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Degradation of carbofuran in aqueous solution by Fe(III) aquacomplexes as effective photocatalysts

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Abstract

The photodegradation of carbofuran by excitation of iron(III) aquacomplexes was investigated under UV irradiation. The degradation rate was strongly influenced by the pH, and initial concentration of Fe(III). The degradation efficiency of carbofuran at the difference pH was in good agreement with the initial concentration of $Fe(OH)^{2+}$ in the solution. An initial carbofuran concentration of 10 mg L^{-1} was completely degraded within 50 min at pH 2.8 with original Fe(III) concentration of 8×10^{-4} mol L^{-1}. This degradation reaction was found to follow the first order kinetics law and the rate constant of $1.60 \times 10^{-3}\ s^{-1}$ was observed. The decrease of TOC content was observed during the photocatalytic process and the removal percentage obtained was about 70% after 25 h. Furthermore, ammonium ion as an end-product was detected in the solution. Therefore, this process based on the catalytic reaction of Fe(II, III) is responsible for the continuous production of hydroxyl radicals in such system. A gas chromatography-mass spectrometry analysis showed the formation of four photoproducts, such as 2,2-dimethyl-2,3-dihydro-benzofuran-7-ol, etc., revealing that the carbamate branch, C-3 and C-2 positions in furan ring were attack targets of hydroxyl radicals. Based on these results, the photocatalytic system could be useful technology for the treatment and the mineralization of compounds like carbofuran.

Keywords: Carbofuran; Fe(III); Aquacomplex; Photodegradation; Mineralization

1. Introduction

Carbofuran ($C_{12}H_{15}NO_3$) is a broad-spectrum insecticide and nematicide. Formulations of carbofuran are used in agricultural applications worldwide, and in 1995, more than five million pounds of carbofuran were applied in the United States [1]. The use of carbofuran has received intensive concern [2–4] not only due to its heavy use but also due to its high oral toxicity. The oral LD50 for carbofuran is 11 mg kg^{-1} body weight in rats [5]. As comparison, the LD50 for parathion, which is an extremely toxic organophosphorus pesticide, is 8 mg kg^{-1} whereas the LD50 for atrazine, which serves as an environmental endocrine disruptor, is 1300 mg kg^{-1} [6]. In addition, carbofuran is an active acetylcholinesterase inhibitor [7,8] and is toxic to fish and mammals [9]. Although in Japan, carbofuran is not registered as pesticide, one is well known to be a metabolite of carbosulfan, benfuracarb and furathiocarb, which are used in agricultural field. Therefore, it is very important to develop the treatment technology for carbofuran urgently.

Hydrolysis and microbial degradation of carbofuran appear to be important pathways in the environment. However, these processes commonly require long times for carbofuran in aqueous solutions. Reported half-lives of the compound in water ranged from 690 days at pH 5 to one week at pH 8 [10]. A variety of effective treatment techniques for aqueous

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carbofuran have been proposed by ultrasonic irradiation [1], direct photolysis [8], UV irradiation in the presence of ozone or Fenton reagent [11,12], anodic Fenton treatment (AFT) [13,14] and TiO_2 as a photocatalyst [2,15].

Recently, it has been pointed out the importance of systems with Fe(III) aquacomplexes for the photogeneration of hydroxyl radicals [16,17]. The interesting point in such system, compared to the photo-Fenton system is that no addition of hydrogen peroxide is needed. Fe(III) aquacomplexes absorb a fraction of the available solar light up to 500 nm [18,19], while TiO_2 photocatalysis can use photon with wavelength close to 380 nm [20]. Therefore, Fe(III)-mediated photogeneration process can be expected to an efficient and inexpensive method for wastewater treatment and promotes the rate of degradation of various organic pollutants. The excitation of $[Fe(OH)(H_2O)_5]^{2+}$, the dominant monomeric species of aqueous ferric iron in acidic solution, is as follows:

