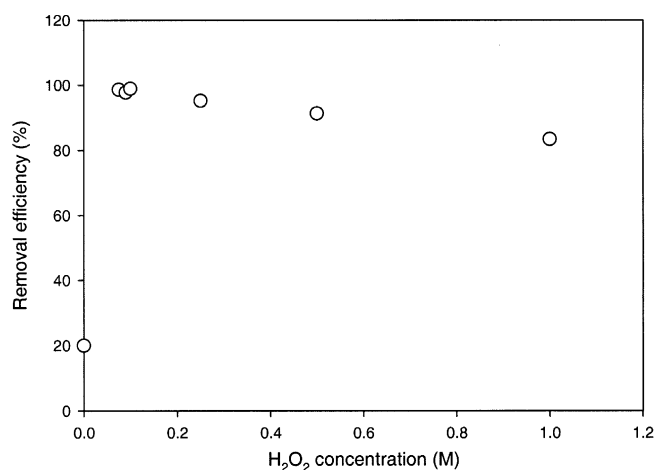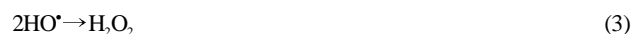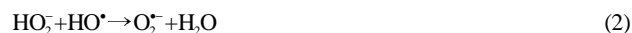Fig. 1. Observation of COD, pH and H_2O_2 concentration in the oxalic degradation.

Fig. 2. Removal efficiency in the degradation of oxalic acid.

of residence time (60 min of operation time), and then became neutral. The pH change is assumed to be related to reduction of oxalic acid in the presence of hydrogen peroxide. It is noted that 98% of organic was degraded at a high rate during the acidic condition during an initial period and the degradation rate remained a constant value in the neutral condition in Fig. 1. Considering concentration of the hydrogen peroxide during process, its concentration decreased with the elapsed time, showing the first order reaction. Furthermore, it is assumed that oxalic acid was degraded to form CO_2 and H_2O considering the high degradation rate of oxalic acid. Therefore, intermediates for oxalic acid degradation were not considered through the study.

In degradation experiments of oxalic acid having initial concentration of 0.08 M, 90% of oxalic acid was degraded at the residence time of 16.7 min in the UV/H_2O_2 system except for extreme conditions, i.e., 0 M and 1.0 M. Conversion of oxalic acid was only 20% at the hydrogen peroxide concentration of 0 M (or UV system) in Fig. 2, showing that an oxidant is necessary for recalcitrant organic degradation. In the case of 1.0 M of the initial concentration, 83.4% of oxalic acid was degraded, which is a lower degradation rate than the other concentrations. In the degradation experiments with the photocatalytic systems, 0.1 M of H_2O_2 is somewhat excessive value containing 0.08 M of oxalic acid [Kolthoff et al., 1972]. It is known that hydrogen peroxide acts as a hydroxyl radical scavenger and a decomposition byproduct of solute during the process [Kosaka et al., 1998, 2001], i.e.:

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \tag{1}$$

$$HO_2^{\bullet} + HO^{\bullet} \rightarrow O_2^{\bullet -} + H_2O \tag{2}$$

$$2HO^{\bullet} \rightarrow H_2O_2 \tag{3}$$

where $HO_2^{\bullet}$ is the hydroperoxyl radical and $O_2^{\bullet -}$ the superoxide anion. The above equations imply that concentration of hydrogen peroxide is related to the treatment efficiency and that the optimal concentration exists, which is dependent on components of organic compounds and their concentrations.

