

Photodegradation of Carbofuran in Aqueous Solution by Fe(III) Aquacomplexes

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Introduction

Carbofuran (C₁₂H₁₅NO₃) is a broad spectrum insecticide and nematocide. The oral LD50 for carbofuran is 11 mg kg⁻¹ body weight in rats [1]. 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 [2]. In addition, carbofuran is an active acetylcholinesterase inhibitor [3] and is toxic to fish and mammals [4]. Therefore, it is very important to develop the treatment technology for carbofuran urgently.

Recently, it has been pointed out the importance of systems with Fe(III) aquacomplexes for the photogeneration of hydroxyl radicals [5]. The interesting point in such system, compared to the photo-Fenton system is that no addition of hydrogen peroxide is needed.

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. The many factors affected on the degradation were evaluated. The progress of mineralization of carbofuran was monitored by total organic carbon (TOC) content and ionic chromatography. Furthermore, the photoproducts of carbofuran during this photocatalytic process have been identified by gas chromatography-mass spectrometry (GC/MS). The degradation pathway was proposed on the base of the evidence of the intermediate formation.

Experimental

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 (10 mg L⁻¹) and the appropriate concentration of Fe(III) solution, was continuously stirred with a magnetic bar. The pH of the sample solution was adjusted with H₂SO₄ and/or NaOH solution. In the majority of the experiments, temperature was kept at 25 ± 1°C with a water bath. The sample solution was illuminated with a Xe lamp. The intensity of the light (2.0 mW cm⁻²) was measured by a UV radio meter.

The progress in the degradation of carbofuran was followed with a HPLC equipped with a UV detector (280 nm). Concentration of Fe(OH)²⁺ was determined by using HQSA. Concentration of Fe(II) formed was determined by the phenanthroline method. The progress of mineralization of carbofuran was monitored by measuring the TOC. TOC of the sample solution was measured with a TOC analyzer. The progress of ammonium and nitrate ion formations was obtained by ionic chromatography equipped with a conductivity detector. The intermediate products during photodegradation of carbofuran were extracted by the solid phase extraction. A mixture of dichloromethane and ethyl acetate (1/1, v/v) was used to

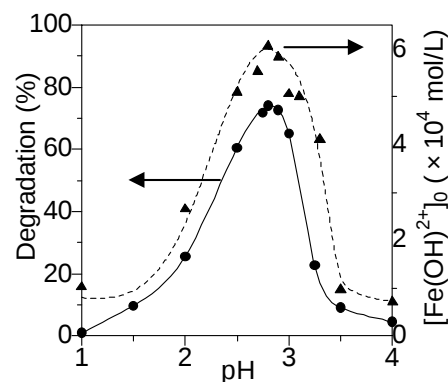


Fig. 1. Effect of pH on carbofuran degradation by Fe(III) aquacomplexes and on Fe(OH)²⁺ formation. Initial concentration of Fe(III): 8×10⁻⁴ mol L⁻¹; light intensity: 2.0 mW cm⁻²; reaction time: 10 min.

elute the intermediate products. A GC/MS was used for separation and detection of the intermediate products.

Results and Discussion

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. These results are shown in Fig. 1, together with the initial concentration of 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. Effect of Fe(III) concentration on the degradation of carbofuran was examined. 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 8×10⁻⁴ mol L⁻¹ within 60 min, while low concentration of Fe(III) did not allow achieving complete degradation in this process. Concentration of Fe(II) increased with increasing the reaction time up to 100 min and then the concentration reached a plateau value.

The progress of the mineralization of the carbofuran solution was monitored by measuring the TOC. 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 indicates that intermediate products were produced during the photocatalytic process. TOC rapidly decreased with decreasing the reaction time up to 10 h, and then decreased gradually. TOC remained about 30% after 25 h irradiation. On the other hand, the formation of ammonium ion during the photocatalytic process was observed. Therefore, carbofuran could be mineralized by the photocatalytic process. Furthermore, 4 intermediate products were detected and the degradation pathway of carbofuran was proposed on the basis of the by-products.

References

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