Available online at www.banglajol.info

Bangladesh J. Sci. Ind. Res. **50(3)**, 211-218, 2015

BCSIR

BANGLADESH JOURNAL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

E-mail: bjsir07@gmail.com

Degradation of carbofuran by V(IV)/H_2O_2 system in aqueous solution

F. Ferdoush[1]*, H. Katsumata[2]*, M. A. N. Russel[2], S. Kaneco[2], T. Suzuki[2] and K. Ohta[2]

[1] *Department of Chemistry for Materials, Graduate School of Engineering, Mie University, Tsu, Mie 514-8507, Japan*
[2] *Environmental Preservation Center, Mie University, Tsu, Mie 514-8507, Japan*

Abstract

Carbofuran is a kind of carbamate pesticide commonly used on major crops. The degradation of carbofuran by V (IV)/H_2O_2 system was investigated. The degradation system was strongly influenced by the pH, and initial concentration of VO^{2+}. The degradation efficiency of carbofuran at the difference pH with the initial concentration of VO^{2+} in system was observed. An initial carbofuran concentration of 10 mg L^{-1} was 95% degraded within 10 min at pH 2.6 with original VO^{2+} concentration of 5×10^{-4} M. The decrease of TOC content was observed during the catalytic process and the removal percentage was obtained about 20% after 24 h. Furthermore, therefore, this process based on the catalytic reaction of VO^{2+} and VO_2^+, and was responsible for the continuous production of hydroxyl radicals in such system. It has also proven that the degradation percentage increase when a little amount of L-ascorbic acid of 5×10^{-4} M was applied, the degradation increase up to 20% more at 10 min. A gas chromatography-mass spectrometry analysis showed the formation of seven products, on the basis of formation of time and its abounded, of all these intermediate products, a reaction mechanism path was submitted.

Keywords: Carbofuran; Fenton; Vanadium; Hydrogen per oxide; L-ascorbic acid

Introduction

Carbofuran (2, 3-dihydro-2, 2-dimethyl-7-benzofuranyl-methylcarbamate) is a pesticide world wide used to control soil and leaves-feeding insects and nematodes. It is an active acetylcholinesterase inhibitor and is toxic to fish and mammals (Katsumata, 2004). It has reported that more than five million pounds of carbofuran were applied in the United States in the year 1995. The use of carbofuran has received intensive concern not only due to its extensive use but also due to its high oral toxicity (Tennakone, 1997; Zhong, 1984; Ferguson, 1984). Due to its long persistence in water, it is increasingly detected in soil surface and wastewater. It exhibits refractory character to bio-degradation method (Benitez, 2001). Hence an effective and inexpensive technique is badly needed for treating such pollutant.

A verity of effective techniques for aqueous carbofuran has been proposed where Fenton has taken a lot of attention because of its low expense and easy technology. Among them Fe(II) based reagent and its modifications have received great attention as means for the degradation of pesticides by Fe(II)/H_2O_2 system. Less attention has been paid to similar reactions based on other transition metal where also Fenton-type reaction undergoes and can lead to the oxidation of different compound (Sutton, 1989; Watanabe, 1998). On this point the interest in transition metal –catalyzed oxidation by hydrogen peroxide has been increased. In part, this interest stems from the discovery of vanadium bromoperoxidase, a vanadium enzyme which catalyzes the oxidation of chloride, bromide, and iodide by hydrogen peroxide (Vilter *et al.,* 1990). All the halides except fluoride can be oxidized by hydrogen peroxide under neutral and acidic conditions. Again the catalytic hydroxylation also observed in The Milas reagent, which consists of V_2O_5 and aqueous H_2O_2 (Milas 1937 and The Merck Index, 1976), is indeed a very effective catalyst for hydroxylation of organic unsaturated substances such as benzene and many types of alkenes. Recently, the reactivity of vanadium (V) peroxide complexes is receiving renewed attention (Butler 1994; Clague, 1995). The formation of the red oxoperoxovanadium (V) ion and a variety of net two-electron oxidation reactions involving hydroxylation of benzene and other arenes and alkanes catalyzed by the peroxovanadium (V) complexes have been reviewed (Butler 1994), Vanadium exists in aqueous solution as tetravalent(IV) vanadyl (VO^{2+}) and pentavalent (V) vanadate (HVO_4^-,VO_3^-,and/or $H_2VO_4^-$) (djordejevitz *et al.,* 1991). A number of monomeric and polymeric tetravalent (V,IV) and pentavalent (V,V) vanadium species can be present in aqueous solutions, their composition depending upon pH and vanadium concentration. In this present study, we have investigated the degradation and mineralization of carbofuran in water by V (IV)/H_2O_2 system. Our this current work, as far from our knowledge is the first investigation to degrade EDC's like carbofuran by vanadium and hydrogen

---

*Corresponding author: E-mail: satuacct@yahoo.com; hidek@chem.mie-u.ac.jp per oxide in acidic condition. Here we also reported the effect of many factors such as pH value, initial concentration of V (IV), reaction time and H_2O_2 concentration on the degradation which were evaluated. It has also shown that the degradation performance increase when organic acid (L-ascorbic acid) added. The progress of mineralization of carbofuran was confirmed by the decrease of total organic carbon (TOC) content and the formation of inorganic ions. Furthermore, the products of carbofuran during this catalytic process have been identified by gas chromatography-mass spectrometry (GC/MS). Based on the formed intermediates, the degradation pathway of carbofuran was proposed.