2. Degradation Efficiencies for Different Advanced Oxidation Processes

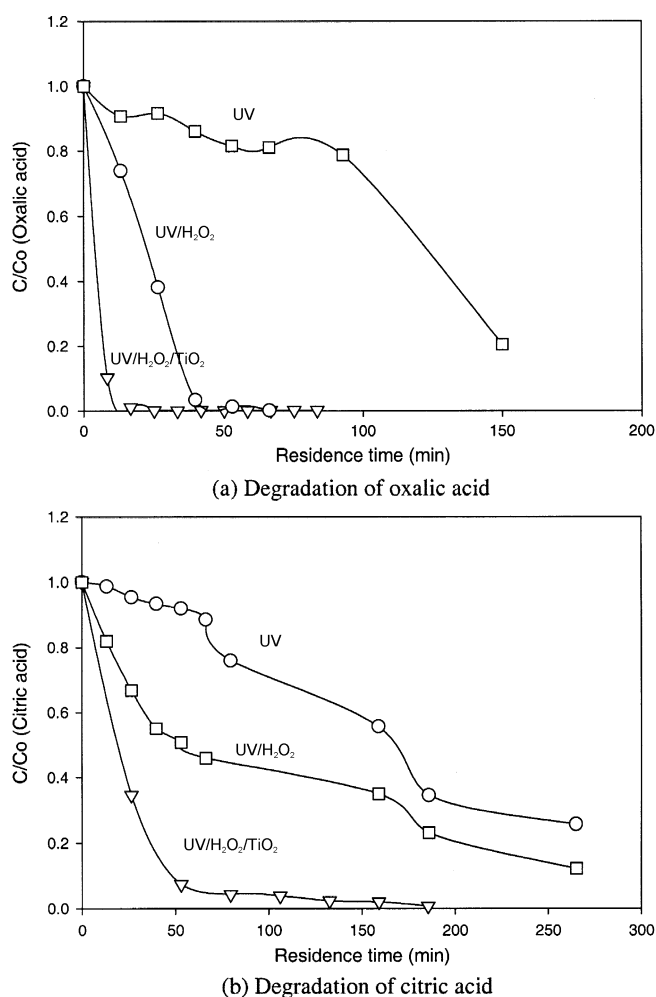Treatment efficiencies of different processes were compared in

(a) Degradation of oxalic acid

(b) Degradation of citric acid

Fig. 3. Different degradation methods for the degradation of organic compounds.

Fig. 4. Degradation rates of citric acid and oxalic acid in the UV/ H_2O_2/TiO_2 system.

the degradation of oxalic acid and citric acid and the results are shown in Fig. 3. The degradation aspects for oxalic acid in three systems show that photocatalytic reaction mediated with TiO_2 showed the highest degradation rate in Fig. 3(a). In absence of hydrogen peroxide and TiO_2, only about 20% of oxalic acid was degraded even with the extended operation. In addition, oxalic acid was almost degraded at elapsed residence time of 40 min in the system of H_2O_2 and UV. In the degradation of citric acid, three different treatment efficiencies were considered as well. It was found that the TiO_2 mediated photocatalysis degraded the organic compound with the highest rate. Therefore, the order of the degradation rate was TiO_2 mediated photocatalysis (UV/H_2O_2/TiO_2)>photocatalysis with H_2O_2 (UV/H_2O_2)>photocatalysis (only UV), similar with the results for oxalic acid (See Fig. 3(b)).

In the case of photocatalysis with TiO_2, the photocatalytic mechanism is based on the activation of the surface of a photo-conductor (usually titanium dioxide in the anatase form) by light [Mazzarino and Piccinini, 1999; Aceiuno et al., 2002; You et al., 2001]. In the presence of oxygen and water, oxygen plays the fundamental role of an electron scavenger by the reaction with the conduction band, thus electron producing the superoxide radical anion $O_2^{\cdot-}$. This prevents the recombination of the electron-vacancy pair. The surface-
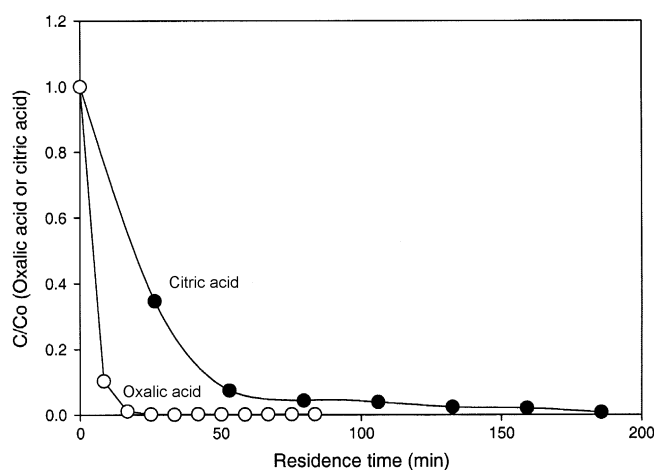
bound water together with hydroxyl groups are oxidized by the vacancies to form $OH^{\cdot}$ as the most active oxidizing species. The hydroxyl radical improves the degradation reaction of organic compounds [Linsebigler et al., 1995; Chai et al., 2000; Choi et al., 2001]. The degradation kinetics should be considered for the quantitative analysis of degradation rate, which is discussed in detail below.

