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CONTENT

OPTIMIZATION STUDY OF THE AZAMETHIPHOS DEGRADATION USING CHLORINE DIOXIDE

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ABSTRACT

In the present study, the degradation of azamethiphos using chlorine dioxide was studied. The optimization of the azamethiphos degradation in terms of chlorine dioxide dosage, different time of degradation and at different pH values, was performed in system with deionized water. The degradation was monitored using high performance liquid chromatography (HPLC-DAD) analysis. It was found that complete degradation was achieved with optimal concentration of 5 mg/dm^3 chlorine dioxide at concentration of azamethiphos solution of 10 mg/dm^3 under light after 1 h treatment and also at pH 9.00 after 30 min treatment at the same concentration of chlorine dioxide. Gas chromatography coupled with triple quadrupole mass detector (GC-QQQ) was also used to identify degradation products of azamethiphos.

INTRODUCTION

Organophosphorous pesticides have been intensively applied worldwide in agriculture as an alternative to organochlorides. Azamethiphos is a systemic organothiophosphorous pesticide that is widely used to kill mites and insects on contact. Pesticide removal from wastewater is today one of the major environmental problems [1-3]. To minimize the risk of pesticide pollution, it is advisable to develop new technologies that would promote easy degradation pesticides. This is the first study on degradation of azamethiphos with chlorine dioxide. Chlorine dioxide is a strong oxidizing agent, bactericide, fungicide, algaecide, and antiseptic. It is a powerful oxidant which can remove pesticides and is effectively used as a disinfecting/oxidizing agent in the treatment of drinking water. The aim of this study was to investigate and optimize degradation of azamethiphos with chlorine dioxide in deionized water and identify degradation products of pesticide using GC-QQQ analysis.

EXPERIMENTAL

Azamethiphos was supplied from Sigma-Aldrich. The pure stock solution of chlorine dioxide (3 g/dm^3) was prepared by mixing sodium chlorite (Superior Water Disinfection Power, TwinOxide®) and sodium bisulphate (Superior Water Disinfection Power, TwinOxide®), in 1 dm^3 of distilled water. The exact concentration of chlorine dioxide in the stock solution was quantified using 4500-ClO_2 DPD method according to the Standard Method. Sodium-thiosulfate ($Na_2S_2O_3$, p.a., Merck) was used as received.

Degradation of azamethiphos solution by chlorine dioxide was performed in a 200 mL closed flasks on rotary shaker. Different dosage of ClO_2 stock solution (5 mg/dm^3 and 10 mg/dm^3) was added in pesticide solution (10 mg/dm^3) to initiate the reaction at room temperature. In different time intervals (30 min, 1 h, 2 h, 3 h, 6 h and 24 h) 10 mL of reaction mixture was taken and chlorine dioxide residues were quenched with $Na_2S_2O_3$ prior to HPLC analysis, which was used to evaluate degradation efficiency. Light conditions were provided using Osram Ultra-Vitalux (300 W) which was used for sunlight simulation and which has radiated power from 315 – 400 nm (UVA) of 13.6 W and from 280 – 350 nm (UVB) of 3.0 W, and dark conditions were provided by placing reaction vessels into enclosed space without any light during reaction period.

Degradation efficiency of pesticide was monitored using high-performance liquid chromatograph (HPLC; Thermo Ultimate 3000 RS) with photodiode array detection (DAD) on Hypersil Gold aQ C18 analytical column (150 mm x 3 mm, 3 μm) at 40 °C. Mobile phase consisted of 0.1% formic acid water solution (Fluka analytical HPLC grade) as component A and acetonitrile (> 99.9%, Sigma-Aldrich HPLC grade) as component B. The chromatographic elution was conducted at flow rate of 0.6 mL/min in gradient mode: 0.0-0.5 min 5% B, 0.5-6.0 min from 5% to 45% B, 6.0-8.0 min from 45% to 95 % B, 8.0-8.1 min from 95% to 5% B, then 5% B for 6 min. Injection volume was 25 μL. Detector was set at 195 nm.

Major degradation products of azamethiphos were analyzed by Agilent Technologies gas chromatograph with triple quadrupole mass detector (GC-QQQ; 7890B/7010). Samples for GC-QQQ analysis were prepared by extraction with methylene chloride (>99.5 %; LGC) and concentrating the organic extract to 1 mL.

RESULTS AND DISCUSSION

This paper studies the reactivity of azamethiphos with chlorine dioxide under conditions that have relevance in the water treatment. In this study, optimization of chlorine dioxide dosage (5 and 10 mg/dm^3), different time of degradation (30 min, 1 h, 2 h, 3 h, 6 h and 24 h) and at different pH values (3.00, 7.00 and 9.00) were performed in system with deionized water. Chlorine dioxide was added in deionized water solution of pesticide. Concentration of pesticide was 10 mg/dm^3.