Materials and methods

Materials

Carbofuran was purchased from Wako Pure Chemical Industries (Osaka, Japan) and was used as received (HPLC grade>98%). Analytical grade of hydrogen peroxide solution (30%,w/w/)was purchased from Wako Pure Chemical Industries (Osaka, Japan). V(IV) solution was prepared by dissolving $VOSO_4$•nH_2O. L-ascorbic acid was obtained from Nacali Tesque (Kyoto, Japan). All other chemicals and solvents were of the purest grade commercially available and were used without further purification. All aqueous solutions were prepared with ultra pure water, which was purified by an ultra pure water system (Addvantec MFS Inc.,Tokyo,Japan) resulting in a receptivity>18MΩcm.

Degradation procedure

Degradation was conducted in a Pyrex glass cell of 30 mL capacity. The reaction mixture inside the cell, consisting of 20 mL of carbofuran solution and the appropriate concentration of V(IV) solution, was continuously stirred with a magnetic bar. The pH of the sample solution was adjusted with H_2SO_4 and/or NaOH solution. The initial concentration of carbofuran in all experiments was 10 mg L^{-1} (4.5×10^{-5} mol L^{-1}). In the majority of the experiments, temperature was kept at 25±1 ˚C in a water bath.

Analyses

After mixing all reagents the sample solution was filtered through a 0.45 µm-membrane filter. The progress in the degradation of carbofuran was followed with a HPLC (JASCO Co., Tokyo, Japan) equipped with a JASCO UVIDEC-100-VI UV detector and a RP-18 GP 150 separation column (150 mm × 4.6 mm i.d., Kanto Chemicals, Tokyo, Japan) . The elution was monitored at 280 nm. The mobile phase was a mixture of acetonitrile and water (2/3, v/v), and was pumped at a flow rate of 0.7 mL min^{-1}. The progress of mineralization of carbofuran was monitored by measuring the TOC. TOC of the sample solution was measured with a Shimadzu TOC analyzer (TOC-V_E) based on CO_2 quantification by non-dispersive infrared analysis after high- temperature catalytic combustion.

The intermediate products during degradation of carbofuran were extracted by the solid-phase extraction (C18 disk, 3 M Empore). A mixture of dichloromethane and ethyl acetate (1/1, v/v) was used to elute the intermediate products. This solution was concentrated under nitrogen flow for the analysis of the by-products. A GC/MS (Shimadzu GC-MS–QP5050A) was used for separation and detection of the intermediate products. The GC was equipped with a HP-5 capillary column (30 m × 0.25 mm i.d.) in helium carrier gas (1.5 mL min^{-1}) and with spit less injection system. The GC oven temperature was programmed to hold 80 ˚C at a rate of 10 ˚C min^{-1} and from 210 to 310 ˚C from 5 min. the injector and interface temperatures were 220 and 250 ˚C, respectively. Mass spectra were obtained by the electron-impact (EI) mode at 70 eV using the full-scan mode.

Results and discussion

Effect of variables on the degradation of carbofuran

The pH influences both the metal chemistry in solution and the protonation/deprotonation of the metal oxide/hydroxide surface. It was showed that vanadium exists in different hydrolyzed forms depending upon its concentration and the pH of the system (Baes, 1976). The effect of pH was observed by changing the initial pH value of the pesticide solution from 2 to 5 and the results are illustrated in Fig.1. The degradation percentage of carbofuran was increased at

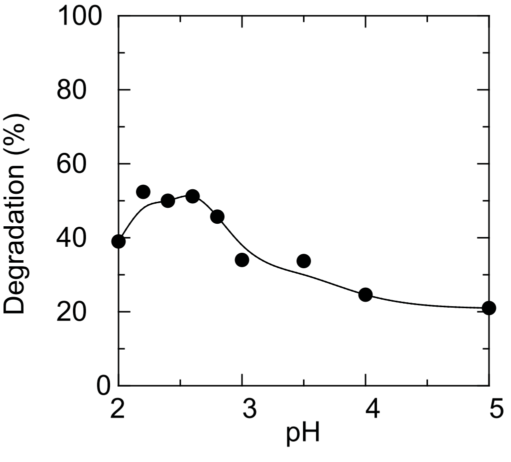


Fig. 1. Effect of pH on the degradation of carbofuran by V(IV)/H_2O_2 system ($[H_2O_2]_{t=0}$: 1.0×10^{-4} M ; $[V(IV)]_{t=0}$: 1.0×10^{-3} M ; Reaction time : 10 min)

low pH range from 2-3 and it gave the highest degradation at pH 2.6. After increasing pH from 4 the degradation rate decreased. Therefore, the rate of carbofuran disappearance is strongly affected by the pH –dependence.