$$Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+} + OH^{\bullet}$$

$$Fe^{2+} \xrightarrow{h\nu, O_2} Fe^{3+}$$

where $Fe(OH)^{2+}$ refers to $[Fe(OH)(H_2O)_5]^{2+}$. Hydroxyl radicals are known to be reactive species involved in the advanced oxidation processes and, in most cases, to cause the complete mineralization of the pollutants. It has been reported that hydroxyl radicals generated upon excitation of Fe(III) aquacomplexes at low concentration were useful for the degradation and mineralization of the organic pollutants [16,17,21–26]. The advantages of the photodegradation process as an oxidative treatment are economical, rapid degradation and simple handling. Therefore, the photocatalytic reaction would be applied to wastewater treatment works as a new developing methodology for reducing levels of pesticides and endocrine disrupting chemicals.

In the present study, we have investigated the degradation and mineralization of carbofuran in water as a result of the excitation of Fe(III) aquacomplexes. Many factors, such as pH value, initial concentration of Fe(III), reaction temperature and light intensity, affected on the degradation were evaluated. 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 photoproducts of carbofuran during this photocatalytic process have been identified by gas chromatography-mass spectrometry (GC/MS). Based on the formed intermediates, the degradation pathway of carbofuran was proposed.

2. Experimental

2.1. Reagents

Carbofuran was purchased from Wako Pure Chemical Industries (Osaka, Japan) and was used as received (HPLC grade > 98%). Iron(III) solution was prepared by dissolving $Fe_2(SO_4)_3 \cdot H_2O$ obtained from Nacalai 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 ultrapure water, which was purified by an ultrapure water system (Advantec MFS Inc., Tokyo, Japan) resulting in a resistivity > 18 MΩcm.

2.2. Photodegradation procedure

Photodegradation 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 Fe(III) 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 $10\,mg\,L^{-1}$ ($4.5 \times 10^{-5}\,mol\,L^{-1}$). In the majority of the experiments, temperature was kept at $25 \pm 1\,°C$ in a water bath. The sample solution was illuminated with a Xe lamp (990 W, Ushio Electronics Co., Tokyo, Japan). In this case, the short UV radiation ($\lambda <$ 300 nm) was filtered out by the vessel wall. The intensity of the light was measured by a UV radiometer (UVR-400, Iuchi Co., Osaka, Japan).

2.3. Analyses

After illumination, the sample solution was filtered through a 0.45 μm-membrane filter. The decrease of UV absorption was monitored with an UVIDEC-610 double-beam spectrometer (JASCO Co., Tokyo, Japan). 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 $0.7\,mL\,min^{-1}$.

Concentration of the most photocatalytic species $[Fe(OH)^{2+}]$ was determined by using 8-hydroxyquinoline-5-sulfonic acid (HQSA) according to the published procedure [16,17]. The absorbance of $Fe(HQSA)_3$ complex was measured at 572 nm ($\varepsilon_{572\,nm} = 5000\,L\,mol^{-1}\,cm^{-1}$). Concentration of Fe(II) formed during the photocatalytic process was determined by the phenanthroline (phen) method. The absorbance of Fe(II)-phen complex was taken at 510 nm ($\varepsilon_{510\,nm} = 1.118 \times 10^4\,L\,mol^{-1}\,cm^{-1}$).

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 progress of ammonium ion formation was obtained by ionic chromatography using a Shimadzu LC-10AT VP pump equipped with a Shimadzu COD-6A conductivity detector and a Shodex catonic column (IC YK-421). Similarly, nitrate ion formation was also analyzed by ionic chromatography using a Hitachi L-6000 pump equipped with a Hitachi L-3270 conductivity detector and a Hitachi anionic column (#2710-SK-IC).

