

Degradation of chemical substances using wet peroxide oxidation under mild conditions

Kiyokazu Okawa^{a,*}, Kazuyoshi Suzuki^b, Toshihiro Takeshita^a, Katsuyuki Nakano^a

^a Fukuoka University Institute for Recycling and Environmental Control System, 10 Koyochō, Wakamatsu-ku, Kitakyūshū 808-0002, Japan

^b Kankyo Engineering Co. Ltd., Technological Laboratory, 10 Koyochō, Wakamatsu-ku, Kitakyūshū 808-0002, Japan

Received 8 April 2005; received in revised form 13 June 2005; accepted 24 June 2005

Available online 2 August 2005

Abstract

The objectives of this study are to clarify the degradation mechanism of chemical substances using wet peroxide oxidation (WPO) under mild condition (150 °C) and to confirm the removal of polychlorinated biphenyls (PCBs) in soil using this oxidation process. Acetic and oxalic acids were mineralized using WPO. TOC removal rate of acetic acid was highest in the solution of pH 2.5. However, TOC removal rate was decreased with the increase in pH and TOC were hardly removed in the solution of pH 7 and 10. The decomposition rate of isobutyric acid by WPO decreased in the presence of radical scavenger (*t*-BuOH). The results suggested that the decomposition of chemical substances using WPO proceeded by hydroxyl radical (OH radical). PCBs in soil were also decomposed by performing WPO at 150 °C.

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Keywords: Hydrogen peroxide; Hydroxyl radical; Low-molecular-weight carboxylic acid; Polychlorinated biphenyl; Soil; Wet peroxide oxidation

1. Introduction

Wet oxidation is a wastewater treatment process known to decompose organic compounds at high temperature and high pressure [1–3]. Generally, wet oxidation has been studied under the condition of more than 200 °C due to enhanced reactivity at higher temperatures [1–3]. Contrarily, with the decrease of temperature, the decomposition rate of organic compounds by wet oxidation is either decreased or stopped [4]. In super critical water, H₂O₂ is known to decompose to hydroxyl radical (OH radicals), which can decompose hazardous chemical compounds, such as polychlorinated biphenyls (PCBs) [5,6]. Consequently, if H₂O₂ can decompose to OH radicals in water at lower temperature (i.e. 150 °C), decomposition of hazardous organic compounds by wet oxidation can be done using milder conditions.

Low-molecular-weight carboxylic acids are known to be intermediates of the chemical oxidation process (i.e.

advanced oxidation process) of various hazardous chemical compounds [7,8] because they are stable against chemical oxidation [9] and are mineralized at longer time [10,11]. Particularly, acetic and oxalic acids have refractory nature to chemical oxidation and they are last intermediates of chemical oxidation of wastewater [12,13]. In addition, because the reactivity of low-molecular-weight carboxylic acids with OH radical are low compared with other organic compounds, wet peroxide oxidation (WPO) of low-molecular-weight carboxylic acids is easily affected by radical scavenger [8]. Therefore, low-molecular-weight carboxylic acids are suitable target compounds for evaluating the role of OH radical in WPO. Previously, some studies have been done on WPO [1,4,14,15], however, only a few literature deals with the study of the mechanism involved in the process [1,15]. Particularly, there have been no reported studies about the use of radical scavenger in studying the mechanism of WPO. The objective of this study is to investigate the degradation mechanism of low-molecular-weight carboxylic acids using WPO under mild condition (150 °C). Using this condition, we also investigated the removal of PCBs in soil using WPO. From the economical point of view, performing WPO at a lower

* Corresponding author. Tel.: +81 93 751 9975; fax: +81 93 751 9976.
E-mail address: okawa@fukuoka-u.ac.jp (K. Okawa).

temperature for PCB removal in soil will provide a low cost for soil remediation of this kind.

2. Experimental

2.1. Materials

Acetic, oxalic, propionic and isobutyric acids (Wako Chemicals) were used as the target compounds. In addition, commercial PCBs, KC-400, KC-500 and KC-600 (GL Sciences) were also used as target compounds. The composition of KC-400, KC-500 and KC-600 are shown in Table 1. Kanto loam soil (organic matter content 16%, pH 7.6) was used as soil sample in this study.