Fig.2 shows the effect of VO^{2+} concentration on the degradation of carbofuran. The degradation rate of carbofuran increased with increasing initial VO^{2+} concentration. About 90% degradation of carbofuran obtained at 5 x 10^{-4}M concentration of VO^{2+} at pH 2.6 within 10 min and then further increase of vanadium concentration it gave a plateau curve of degradation. No further change observed in the degradation rate. This plateau assumed the stationary equilibrium between VO^{2+} and VO_2^+ that regenerates the absorbing species and gives an interesting catalytic aspect. That's why further application of vanadium no change occur. Under neutral and alkaline conditions, at vanadium concentrations below 0.5 mM, vanadium (V) exists primarily as a nonnumeric oxyanion (VO_4^{3-}, HVO_4^{2-}, $H_2VO_4^{2-}$) (Peacock, 2004; Naeem, 2007) while under acidic condition, the predominant species is *cis*-VO_2^+ (Mustafa, 2002). Under neutral and basic conditions, coordination of hydrogen peroxide to vanadate gives anionic peroxovanadates, with one to four coordinated peroxide ligands, and peroxodivanadates (Gresser *et al.,* 1985). Effect of initial H_2O_2 concentration on the degradation of carbofuran with the use of V (IV)/H_2O_2 system was investigated in the rage of 0 -1.0 × 10^{-2} M at pH 2.6. The degradation rate of carbofuran increased with increasing the initial concentration of H_2O_2 up to 2×10^{-4} M. After further application of H_2O_2 the degradation rate decreased. Therefore, the rate of carbofuran disappearance is dependent on the initial concentration of H_2O_2 in the solution as shown in Fig. 3.

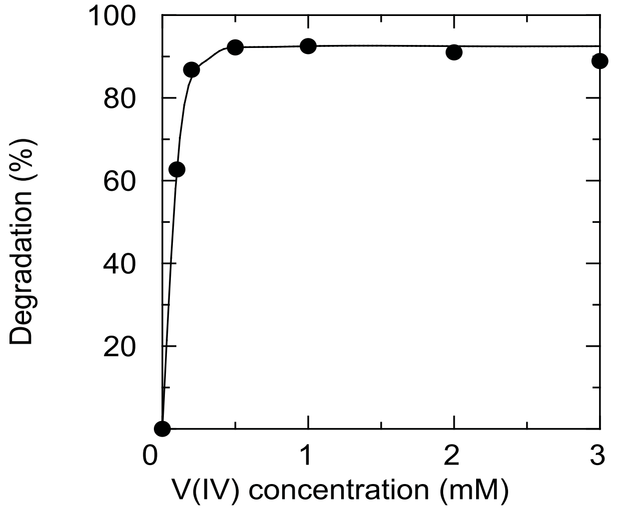


Fig. 2. Effect of V(IV) concentration on the degradation of carbofuran by V(IV)/H_2O_2 system (pH : 2.6; $[H_2O_2]_{t=0}$: 1.0×10^{-3} M; Reaction time : 10 min)

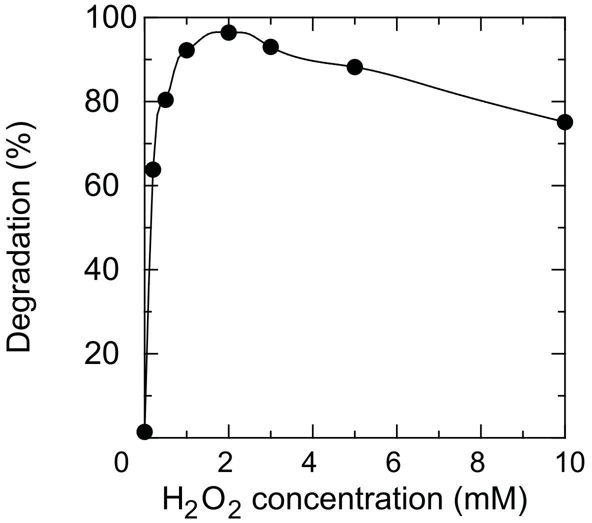


Fig. 3. Effect of H_2O_2 concentration on the degradation of carbofuran by V(IV)/H_2O_2 system (pH :2.6; $[V(IV)]_{t=0}$: 5.0×10^{-4} M; Reaction time :10 min)

Fig. 4 shows the degradation characteristic of carbofuran in the V(IV)/H_2O_2 system at pH 2.6 because of faster generation of ·OH radical than the conventional Fenton reaction. About 95% degradation has been completed within 40 min. These results could be an evidence for the extension of OH radical production from H_2O_2 by using other transition metal, such as V.

