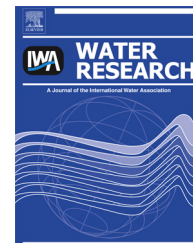


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Degradation of methiocarb by monochloramine in water treatment: Kinetics and pathways

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ABSTRACT

The micropollution of drinking water sources with pesticides has become a global concern. This work investigated the degradation of methiocarb (MC), a most commonly-used carbamate pesticide, by monochloramine (NH₂Cl) under simulated water treatment conditions. Results indicate that the reaction was of first-order in MC and varied orders in NH₂Cl depending on water pH. The observed rate constant of MC degradation decreased quickly with either a decrease in the molar ratio of chlorine to ammonia (Cl₂:N) or an increase in water pH. The apparent activation energy of the reaction was determined to be 34 kJ mol⁻¹. The MC degradation pathways also exhibited a strong pH dependence: at pH 6.5, MC was first oxidized by NH₂Cl to methiocarb sulfoxide (MCX), and then hydrolyzed to methiocarb sulfoxide phenol (MCXP); while at pH 8.5, MCX, MCXP and methiocarb sulfone phenol (MCNP) were formed successively through either oxidation or hydrolysis reactions. Based on the identified byproducts and their concentrations evolution, the proposed pathways of MC degradation in the presence of NH₂Cl were further validated through kinetic model simulations.

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1. Introduction

Methiocarb (mesurol, 3,5-dimethyl-4-(methylthio)phenyl methylcarbamate) (MC) is one of the most commonly-used carbamate pesticides worldwide (Keum et al., 2000; Gitahi et al., 2002; Altinok et al., 2006). It has been frequently detected in groundwater in various countries at concentrations ranging from 0.03 to 5.40 µg L⁻¹ (Barcelo et al., 1996; Garcia de Llasera and Bernal-Gonzalez, 2001; Squillace et al., 2002; APVMA, 2005). Although the detected concentrations of MC in natural waters are generally low, it poses a serious health threat to aquatic life and human considering

its high toxicity. The oral LD₅₀ in rats for MC is in the range of 13–130 mg kg⁻¹ body weight (bw) (Marrs, 1998). In aqueous environments, MC can be degraded to methiocarb sulfoxide (MCX) or lose its carbamate group to yield methiocarb phenol (MCP) (UNFAO and WHO, 1999; APVMA, 2005). The byproduct MCX is more toxic than MC, with an oral LD₅₀ in rats of 6–43 mg kg⁻¹ bw (Marrs, 1998). MCX is hence listed in the Priority List of Transformation Products in Great British Drinking Water Supplies as a result of comprehensive evaluations based on pesticide usage, toxicity, transformation products, mobility, and persistence (Sinclair et al., 2006).

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Nomenclature

MC	Methiocarb
MCN	Methiocarb sulfone
MCNP	Methiocarb sulfone phenol
MCP	Methiocarb phenol
MCX	Methiocarb sulfoxide
MCXP	Methiocarb sulfoxide phenol

Monochloramine (NH_2Cl) has been increasingly used as an alternative disinfectant to free chlorine or as a secondary disinfectant post chlorination because it is less reactive towards natural organic matter (NOM) and thus produces a lower level of regulated disinfection byproducts (DBPs) (Duirk et al., 2002; Greynshock and Vikesland, 2006). Extensive researches have been conducted on the formation of DBPs during water monochloramination (Choi and Valentine, 2002; Qi et al., 2004). Though NH_2Cl has a low reactivity towards NOM, it can still react with many chemical contaminants with reaction rates dependent on water pH and the molar ratio of chlorine to ammonia ($\text{Cl}_2:\text{N}$) (Heasley et al., 2004; Sandín-España et al., 2005; Chamberlain and Adams, 2006; Greynshock and Vikesland, 2006). In general, its reactivity towards a chemical contaminant increases as water pH decreases. It was also reported that the degradation of triclosan by NH_2Cl slowed down as the $\text{Cl}_2:\text{N}$ ratio decreased (Greynshock and Vikesland, 2006).