2.2. WPO of low-molecular-weight carboxylic acids

Three hundred fifty milliliters of distilled water containing low-molecular-weight carboxylic acids was placed in stainless steel reactor (6 cm i.d., 16 cm depth). The solution was agitated at 500 rpm and heated at 150 °C. The reaction was done with continuous supply of H₂O₂ (50 g/L) at a flow rate of 1.0 mL/min. The pressure in the reactor was 0.5–1.5 MPa. The desired initial pH for every experiment was adjusted by adding HCl or NaOH. WPO of isobutyric acid using the batch reactor was also carried out in the presence of *t*-BuOH (500 mg/L) as radical scavenger. Ten milliliter of the sample solution was periodically taken from the reactor.

2.3. WPO of PCBs in soil

Fig. 1 displays the schematic diagram of a batch reactor system used for the degradation of PCBs in soil. KC-400, KC-500 and KC-600 were spiked to soil and then the amount of KC-400, KC-500 and KC-600 in soil were analyzed to be 137, 96 and 108 mg/kg, respectively. Soil contaminated PCBs and distilled water were mixed in slurry tank and then the specific gravity of slurry adjusted to 1.2 (soil/water = 0.35, w/w). One liter of distilled water (pH 2.5) was placed in stainless steel reactor (15 cm i.d., 28 cm depth) and the water heated until 150 °C. The slurry containing H₂O₂ (100 mg/g soil) was supplied at a flow rate of 0.2 L/min until the pressure

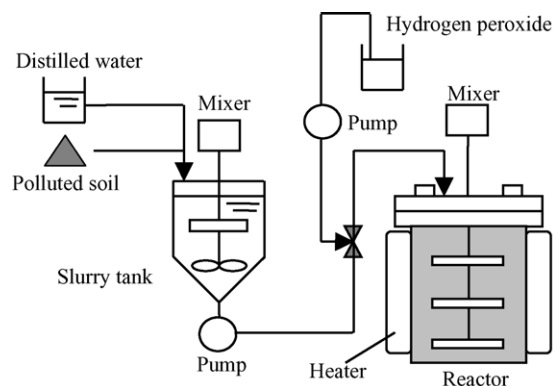


Fig. 1. Schematic diagram of the reactor used for the removal of PCBs in soil.

in the reactor reached 2.5 MPa. After that, the mixture in the reactor was agitated for 30 min at 500 rpm to treat PCBs in soil. The PCBs remaining in the treated soil (5 g) was extracted using an accelerated solvent extractor (ASE200, DIONEX; Solvent: *n*-hexane (50 mL)) and were analyzed by gas chromatography.

2.4. Analytical method

TOC analyzer (TOC-5050A, Shimadzu) was employed to measure TOC in the sample solution. Isobutyric acid concentration was measured using ion chromatography (DX-120, Dionex; Column: IonPac AS16). PCBs were analyzed using a gas chromatograph with an electron capture detector (G2700, Yanako; Column: Quadrex-MS). GC/MS (Hewlett-Packard 6890; Column: HP-WAX) was used to analyze by-products formed during the WPO of propionic acid.

3. Result and discussion

3.1. Degradation of low-molecular-weight carboxylic acids by WPO

Before performing this oxidation process it was confirmed that low-molecular-weight carboxylic acids used in this study cannot be decomposed in heated water (150 °C). Fig. 2 shows

Table 1
Composition of commercial PCBs

	KC-400 (wt%)	KC-500 (wt%)	KC-600 (wt%)
Monochlorobiphenyls	0.01	0.008	0.008
Dichlorobiphenyls	0.48	0.38	0.23
Trichlorobiphenyls	17.47	1.72	0.65
Tetrachlorobiphenyls	51.43	10.31	1.09
Pentachlorobiphenyls	27.92	51.80	8.58
Hexachlorobiphenyls	2.55	32.49	42.34
Heptachlorobiphenyls	0.14	3.23	39.19
Octachlorobiphenyls	0.00	0.06	7.44
Nonachlorobiphenyls	0.00	0.00	0.47
Decachlorobiphenyls	0.00	0.00	0.006