The intermediate products during photodegradation 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 5050 A) 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 splitless injection system. The GC oven temperature was programmed to hold 80 °C for initial 5 min, to increase from 80 to 210 °C at a rate of 10 °C min^{-1} and from 210 to 310 °C at a rate of 30 °C min^{-1} and to hold at 310 °C for 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.

3. Results and discussion

3.1. Effect of variables on the degradation of carbofuran

The time courses of the UV absorption spectra of carbofuran solution in the photocatalytic degradation by $\mathrm{Fe(OH)^{2+}}$ was observed in the range of 0–50 min. The experimental conditions were $[\mathrm{Fe(III)}]_0 = 8.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$, pH = 2.8 and light intensity = 2.0 mW cm^{-2}. Other conditions were described in Section 2. The UV spectrum of carbofuran solution before illumination presented one absorption maximum at 280 nm. The disappearance of 280 nm absorption band was observed with increasing reaction time. Consequently, it was confirmed that the monomeric Fe(III), $\mathrm{Fe(OH)^{2+}}$, was effective photocatalyst for the decomposition of carbofuran under UV illumination.

Effect of pH on the degradation of carbofuran by use of Fe(III) aquacomplex as a photocatalyst was investigated over the pH range of 1.0–4.0 because much precipitation of $\mathrm{Fe(OH)_3}$ occurred above pH 4.0. These results are shown in Fig. 1 together with the initial concentration of $\mathrm{Fe(OH)^{2+}}$ at the different pH. The degradation percentage of carbofuran rapidly increased with increasing pH value up to 2.8, decreasing at pH above 2.8. Therefore, the rate of carbofuran disappearance is strongly affected by the pH-dependence. In other words, its rate is dependent on the initial concentration of $\mathrm{Fe(OH)^{2+}}$ in the solution as shown in Fig. 1. In our experimental conditions, 75% of $\mathrm{Fe(OH)^{2+}}$ with [Fe(III)total] $= 8 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ was formed at pH 2.8, i.e. at the beginning of the irradiation $[\mathrm{Fe(OH)^{2+}}] = 6.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$. These results are related to the nature of Fe(III) hydroxo species present in solution, $\mathrm{Fe(OH)^{2+}}$ being the one with the largest light absorption coefficient and quantum yield for $\mathrm{OH^{\bullet}}$ radical production, along with Fe(II) generation, in the range 280–370 nm [18,19]. Furthermore, it was shown that the higher initial quantum yield of degradation compounds was obtained at a higher percentage of $\mathrm{Fe(OH)^{2+}}$ [16,24]. Therefore, the results of pH-dependence obtained in the photocatalytic degradation of carbofuran by $\mathrm{Fe(OH)^{2+}}$ were reasonable. Consequently, pH 2.8 was selected for the optimum experimental conditions.

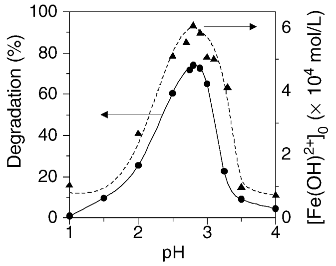


Fig. 1. Effect of pH on carbofuran degradation by Fe(III) aquacomplexes and on $\mathrm{Fe(OH)^{2+}}$ formation. Initial concentration of Fe(III): $8 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$; light intensity: 2.0 mW cm^{-2}; reaction time: 10 min.

Effect of temperature on the degradation of carbofuran in the presence of Fe(III) was examined in the range of 10–40 °C. Although the degradation efficiency of carbofuran gradually increased as the temperature increased, the appreciable change was not observed in the temperature range. Since the photonic activation seems to occur at a considerably high speed, the photocatalytic system may be not so sensitive to the temperature [27]. Hence, all subsequent experiments were performed at 25 °C, considering practical application and the operating cost for the degradation system.