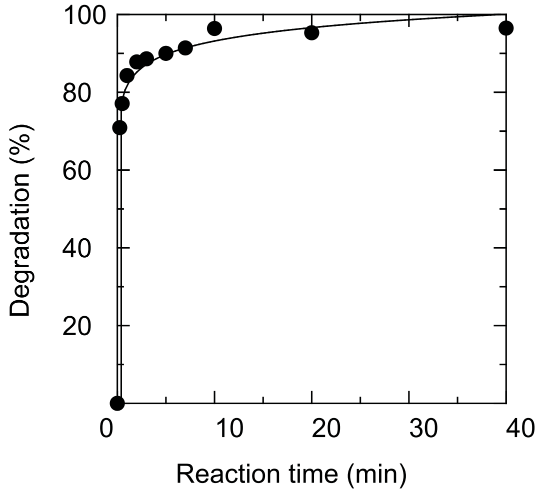


Fig. 4. Effect of reaction time on the degradation of carbofuran by V(IV)/H_2O_2 system (pH : 2.6; $[H_2O_2]_{t=0}$: 2.0×10^{-3} M; $[V(IV)]_{t=0}$: 5.0×10^{-4} M

The progress of the mineralization of the carbofuran solution was monitored by measuring the TOC. As shown in Fig.5, the complete mineralization of carbofuran was not achieved after 24h, although carbofuran was not present in the solution after the degradation time (Fig.4). This indicates that intermediate products were produced during the degradation processes which contain TOC. However, TOC rapidly decreased with decreasing the reaction time up to 3 h, and then decreased gradually. TOC remained about 80% after 24 h degradation. This result indicates the formation of persistent intermediate compounds, which are difficult to degrade by this degradation system. The complete mineralization of carbofuran was not achieved but AFT (Zhong, 1984) and photo-Fenton reaction (Howarth, 1979).).

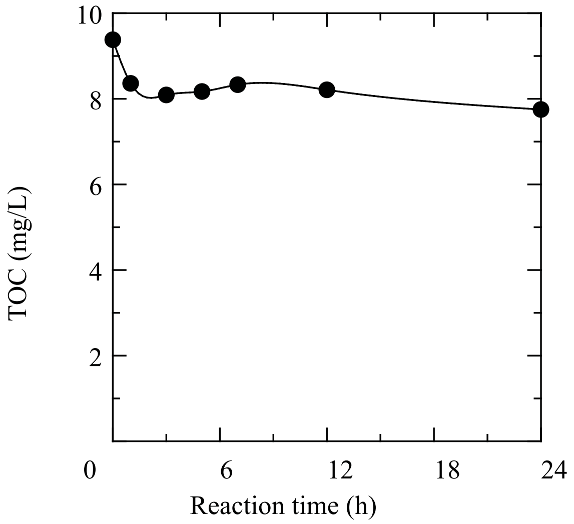


Fig. 5. Time evolution of TOC during degradation of carbofuran by V(IV)/H_2O_2 system (pH : 2.6; $[H_2O_2]_{t=0}$: 2.0×10^{-3} M; $[V(IV)]_{t=0}$: 5.0×10^{-4} M)

A metal-mediated site-specific mechanism for free radical-induced biological damage has also been proposed (Harrison *et al.,* 1985), where $OH^{\cdot}$ is formed site-specifically in the vicinity of the target molecule (Biol) and reacts at the site of its production.

$\text{Biol} + \text{Mn}^{+} \longrightarrow \text{Biol-Mn}^{+}$ ....(1)

$\text{Biol-Mn}^{+} + O_2^{\cdot -} \longrightarrow \text{Biol-M}^{(n-1)+} + O_2$ ....(2)

$\text{Biol-M}^{(n-1)+} + H_2O_2 \longrightarrow (\text{Biol-M}^{n+}..\text{HO}^{\cdot}) + OH^{-}$ ....(3)

Other reluctant present in cells (such as ascorbate) might be able to replace super oxide in the Haber-Weiss cycle and , therefore, promote the toxicity of a metal/hydrogen peroxide system. From Fig. 6 it has shown that degradation of carbofuran in the system of V(IV)/H_2O_2/L-ascorbic acid (where the initial concentration of $[V(IV)]_0=1.0\times10^{-4}$M; $[H_2O_2]_0= 1.0\times10^{-3}$M and [L-ascorbic acid]$_0=5.0\times10^{-4}$M). With the absent of L-ascorbic acid the degradation rate was 55% but at the present of L-ascorbic acid the degradation % increase up to 20 times more and reached to about 80%. So it could assume that with the present of L-ascorbic acid production of OH radical increase by the eq.(8)