It is known that the degradation of organic compounds is related to organic species, their concentration and degradation methods. Degradation aspects of oxalic acid and citric acid were compared with UV, UV/H_2O_2, and UV/H_2O_2/TiO_2 systems. Of the methods considered, the UV/H_2O_2/TiO_2 system showed the highest rate compared with the other methods. While 95% of oxalic acid was demineralized at the residence time of 17 min, it took 80 min of residence time for citric acid to be degraded with 95% (See Fig. 4). It is assumed that the slow degradation rate of citric acid is due to more complex chemical structures than oxalic acid [Karpel Vel Leitner and Dore, 1996, 1997]. According to the reported results, the carboxylic acids substituted with one hydroxyl group led to the formation of the corresponding ketone (or aldehyde) in oxygenated solution, resulting in a slow reaction rate.

3. Degradation Kinetics of Organic Compounds

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 having excess hydrogen peroxide as follows:

$$\frac{dC}{dt} = -kC \qquad (4)$$

$$\ln\frac{C}{C_0} = -kt \qquad (5)$$

where C is the concentration of organic compound (M), k the rate constant (1/min), t the elapsed residence time (min) and subscript 0 means an initial condition. The plots of the logarithm of organic concentrations and residence time were obtained to determine the reaction order of organic compounds as shown in Fig. 5. The y-axis of the plots for organic compounds was represented as TOC or COD (mg/L). It was found that the degradation of oxalic acid and citric acid was the first order reaction, giving linear slopes as
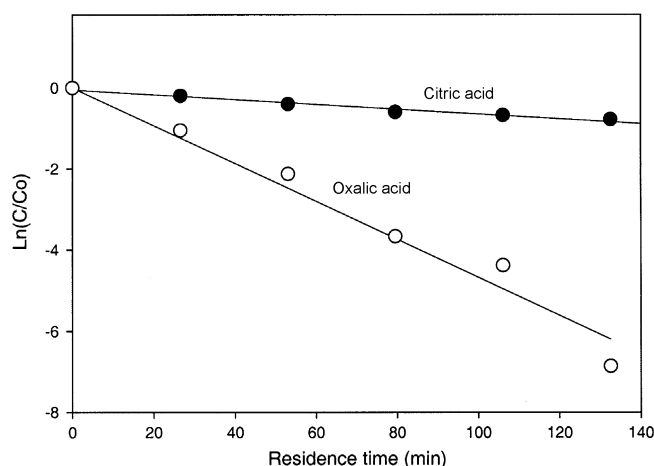
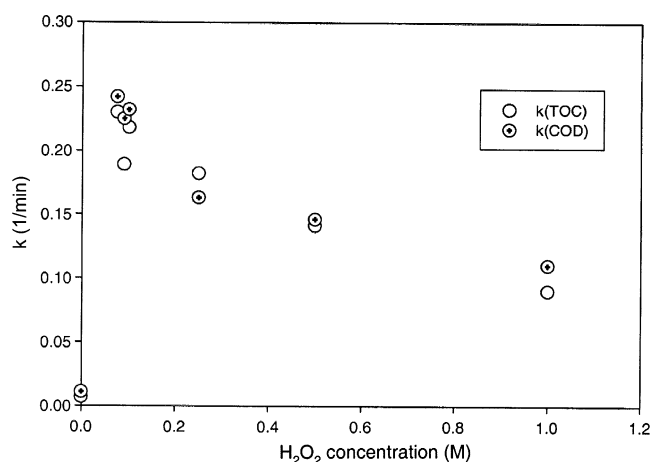**Fig. 5. Degradation kinetic constants in the organics degradation in the system of UV/H_2O_2.**

Fig. 6. Degradation kinetic constants of oxalic acid as a function of H_2O_2 concentration.

the degradation rate constant, k (1/min).

The rate constants of oxalic acid were compared in the experiments of different concentration of hydrogen peroxide. Fig. 6 shows the degradation results for oxalic acid as a function of hydrogen peroxide concentration measured by TOC (ppmC). It was clearly observed that the reaction rate increased by addition of hydrogen peroxide. And, it was verified that 0.1 M of H_2O_2 showed the highest value of the rate constant. When the stoichiometric demand is considered, the hydrogen peroxide concentration of 0.1 M was slightly excessive considering that oxalic acid in the feed solution was

Table 1. Degradation rates of oxalic acid and citric acid with different methods

Experimental conditions*	Oxalic acid k (Oxal) (1/min)	Citric acid k (Cit) (1/min)	k (Oxal)/ k (Cit)
UV system	0.0068	0.0045	1.5
UV/H_2O_2	0.2180	0.0246	8.9
UV/H_2O_2/TiO_2	0.2895	0.0315	9.2

*Results are shown for 0.1 M of H_2O_2 and 0.2% of TiO_2.