Influence of light intensity on the photocatalytic decomposition of carbofuran was carried out in the range of 0–2.5 mW cm^{-1}. The degradation rate of carbofuran rapidly increased with increasing light intensity up to 1.5 mW cm^{-1}, and then the rate gradually increased. Ollis [28] reviewed the effect of light intensity on the kinetics of photocatalysis and mentioned that (i) at low light intensities, the rate would increase linearly with increasing light intensity; (ii) at middle light intensities, the rate would depend on the square root of the light intensity; and (iii) at high light intensities, the rate would be independent of light intensity. These phenomena were in good agreement with the present results in the photocatalytic degradation of carbofuran. All subsequent degradation of carbofuran was carried out under light intensity of 2.0 mW cm^{-1} corresponding to the intensity of sunny day.

Fig. 2 shows the effect of Fe(III) concentration on the degradation of carbofuran. The degradation of carbofuran scarcely occurred within 60 min in the absence of Fe(III). On the other hand, the degradation rate of carbofuran increased with increasing initial Fe(III) concentration. Complete degradation of carbofuran under these conditions was reached at Fe(III) concentration of above $8 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ within 60 min, while low concentration of Fe(III) did not allow achieving complete degradation in this process. This

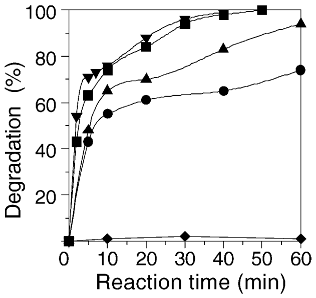


Fig. 2. Effect of Fe(III) initial concentration on carbofuran degradation by Fe(III) aquacomplexes. (♦): 0; (●): 0.2; (▲); 0.4; (■): 0.8; (▼): 1.6 × 10^{-3} mol L^{-1}. pH: 2.8; light intensity: 2.0 mW cm^{-2}.

can be explained by the effect of the additionally produced OH$^\bullet$ radicals. At the same time, the concentration of Fe(II) formed during the process was measured using phenanthroline method (Fig. 3). Concentration of Fe(II) increased up to 1.8 × 10^{-4} mol L^{-1}, a plateau value reached after about 100 min of irradiation, while the degradation of carbofuran and its photoproducts keeps going on. This plateau can be assigned to a photostationary equilibrium between Fe(II) and Fe(III) that regenerates the absorbing species and gives an interesting catalytic aspect [22,23]. Accordingly, a continuous formation of OH$^\bullet$ radicals is observed allowing the complete mineralization of carbofuran.

The photocatalytic reaction of carbofuran with Fe(OH)$^{2+}$ under these experimental conditions presented in Fig. 2 was estimated to follow a pseudo first-order kinetic law, according to the equation,

$$\frac{dC_{\mathrm{subs}}}{dt} = -k_{\mathrm{obs}}C_{\mathrm{subs}}$$

where C_{subs} is carbofuran concentration and k_{obs} is the observed first-order rate constant. In order to confirm the speculation, ln(C/C_0) was plotted as a function of the reaction time. The calculated results indicated that the first-order model gives a better fit (data not shown). Therefore, the primary photodegradation dynamics of carbofuran would be pseudo first-order kinetics. The substrate half-lives, 90% conversion times and first-order rate constant for the degradation of carbofuran calculated from the equation are summarized in Table 1. The concentration of Fe(III) affected the degradation of carbofuran during the photocatalytic reaction as described above. As seen in Table 1, the increasing of Fe(III) concentration from 2 × 10^{-4} to 1.6 × 10^{-3} mol L^{-1} clearly intensified the degradation of carbofuran. The 90% conversion time for carbofuran was shortened by factor 5 (from 5200 to 1100 s) in the photocatalytic process. Similar phenomena were reported by many researchers [29–32], who suggested positive effects on the Fenton and photo-Fenton treatments by the increasing of Fe(II) and H_2O_2 concentrations.