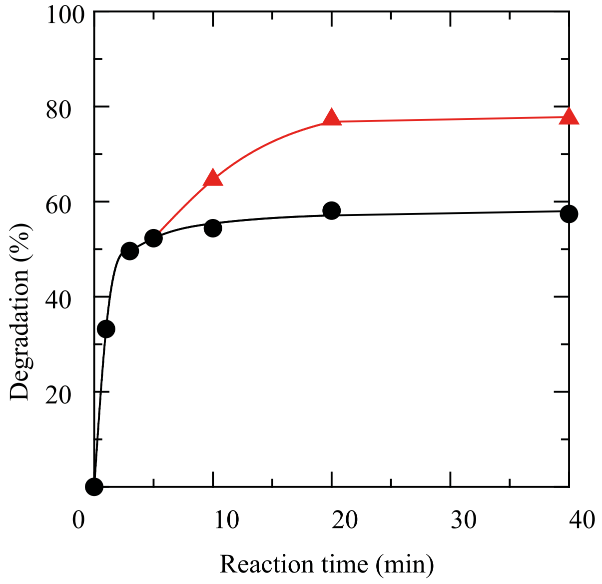
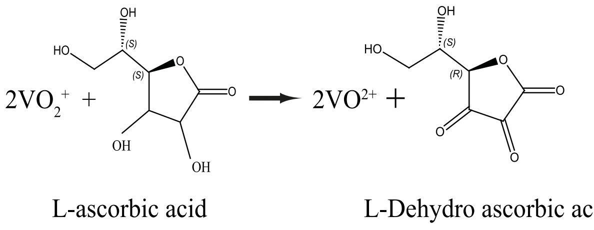


Fig. 6. Effect of L-ascorbic acid on the degradation characteristics of carbofuran by V(IV)/H_2O_2 system in the presence (▲) and absence(●) of L-ascorbic acid (pH: 2.6; $[H_2O_2]_{t=0}$: 1.0×10^{-3} M; $[V(IV)]_{t=0}$: 1.0×10^{-4} M; [L-ascorbic acid]$_{t=0}$: 0 or 5.0×10^{-3} M)

●: V(IV)/H2O2 system

▲: V(IV)/H2O2/L-ascorbic acid system

It has also been previously demonstrated that the combination of ascorbate and Cu^{2+} causes damage to macromolecule structures such as polysaccharides and proteins through generation of reaction oxygen species (Chevion *et al.,* 1988). From Fig.6 it can also assumed that TOC removal of carbofuran degradation with L-ascorbic could be more then with the absence of L-ascorbic acid.



.....(4)

Identification of products and degradation mechanism

A total of 7 major intermediates from the degradation of carbofuran by the system of V(IV)/H_2O_2 in 2-180 min were analyzed by GC-MS-EI. The GC-MS-EI results including the mass weight and retention time are summarized in table 1, where the intermediates were presumably subjected to cleavage of the side chains attached to the nitrogen atoms and aromatic ring.

Scheme 1 illustrates the proposed degradation mechanism of the V(IV)/H_2O_2 system. The results have been compared to those from previous research with analogous degradation mechanisms such as carbofuran degradation by hydrolysis (Uchida, 1986), photolysis (Shinar, 1983), TiO_2 photo catalysis (McMurray, 1992) and AFT treatment (Zhong, 1984), semiconductor oxides (Wang, 2002) and photolysis/photo catalysis of a similar herbicide, which supported our findings.

By mass spectrum confirmation and the authentic standard comparison, the product no. 7 was found to be carbofuran, the parent product. By interpreting the mass spectrum, the intermediate product no. 1 was the product due to the cleavage of the carbamate group from carbofuran. This product was also detected in (Uchida *et al.,* 1986) carbofuran degradation. The products no. 4 and 3 were identified as 2,2-dimethyl-2,3-dihydro-benzofuran-3,7-diol and 7-hydroxy-2,2-dimethyl-benzofuran-3-one, respectively. Both of them were formed by further continuous oxidization of 2,2-dimethyl-2,3-dihydro-benzofuran-7-ol (product-1) on the furan ring attacking by OH radical. Wang and Lemley (Zhong, 1984) also reported these products as intermediates of carbofuran by AFT treatment. Product 6 with the name of 2,2-dimethyl-3-oxo-2,3-dihydro-benzofuran-7-yl ester was obtained by the attack of OH radical on the furan ring of carbofuran as a primary intermediate product. After continuous degradation methyl-carbamic acid (product 5) and then product 3 obtained as secondary intermediate products. It was also assumed that product 4 could be further attacked of product 6 by OH radical after this it goes to continuous degradation. It was also assumed that product 1 was obtained by the cleavage of carbamate group from carbofuran (parent product) and further attack by OH radical to product 2. In addition to these 7 compounds, other degradation products still possibly exist in the degradation system but were not detected because of their low sensitivity in GC/MS.

Based on the intermediate products listed in Table 1 and the results obtained by other researchers (Shinar, 1983; Wang, 2002) the possible degradation pathway for carbofuran is proposed in Scheme 1. The first step of the catalytic reaction of carbofuran in water was similar to its base hydrolysis reaction. Namely, the carbonate group appeared to be the primary attack site by the hydroxyl radical and the group removed during this process. At the same time, carbamic acid was formed (Shinar, 1983). The product, which is known to be unstable (Mahalakshmi, 2007), rapidly degraded to methylamine a carbon dioxide, both of which are gases at room temperature. In addition formic acid 2, 2-dimethyle-2, 3-dihydro-benzofuran-7-yl ester, which formed through partial cleavage of the carbamate branch, has been found in AFT treatment (Zhong, 1984). After the carbamate group removal, the hydroxyl radicals continued attack by a substituting a hydroxyl group for one of the H atoms at C-3 position of the furan ring. Further oxidation eliminated another H atom at C-3 position and a carbonyl group was formed. The hydroxyl radicals attack at C-2 position of the furan ring and further lead to the cleavage of the ring and demethylation. The aromatic intermediate was presumable further oxidized through ring-rupturing reaction into aliphatic compounds (McMurray *et al.,* 1992). Based on the decrease of TOC during the degradation process (Fig. 5), it could be anticipated that the benzene ring was opened and the mineralization reaction to carbon dioxide occurred.