The percentage of degradation was monitored by HPLC analysis on the basis of the pesticide peak area reduction after degradation compared to the peak area of the pesticides prior to degradation. The HPLC results showed that chlorine dioxide was effectively used for degradation of azamethiphos. The high degradation efficiency (88-100%) was achieved under different experimental conditions.

The results of HPLC analysis for azamethiphos showed that at a concentration of 5 mg/dm^3 ClO_2, high efficiency of degradation was achieved in the light and in the dark (in the light, after 1 h, 100%, after 24 h, 98.90% and in the dark, after 24 h, 97.77%;) (Fig. 1 a). Moreover, at concentration of 10 mg/dm^3 ClO_2 somewhat lower, but good efficiency of degradation also was achieved in the light (99.56% after 3 h). Good degradation efficiency was achieved in the dark, but slightly lower than for that in the light (after 24 h, 97.44% at a concentration of 10 mg/dm^3 ClO_2) (Fig. 1 a). The results showed that the best degradation efficiency of 100% was achieved after 1 h under light condition, at concentration of 5 mg/dm^3 ClO_2, and after 30 min at pH 9.00 at the same concentration of ClO_2. On the other pH values (Fig. 1 b), at pH 3.00 and 7.00 and at concentration of 5 mg/dm^3, satisfactory degradation efficiency was observed (at pH 3.00, after 24 h, 94.92%; at pH 7.00, after 24 h, 94.63%) (Fig. 1 b), but at concentration of 10 mg/dm^3 ClO_2, at pH 3.00 and 7.00 similar degradation efficiency was achieved (at pH 3.00, after 24 h, 93.57%; at pH 7.00, after 24 h, 95.76%) (Fig. 1 b).

The degradation products of azamethiphos obtained under optimal conditions (i.e. 10 mg/dm^3 azamethiphos with 5 mg/dm^3 ClO_2 under light and after 1 h) were analyzed by GC-QQQ. They were identified according to the corresponding spectral characteristics: mass spectra, accurate mass and characteristic fragmentation. Chromatogram has showed four degradation products of azamethiphos: O,O,S-trimethyl phosphorothioate (m/z 155; retention time 5.33 min), 6-chlorooxazolo[4,5-b]pyridin-2(3H)-one (m/z 169; retention time 10.237 min), S-(aminomethyl) O,O-dimethyl phosphorothioate (m/z 169; retention time 11.325 min), 6-chloro-3-(mercaptomethyl)oxazolo[4,5-b]pyridin-2(3H)-one (m/z 215; retention time 13.033 min).

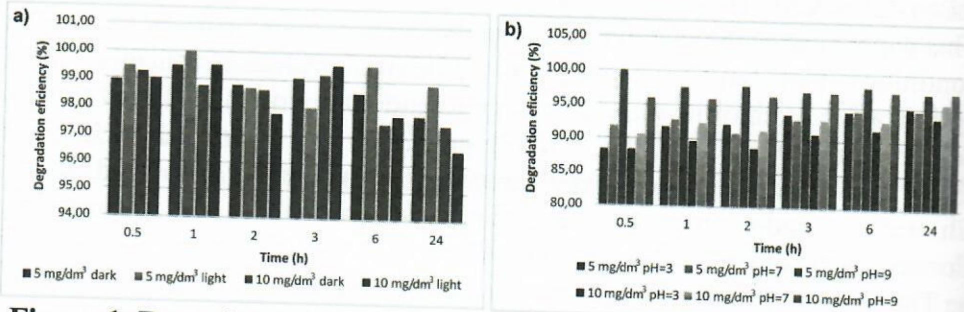

Figure 1. Degradation efficiency of azamethiphos: at concentrations 5 and 10 mg/dm^3 ClO_2 under (a) light and dark conditions and (b) at different pH values

CONCLUSION

This study reports the results for the degradation of organophosphorous pesticide, such as azamethiphos by chlorine dioxide in deionized water under light and dark conditions with different dosage of chlorine dioxide, at different time of degradation and at different pH values. The most efficient degradation (100%) of azamethiphos was obtained in the light at a concentration of 5 mg/dm^3 ClO_2, and also at concentration of 5 mg/dm^3 ClO_2, pH 9.00. Under other conditions, degradation efficiency was also high and was in the range from 88 to 99%. After treatment with chlorine dioxide four degradation products were identified. It was concluded that chlorine dioxide was effectively used for degradation of azamethiphos and these results made the application of chlorine dioxide for degrading organic pollutants from aqueous solution more practical.

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