Although water treatment processes can sometimes reduce the concentrations of many pesticides (Ormad et al., 2008), the formation of byproducts may increase the toxicity of treated water (Wu and Laird, 2003). Our previous study has found that the toxicity of MC solution increased after ClO_2 treatment (Tian et al., 2010). However, to date, little is known about the kinetics and mechanism of MC degradation by NH_2Cl , particularly in terms of degradation byproducts. Therefore, the aim of this study was to determine the reaction kinetics, identify major degradation byproducts, and elucidate the pathways of MC degradation in the presence of NH_2Cl . The results would clarify the fate and behavior of MC during water disinfection with NH_2Cl , thus help ensure the drinking water safety.

2. Materials and methods

2.1. Chemicals

MC (98.5%) was purchased from Dr. Ehrenstorfer GmbH, and MCX (98.2%), MCN (94.4%) and *N,O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane were from Sigma–Aldrich. Methanol, acetone, and acetonitrile of high performance liquid chromatography (HPLC) grade were obtained from Fisher Scientific, and methyl *tert*-butyl ether (MTBE, HPLC grade) was from Tedia. Other chemicals were of at least analytical grade and used without further purification.

The stock solutions of MC, MCX and MCN were prepared individually in methanol with a concentration of about

200–300 mg L^{-1} . The mixed calibration standards containing MC, MCX and MCN (0.25–10.0 μM) were prepared from their stock solutions and 0.1 M HCl was added to prevent hydrolysis. The standard solutions of MCP, MCXP and MCNP were prepared respectively by hydrolyzing a desired volume of the stock solutions of MC, MCX and MCN with 1 mL of 2.0 M NaOH for about 1 min, and then acidifying with 5 mL of 2.0 M HCl. The completeness of hydrolysis was confirmed by liquid chromatography/photodiode array/mass spectrometry (LC/PDA/MS, Alliance 2695 HPLC and ZQ4000 MSD, Waters) analysis. NH_2Cl was freshly prepared by mixing NaOCl and NH_4Cl solutions at a $\text{Cl}_2:\text{N}$ molar ratio of 0.8 at about pH 10 except otherwise stated. NH_4Cl was purposely applied in excess to achieve a 100% yield of NH_2Cl and suppress the spontaneous decomposition of the formed NH_2Cl as well (Qiang and Adams, 2004). All reaction solutions were prepared with ultrapure water produced by a Milli-Q system (Advantage A10, Millipore) and buffered with 10 mM phosphate in the pH range of 6.1–8.9.

2.2. Hydrolysis experiments

The hydrolysis kinetics of MC, MCX and MCN was studied separately in 60 mL brown glass reactors to exclude potential light influence. The reaction solution of a target compound was freshly prepared by diluting its stock solution with ultrapure water containing 10 mM KH_2PO_4 . The hydrolysis reaction was initiated by addition of a desired volume of 2.0 M NaOH solution and terminated by addition of 2.0 M HCl solution. Samples were withdrawn at pre-selected time intervals and analyzed for the residual MC concentrations with HPLC/PDA.

2.3. Degradation experiments

MC degradation by NH_2Cl was studied under pseudo-first-order conditions with at least 10-fold excess of NH_2Cl in a pH range of 6.1–8.9 and a temperature range of 6–33 °C. Experiments were conducted in 250 mL brown glass reactors to exclude potential light influence. To restrain MC from hydrolysis, the reaction solution of MC (10 μM) was freshly prepared by spiking a desired volume of its stock solution into 100 mL of ultrapure water buffered with 10 mM KH_2PO_4 . Note that the presence of methanol, at a level of below 1.0% (v/v), has negligible impact on the reaction of NH_2Cl towards an organic compound (Greynshock and Vikesland, 2006). Our preliminary experiment had also confirmed that 0.8% (v/v) methanol exerted insignificant influence on MC degradation by NH_2Cl in this study.

After adjusting the reaction solution pH, a desired volume of NH_2Cl stock solution was spiked to initiate the reaction. Samples were withdrawn at pre-selected time intervals, and the residual oxidant was immediately quenched with pre-added Na_2SO_3 solution. Each sample was extracted with 2 mL of MTBE, and then analyzed with gas chromatography/mass spectrometry (GC/MS, 7890 GC and 5975 MSD, Agilent) to determine the residual MC concentration. The degradation experiments were conducted in duplicate, and the relative standard deviations of all measurement data were determined to be below 5%.

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