Verification of the proposed degradation pathways and end products.

The proposed mechanism was further verified by Fig. 7,

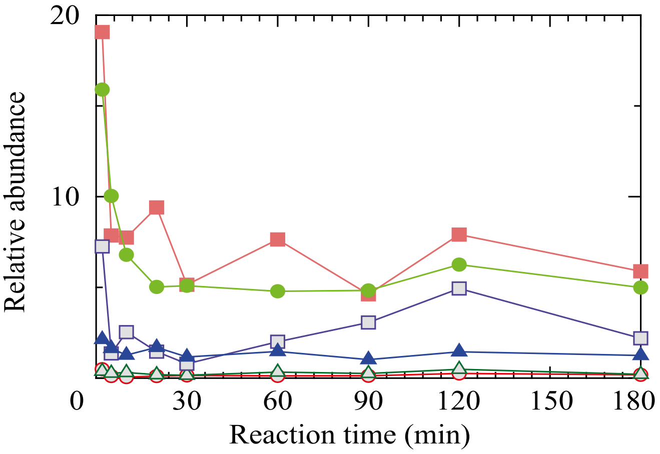
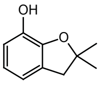
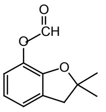
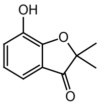
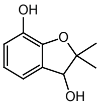
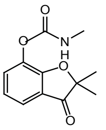
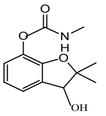
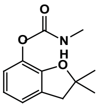
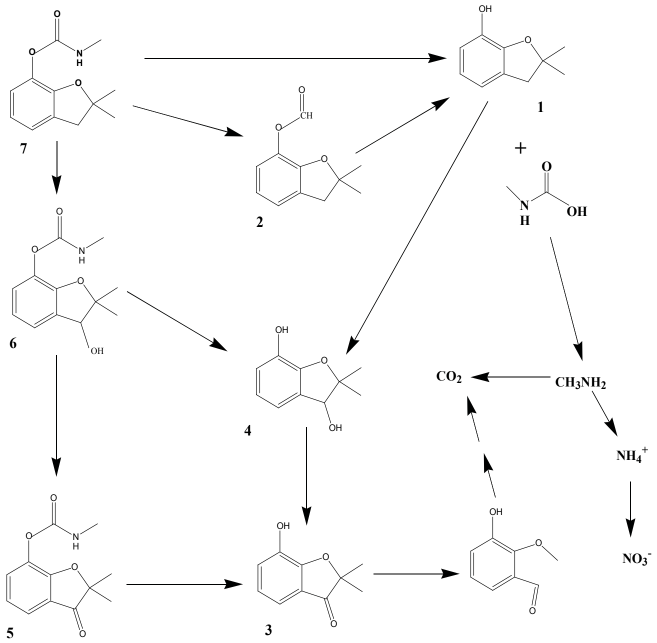


Fig. 7. Effect of reaction time on the intermediates in the V(IV)/H_2O_2 system (pH : 2.6; $[H_2O_2]_{t=0}$: 2.0×10^{-3} ; $[V(IV)]_{t=0}$: 5.0×10^{-4} M

● : 2,2-Dimethyl-2,3-dihydro-benzofuran-7-ol
▲ : 7-Hydroxy-2,2-dimethyl-benzofuran-3-one
■ : Methyl-carbamic acid 2,2-dimethyl-3-oxo- 2,3-dihydro-benzofuran-7-yl ester
○ : Formic acid 2,2-dimethyl-2,3-dihydro- benzofuran-7-yl ester
△ : 2,2-Dimethyl-2,3-dihydro-benzofuran- 3,7-diol
□ : Carbamic acid 3-hydroxy-2,2-dimethyl- 2,3- dihydro-benzofuran-7-yl ester

Table I. Degradation products from carbofuran

Peak No.	Retention time (min)	Molecular weight (m/z)	Compound
1	9.48	164	
2	10.96	192	
3	11.33	206	
4	12.00	180	
5	16.75	235	
6	17.45	237	
Carbofuran (7)	11.96	221	



Scheme 1. Proposed degradation mechanism of carbofuran in the aqueous system.

which shows the decay and generation of carbofuran, the 7 identified reaction intermediates and some unidentified low-molecular-weight intermediates and/or end products during the hydrogen peroxide catalyzed the degradation reaction. A study of the evolution profiles offers useful information in supporting the proposed mechanism. For instance, in Fig.7, the decay of carbofuran leads to the generation of primary intermediates such as compounds 2,5 and 6, whereas the decay of these two primary intermediates generates secondary intermediates such as compounds 1, 4, 3 and 7 respectively. The gradual increases of the small molecular weight compounds (i.e. NH_4^+, NO_3^-, CO_2, H_2O etc.) were probably the polar end products formed after the cleavage of the benzene ring. These end products are apparently resistant to free radical attack, as their ion intensity was maintained at high levels even at an extended reaction time of 20 h.