Table 1
Pseudo-first order constant (k), correlation coefficient (R^2), half-lives ($t_{1/2}$) and 90% degradation ($t_{90\%}$) times of carbofuran degradation

[Fe(III)]$_0$	k (s^{-1})	R^2	$t_{1/2}$ (s)	$t_{90\%}$ (s)
2.0 × 10^{-4}	4.43 × 10^{-4}	0.990	1600	5200
4.0 × 10^{-4}	8.32 × 10^{-4}	0.960	830	2800
8.0 × 10^{-4}	1.60 × 10^{-3}	0.954	430	1400
1.6 × 10^{-3}	2.12 × 10^{-3}	0.944	330	1100

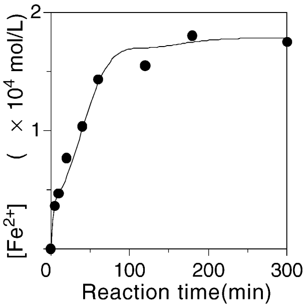


Fig. 3. Formation of Fe(II) during the photocatalytic process as a function of reaction time. Initial concentration of Fe(III): 8 × 10^{-4} mol L^{-1}; pH: 2.8; light intensity: 2.0 mW cm^{-2}.

Fig. 4 shows a comparison of the degradation of carbofuran in both dark and light environment. In the absence of Fe(III), the degradation of carbofuran was slightly observed after 60 min of irradiation (<5%). On the other hand, in the presence of Fe(III) no decrease of carbofuran was observed in the dark after 60 min. Furthermore, the degradation of carbofuran with Fe(III) in the dark was evaluated. For this case, although about 60% of carbofuran was degraded after 60 min at pH 2.8, complete degradation was difficult to achieve. This phenomenon was presumably due to the redox reaction (not radical reaction) of carbofuran with Fe(III). These results indicate that the photocatalytic reaction using Fe(III) aquacomplex is useful for the treatment of wastewater containing carbofuran.

3.2. Mineralization

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 60 min, although carbofuran was not present in the solution after the irradiation time. This difference

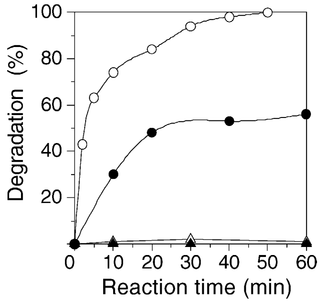


Fig. 4. Degradation characteristics of carbofuran under dark and light conditions. (▲): dark; (△): light; (●): dark/Fe(III); (○): light/Fe(III). Initial concentration of Fe(III): 8 × 10^{-4} mol L^{-1}; pH: 2.8; light intensity: 2.0 mW cm^{-2}.

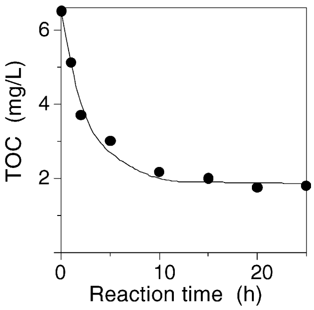


Fig. 5. Time evolution of TOC during irradiation of carbofuran. Initial concentration of Fe(III): $8 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$; pH: 2.8; light intensity: $2.0\,\mathrm{mW\,cm^{-2}}$.

indicates that intermediate products were produced during the photocatalytic process. The generated photoproducts are attacked in their turn by hydroxyl radicals which are formed in a continuous manner via a homogeneous photocatalytic process involving Fe(III, II) [23,25]. However, TOC rapidly decreased with decreasing the reaction time up to 10 h, and then decreased gradually. TOC remained about 30% after 25 h irradiation. This result indicates the formation of persistent intermediate compounds, which are difficult to degrade by this photocatalytic system. The complete mineralization of carbofuran was not achieved by AFT [13] and photo-Fenton reaction [11]. However, carbofuran might be able to be completely mineralized by longer irradiation since the decrease of TOC was continued after 25 h.