0.08 M, corresponding to the reported results [Ince and Apikyan, 2000].

To observe degradation efficiencies for degradation experiments, concentrations of oxalic acid and citric acid in the feed solution were set as 1.0%, which corresponds to 0.08 M and 0.05 M, respectively. The reaction constants for oxalic acid and citric acid were compared in three experimental conditions: (i) the photocatalysis (UV system), (ii) the photocatalysis by addition of hydrogen peroxide (UV/H_2O_2 system) and (iii) the TiO_2 mediated photocatalysis (UV/H_2O_2/TiO_2 system). Table 1 summarizes the degradation experimental results for oxalic acid and citric acid. It was observed that the reaction rate of the TiO_2 mediated photocatalysis was much higher than that of photocatalysis with hydrogen peroxide. The photocatalysis with TiO_2 showed the highest rate for both organic compounds, implying that organic compounds were easily degraded to form CO_2 and H_2O. Considering the rate constants for the photocatalysis and the TiO_2 mediated photocatalysis, the rate of the latter was 155 times higher than that of the former in the oxalic acid degradation experiments. In the case of citric acid degradation, the rate increased 26 times in the TiO_2 mediated photocatalysis. In addition, oxalic acid was degraded with higher rate than citric acid irrespective of different methods due to chemical structures.

The degradation rate constant of the photocatalysis at the first row was 0.0068 1/min for oxalic acid, 1.5 times higher rate than that of citric acid. According to the reported results, the degradation rates of oxalic acid and citric acid with respect to $OH^\bullet$ were the second order reaction and the rate constants were $1.4 \times 10^6\ M^{-1}s^{-1}$ and $5.0 \times 10^7\ M^{-1}s^{-1}$, respectively [Buxton et al., 1988; Getoff et al., 1971]. In the results, hydrogen peroxide was produced by radiolysis of water, thus resulting in the second order reaction in the degradation of oxalic acid and citric acid. The higher degradation rate of oxalic acid in this study is thought to be due to experimental conditions, especially excess hydrogen peroxide. Considering the effect of H_2O concentration, it is accepted that water molecule dissociates to form $OH^\bullet$ by collision with electrons or reaction with atomic oxygen and the H_2O concentration strongly influences on $OH^\bullet$ density [Ono and Oda, 2002]. Since the degradation of organic compounds was considered in the aqueous solution with excess hydrogen peroxide in this study, the effect of water molecules was not considered.

The reaction rates between oxalic acid and citric acid increased much more at the photocatalysis with hydrogen peroxide and TiO_2, showing that oxalic acid degraded at about nine times higher rates than citric acid. Through the study, it was clearly observed that recalcitrant organic compounds existing in a decontamination process could degrade effectively by using H_2O_2 and TiO_2 in the UV system.

As mentioned before, a chemical decontaminating agent consists of oxalic acid, citric acid and EDTA, which form metal complex with dissolved metals (Fe, Cr and Ni as major components and Co as minor component) from the deposited metal oxides on the surface of pipes, valves, pumps etc. It is known that organic compounds of metal complex show different aspects compared with those without metal complex [Yang and Davis, 2000; Davis and Green, 1999; Yang and Davis, 2001]. As a further study, the degradation of EDTA and its metal complex existing in decontamination processes will be considered using advanced oxidation processes.

CONCLUSION

In this study, degradation aspects and kinetics were considered in the degradation experiments of photocatalysis, photocalysis with hydrogen peroxide and TiO_2. In the degradation of oxalic acid with different concentrations of H_2O_2 concentrations, it was found that degradation was the first order reaction during AOP using hydrogen peroxide. Also, the highest degradation rate was found at 0.1 M of H_2O_2 which is slightly higher than the stoichiometric demand for oxalic acid. Degradation rate of oxalic acid was much higher than that of citric acid, assuming that degradation aspects are related to chemical structures. Of methods, the TiO_2 mediated photocatalysis showed the highest rate constants for oxalic acid and citric acid. The results in the study imply that AOP can degrade oxalic acid and citric acid existing in the decontamination process.

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