TOC analysis also carried out simultaneously with GC-MS-EI analysis to verify the conversions (decay/generation) of different molecular size species (see Fig. 5). The degradation of carbofuran could be analysis by degradation of carbofuran into high molecular intermediate compound and then to low molecular intermediate compound. From Fig. 7 it has shown that the relative abundance of primary and secondary intermediate products is high unto 3 h but the abundance decrease gradually, which support Fig. 5 that up to 24 h TOC was remain about 80% though carbofuran degraded to 95% within 40 min (Fig. 4).

Conclusion

The degradation of carbofuran in aqueous solution was investigated by VO^{2+} aqua complex. The degradation rate was strongly affected by the pH value and the initial concentration of V(IV) and H_2O_2. The almost 95% degradation was achieved for carbofuran after 10 min under the optimum conditions. It was also showed that at low pH (acidic) degradation performed very well. In this process optimum pH was taken 2.6. The disappearance of TOC was observed during the degradation process about 20 % though the degradation was found 95% at 10 min. Maybe degradation product contains TOC. By using L-ascorbic acid it was also found that at low concentration degradation rate increase 20 times high. Furthermore we have identified 7 kinds of intermediate products of carbofuran during the degradation process. The degradation pathway of carbofuran was proposed based on the identified by-produts.

Acknowledgement

We gratefully acknowledge the financial support of this study by Grant-in-Aid for Young Scientists (B) No. 18710063 from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

Benitez FJ, Acero JL, Real FJ, Rubio FJ and Leal AI (2001), The role of hydroxyl radicals for the decomposition of p-hydroxy phenylacetic acid in aqueous solutions, *Water Research*. **35:** 1338-1343.

Baes CF and Mesmer RE (1976), The Hydrolysis of Cations. Wile, New York.

Butler A, Clague MJ and Meister GE (1994), Vanadium Peroxide Complexes, *Chem.* Rev. **94:** 625-638.

Butler A, Walder JV (1993), Marine haloperoxidases, *Chem.* Rev. **93:** 1937-1944.

Campbell NJ, Dengel AC and Griffith WP (1989), Studies on transition metal peroxo complexes—X. The nature of peroxovanadates in aqueous solution, *Polyhedron,* **8:** 1379-1386.

Clague MJ and Butler A (1995), On The Mechanism of cis-Dioxovanadium(V)-Catalyzed Oxidation of Bromide by Hydrogen Peroxide: Evidence for a Reactive, Binuclear Vanadium(V) Peroxo Complex, *J.Am.Chem.Soc.* **117:** 3475-3484.

Chevion M (1988), A site-specific mechanism for free radical induced biological damage: The essential role of redox-active transition metals, *Free Radic. Biol. Med.* **5:** 27-37.

Chiou SH (1983), DNA- and Protein-Scission Activities of Ascorbate in the Presence of Copper Ion and a Copper-Peptide Complex, *J. Biochem.* **94:** pp. 1259–1267.

Catastini C, Sarakha M, Mailhot G and Bolte M (2002), Iron (III) aquacomplexes as effective photocatalysts for the degradation of pesticides in homogeneous aqueous solutions, *Sci. Total Environ.* **298:** 219-228.

Catasini C, Rafqah S, Mailhot G and Sarakha M (2004), Degradation of amitrole by excitation of iron(III) aquacomplexes in aqueous solutions, *J. Photochem. Photobiol. A: Chem.* **162:** 97-103.

Djordejevitz C and Wampler GL (1985), Antitumor-activity and toxicity of perxo heteroligand vanadates (V) in relation to biochemistry of vanadium. *J Inorg Biochem.* **25:** 51-55.

Ferguson PW, Dey MS, Jewell SA and Krieger RI (1984), Carbofuran metabolism and toxicity in the rat, *Toxicological* Sciences **4:** 14-21.

Gordon JA (1991), Use of vanadate as protein-phsphotyrosine phosphate inhibitor. *Methods Enzymol.* **201:** 478-82.

Gresser MJ and Tracey AA (1985), Vanadium (V) oxyanions: the esterification of ethanol with vanadate, *J.Am.Chem.Soc.* **107:** 4215-4220.

Goldstein S and Czapski G (1990), Transition metal ions and oxygen radicals, *Int. Rev.Exp. Pathol.* **31:** 133-164.

Harnung SC Larsen C and Pedersen E (1993), Structure of monovanadates in aqueous solution, *Acta Chem.Scand.* **47**: 674-682.

Hong A and Zeng Y (2002), Degradation of pentachlorophenol by ozonation and biodegradability of intermediates, *Water Res.* **36:** 4243-4254.