The formations of ammonium and nitrate ions during the photocatalytic process as a function of reaction time are presented in Fig. 6. Tennakone et al. [2] studied the photomineralization of carbofuran using TiO_2 and found ammonium, nitrite and nitrate in solution at the termination photolysis. Detection of nitrite and nitrate during sonolysis of carbofuran has been reported [1]. This information suggested that this photocatalytic degradation of carbofuran would also yield these ions as breakdown products. However, nitrate ion was not formed from carbofuran in this system within 25 h, as seen in Fig. 6. On the other hand, ammonium ion was rapidly formed with increasing reaction time up to 10 h and then it was reached plateau. After 25 h irradiation, $1.3 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ of ammonium ion was produced, corresponding to ca. 30% of initial nitrogen from carbofuran. Therefore, a part of nitrogen atoms from carbofuran could be mineralized by this photocatalytic system. This incomplete nitrogen mass balance has been frequently observed in similar process [33–35] and indicates that other nitrogen-containing compounds must be present in the solution or evaporated during the process. The possible explain of alkyl nitrogen, cianno derivatives [36], carbamic acids and amines could explain the residual TOC, but the analytical procedures applied to the samples have not been able to detect them. Other authors described N_2 [37] and/or hydroxylamine [38] evolving from nitrogen-containing compounds degraded by photocatalysis.

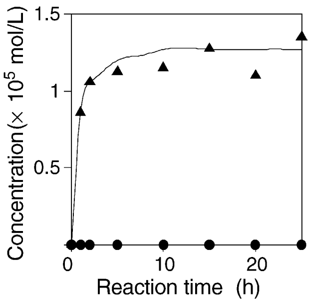
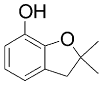
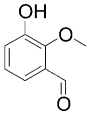
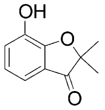
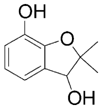
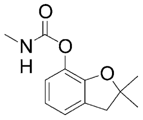


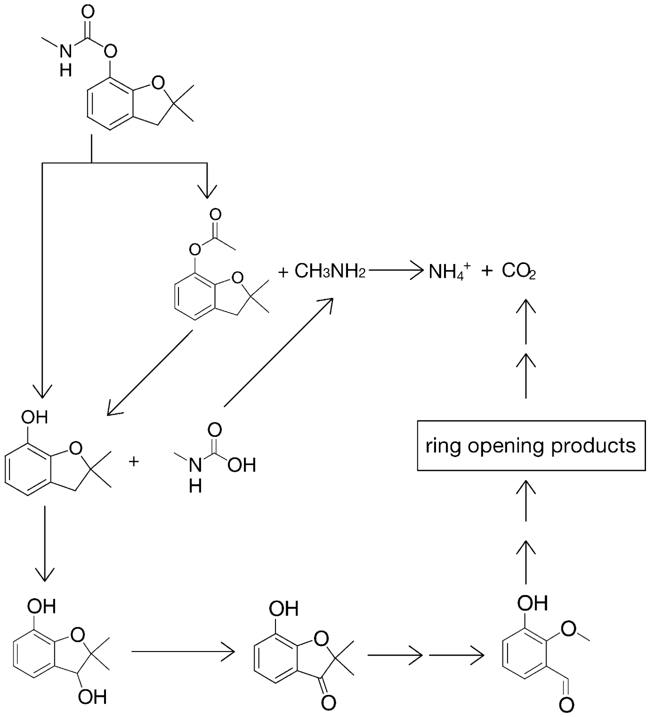
Fig. 6. Time evolution of ammonium and nitrate ion concentrations during irradiation of carbofuran. (●): nitrate ion; (▲): ammonium ion. Initial concentration of Fe(III): $8 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$; pH: 2.8; light intensity: $2.0\,\mathrm{mW\,cm^{-2}}$.