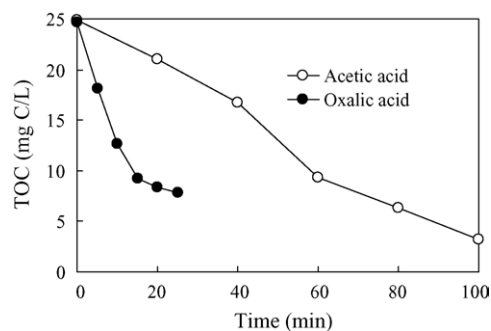


Fig. 2. TOC removal of acetic and oxalic acids by wet peroxide oxidation.

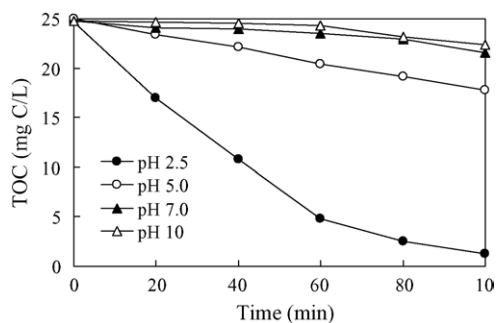


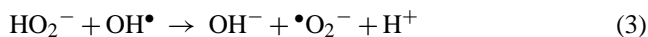
Fig. 3. TOC removal of acetic acid by wet peroxide oxidation at different initial pH.

the decomposition of TOC during WPO of acetic and oxalic acids in this system. The pH values of the acetic and oxalic acids solutions were 3.3 and 2.5, respectively. After WPO at 150 °C, TOC in the solution containing acetic and oxalic acids decreased, indicating that acetic and oxalic acids were mineralized using the process. It is reported that acetic and oxalic acids are stable compounds against oxidation and only OH radical can oxidize these compounds in wastewater treatment using advanced oxidation process [9].

TOC removals of acetic acid by the WPO at different initial pH are shown in Fig. 3. TOC removal rate was highest in the solution at pH 2.5. However, TOC removal rate decreased with the increase of pH. TOC was hardly removed in the solution of pH 7 and 10. It is reported that OH radical rapidly converted to the conjugated base $O^{\bullet-}$ in alkaline solution [1], leading to a loss of the strong OH^{\bullet} oxidant.



In addition, H_2O_2 ionizes to HO_2^{-} which is strong radical scavenger in alkaline solution [16].



Thus, the decomposition rate of acetic acid decreased with the rise of pH.

Fig. 4 shows the decomposition of isobutyric acid by the WPO in the presence/absence of *t*-BuOH. In the presence of *t*-BuOH, which is a radical scavenger, the decomposition

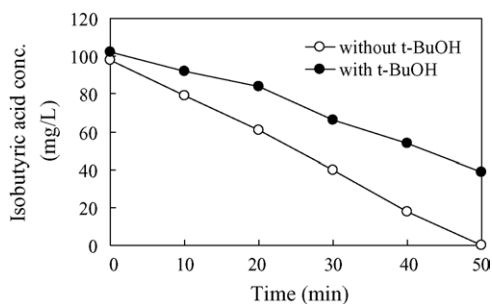


Fig. 4. Decomposition of isobutyric acid by wet peroxide oxidation in the presence/absence of *t*-BuOH.