Huston PL and Pignatello JJ (1999), Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction, *Wat. Res.* **33:** 1238-1246.

Harrison AT and Howarth OW (1985), Oxygen-exchange and protonation of polyanions – a multinuclear magnetic - resonance study of tetradecavanadophosphate (9-) and decavanadate (6-), *J. Chem.Soc.,* Dalton Trans., 1173-1177.

Howarth OW and Hunt JR (1979), Peroxo-complexes of vanadium (V) – V-51 nuclear magnetic-resonance study, *J.Chem.Soc.*, Dalton Trans., 1388-1391.

Katsumata H, Matsuba K, Kaneco S, Suzuki T, Ohta K and yobiko Y (2004), Degradation of carbofuran in aqueous solution by Fe(III) aquacomplexes as effective photocatalysts, *J. Photochem. Photobiol., A: Chem.* **170:** 239-245.

Kuo WS and Lin Y (2000), Photocatalytic oxidation of xenobiotics in water with immobilized TiO_2 on agitator, *J. Environ. Sci. Health B.* **35:** 61-75.

Milas NA (1937), The Hydroxylation of Unsaturated Substances. III. The Use of Vanadium Pentoxide and Chromium Trioxide as Catalysts of Hydroxylation, *J. Am. chem. Soc.* **59:** 2342-2344.

Morinville A, Maysinger D and Shaver A (1998), From Vanadis to atropos:vanadium compounds as pharmacological tools in cell death signaling, *TIPS* **19:** 452-460.

Mustafa S, Nawab S and Dilara B (2002), The sorptionof divalent metal ions on $AIPO_4$, *J.Colloid Interface Sci.* **252:** 6-14.

Mahalakshmi M, Banumathi Arabindoo, Palanichamy M and Murugesan V (2007), Photocatalytic degradation of carbofuran using semiconductor oxides, *Journal of Hazardous Materials.* **143:** 240-245.

McMurray J (1992), Organic Chemistry,third ed., Brooks/Cole publishing, Belmont, CA.

Marx G and Chevion M (1985), Site-specific modification of albumin by free-radicals – reaction with copper(II) and ascorbate, *Biochem. J.* **236**: 397–400.

Naeem A, Westerhoff P and Mustafa S (2007), Vanadium removal by metal (hydr)oxide adsorbents, *Water research.* **41:** 1596-1602.

Peacock CL and Sherman DM (2004), Vanadium (V) adsorption onto goethite at pH 1.5 to 12; a surface complexation model based on ab initio molecular geometries and EXAFS spectroscopy, *Geochimica et Cosmochimica Acta.* **68:** 1723-1733.

Pope MT and Dale BWQ (1968), Isopoly-vanadates –niobates and –tantalates, *Quart. Rev.* **22**: 527-548.

Soedjak HS and Butlern A (1990), Chlorination catalyzed by vanadium bromoperoxidase, *Inorg.chem.* **29:** 5015-5017.

Sutton HC and Winterbourn CC (1989), On the participation of higher oxidation states of iron and copper in fenton reactions. *Free Radic. Biol. Med*. **6:** 53-60.

Shinar E, Navok T and Chevion M (1983), The analogous mechanisms of enzymatic inactivation induced by ascorbate and superoxide in the presence of copper, *J. Biol. Chem.* **258**, pp. 14778–14783.

Tennakone K, Tilakaratne CTK and Kottegoda IRM (1997), Photomineralization of carbofuran by TiO_2-supported catalyst, *Water Res.* **31:** 1909-1912.

The Merck Index, 9th Edition, 1976, ONR-61, many references cited therein on Milas hydroxylation of olefins.

Uchida K and Kawakishi S (1986), Oxidative Depolymerization of Polysaccharides Induced by the Ascorbic Acid-Copper Ion Systems, *Agric. Biol. Chem.* **50:** pp. 2579–2583.

Vilter H (1984), Peroxidases from phaeophyceae: A vanadium(V)-dependent peroxidase from Ascophyllum nodosum, *Phytochemistry* **23:** 1387-1390.

Watanabe T, Koller K and Messner K (1998), Copper-dependent depolymerization of lignin in the presence of fungal metabolite, pyridine, *J. Biotechnol.* **62:** 221-230.

Wever R and Krenn BE (1990), In; Vanadium in biological system; Chasteen,N.D., Ed.;Kluwer Academic Publishers: Dordrecht, pp. 81-97.

Wang Q and Lemley AT (2002), Oxidation of Carbaryl in Aqueous Solution by Membrane Anodic Fenton Treatment, *J. Agric. Food Chem.* **50**: 2331-2337.

Wu C, Lir X, Wei D, Fan J and Wang L (2001), Photosonochemical degradation of Phenol in water, *Water Res.* **35:** 3927-3933.

Zhong WZ, Lemley AT and Spalik J (1984), Quantitative determination of ppb levels of carbamate pesticides in water by capillary gas chromatography, *Journal of Chromatography A.* **299:** 269-274.

Received: 16 March 2014; Revised: 13 January 2015;

Accepted: 14 January 2015.