3.3. Identification of photoproducts and degradation mechanism

The photoproducts formed in this photocatalytic degradation of carbofuran in the aqueous solution for 20 min were investigated by GC/MS analysis. Four products were identified by the molecular ion and mass fragment ions, and also through comparison with NIST library data. Table 2 summarizes the molecular weight obtained for these photoproducts. The similarities of these compounds to the NIST library data were more than 85%. By mass spectrum confirmation and the authentic standard comparison, the product 5 was found to be carbofuran, the parent compound. By interpreting the mass spectrum, the photoproduct 1 was assigned to 2,2-dimethyl-2,3-dihydro-benzofuran-7-ol, which was the product due to the cleavage of the carbamate group from carbofuran. This photoproduct was also detected in the hydrolysis [4], photolysis [8], TiO_2 photocatalysis [15] and AFT treatment [13] of

Table 2
Photoproducts obtained by degradation of carbofuran

Product no.	Retention time (min)	Molecular weight (*m*/*z*)	Photoproduct
1	8.26	164	
2	9.72	152	
3	9.93	178	
4	10.50	180	
5	14.18	221	



Scheme 1. Proposed degradation mechanism of carbofuran by Fe(III) aquacomplexes.

carbofuran. The photoproducts 3 and 4 were identified as 7-hydroxy-2,2-dimethyl-benzofuran-3-one and 2,2-dimethyl-2,3-dihydro-benzofuran-3,7-diol, respectively. Both of them were formed by further oxidizing 2,2-dimethyl-2,3-dihydro-benzofuran-7-ol (photoproduct 1) on the furan ring. Wang and Lemley [13] also reported these products as intermediates of carbofuran by AFT treatment. The photoproduct 2 was attributed to 3-hydroxy-2-methoxy-benzaldehyde, which was formed by opening the furan ring and demethylation from 7-hydroxy-2,2-dimethyl-benzofuran-3-one (photoproduct 3). In addition to these four compounds, other degradation products still possibly exist in the photocatalytic system but were not detected because of their low concentration, extraction efficiency and limited sensitivity in GC/MS.

Based on the intermediate products listed in Table 2 and the results obtained by other researchers [8,13], the possible degradation pathway for carbofuran is proposed in Scheme 1. The first step of the photocatalytic reaction of carbofuran in water was similar to its base hydrolysis reaction. Namely, the carbamate 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 [8]. The product, which is known to be unstable [39], rapidly degraded to methylamine and carbon dioxide, both of which are gases at room temperature. It is considered that the nitrogen mass balance was incompleted (Fig. 6) in order to these facts. In addition, formic acid 2,2-dimethyl-2,3-dihydro-benzofuran-7-yl ester, which formed through partial cleavage of the carbamate branch, has been found in AFT treatment [13] although this compound was not detected in this study. 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 presumably further oxidized through ring-rupturing reaction into aliphatic compounds [40–43]. Based on the decrease of TOC during the photocatalytic process (Fig. 5), it could be anticipated that the benzene ring was opened and the mineralization reaction to carbon dioxide occurred.

4. Conclusions

The photodegradation of carbofuran in aqueous solution was investigated by Fe(III) aquacomplex. The degradation rate was strongly affected by the pH value and the initial concentration of Fe(III). The complete degradation was achieved for carbofuran after 50 min under the optimum conditions. It was found that the primary photocatalytic decomposition reaction followed a pseudo first-order kinetic law and the rate constant, k, was $1.60 \times 10^{-3}\,\mathrm{s}^{-1}$.

The disappearance of TOC was observed during the photocatalytic process and the remaining TOC achieved $1.8\,\mathrm{mg\,L}^{-1}$ after 25 h (about 70% mineralization). The formation of ammonium ion was also observed. Therefore, we could reach the mineralization of the starting compound. Furthermore, we identified four kinds of intermediate products of carbofuran during the photocatalytic process. The degradation pathway of carbofuran was proposed based on the identified by-products.

Acknowledgments

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