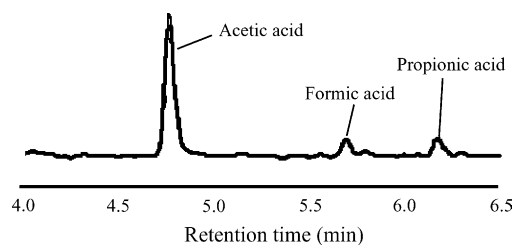
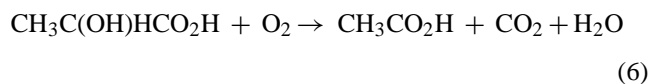


Fig. 5. GC/MS chromatogram of propionic acid after 40 min reaction (Column: HP-WAX (30 m × 0.25 mm × 0.25 μm)).

rate of isobutyric acid is slower than that with no *t*-BuOH. These results suggest that OH radical resulting from decomposition of H_2O_2 was scavenged by *t*-BuOH and oxidation of isobutyric acid was prevented. Therefore, this suggested that degradation of low-molecular-weight carboxylic acids by this oxidation process involves OH radical reaction. H_2O_2 is known to decompose to OH radicals in super critical water that leads to decomposition of PCBs [5,6]. In addition, PCBs, dioxins and endocrine disruptors are known to be mineralized by OH radical [17–21]. Gunten [22] also reported that OH radical have much higher reactivity for any hazardous chemical compounds than those of other oxidants such as ozone and the rate constants ($M^{-1} s^{-1}$) are 7–10 orders of magnitude. Accordingly, it is suggested that H_2O_2 can decompose to OH radicals in water even at mild condition, i.e. 150 °C and any hazardous chemical compounds, such as PCBs, can be decomposed using this oxidation process.

GC/MS chromatogram of propionic acid after WPO at 40 min reaction time is presented in Fig. 5. This figure shows that during the WPO of propionic acid, the main intermediate product was acetic acid plus a small amount of formic acid, a result which also supports the hypothesis that decomposition of low-molecular-weight carboxylic acids using WPO proceed by OH radical. It is reported that oxidation of carboxylic acids proceeds by consecutive oxidation of higher molecular weight to lower molecular weight carboxylic acids by OH radical [23]. Gomes et al. [24] also reported that propionic acid is oxidized to acetic acid by OH radical. The reactions involved are:



3.2. Degradation of PCBs in soil by WPO

To investigate the application of removal of PCBs in soil using WPO, oxidation of PCBs in soil were carried out using this process. After WPO, the remaining PCBs in soil were extracted by *n*-hexane and analyzed by GC. The amount of PCB removed was obtained by difference. Removal of PCB in soil after WPO for different type of PCBs is shown

Table 2
Removal of PCB after wet peroxide oxidation for different type of PCBs

Type of PCBs	Removal of PCBs (%)
KC-400	97
KC-500	94
KC-600	93

Duration of treatment was 30 min.

in Table 2. The removal percent of KC-400, KC-500 and KC-600 were 97, 94 and 93%, respectively, indicating that differences among the composition of PCBs in the soil has little effect on the oxidation process. It is known that the dielectric constant of water is decrease with the rise of temperature [25] and the solubility of organic substances increase due to the rise of hydrophobic property of water [26]. It is therefore considered that PCBs in soil were extracted into water from soil and they were decomposed in aqueous phase under the condition of this oxidation process.

Moreover, it is known that some metal oxides present in soils, such as MnO_2 and Fe_2O_3 , can behave as catalysts of various oxidation processes [27–29]. Consequently, it is presumed that during WPO, the metal oxides present in soil contributed to a more efficient removal of PCBs in soil. These results suggested that WPO under mild condition could be applied for treatment of soil contaminated with hazardous chemical compounds as well as treatment of wastewater.

4. Conclusions

From this study the following conclusions were derived:

1. Acetic and oxalic acids were mineralized using WPO under mild condition (150°C). TOC removal rate of acetic acid was highest in the solution of pH 2.5. However, TOC removal rate was decreased with the increase of pH and TOC were hardly removed in the solution of pH 7 and 10.
2. The decomposition rate of isobutyric acid by WPO was decreased by the presence of radical scavenger (*t*-BuOH). The results suggested that the decomposition of chemical substances using WPO proceeds by OH radical.
3. Applying WPO at 150°C in PCB polluted soil effectively removed PCB in the soil and, thus, gives a low cost remediation technique for soil contaminated with PCBs.

Acknowledgments

The authors wish to thank A.B. Hizon of Department of Material Science and Chemical System of Hiroshima University for her various help in this paper.

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