



Methiocarb degradation by free chlorine in water treatment: Kinetics and pathways

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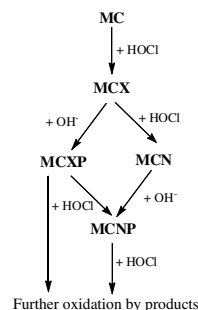
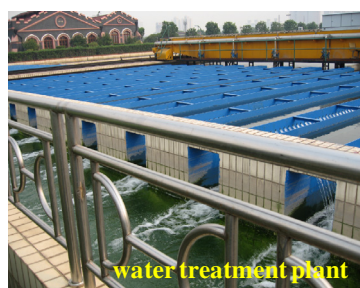
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HIGHLIGHTS

- A stoichiometric ratio of 1:1 was determined for MC reacting with free chlorine.
- MC reacted with free chlorine at an intrinsic rate constant of $2.42 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.
- MCX and MCN were identified as the major degradation byproducts.
- The further degradation of MCX to MCN (or MCXP) was highly pH dependent.
- The toxicity of MC solution increased obviously after chlorination.

GRAPHICAL ABSTRACT



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ABSTRACT

Methiocarb (MC) reacted with free chlorine at a stoichiometric ratio of 1:1, and the apparent rate constant was determined to be $(1.19\text{--}2.46) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in the pH range of 5.6–7.5 by competition kinetics. Methiocarb sulfoxide (MCX) and methiocarb sulfone (MCN) were identified to be the major byproducts of MC degradation. MCX could be further oxidized by free chlorine to MCN under acidic and neutral conditions, or hydrolyze to methiocarb sulfoxide phenol (MCXP) under basic conditions. MCN was hardly oxidized by free chlorine but hydrolyzed to methiocarb sulfone phenol (MCNP). Once formed, both MCXP and MCNP reacted with free chlorine too fast to be detectable. Due to the formation of MCX (more toxic than MC), the toxicity of the reaction solution obviously increased after chlorination. This enhanced toxicity raises a serious concern about the safety of drinking water if source water contains MC as a micropollutant.

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1. Introduction

Methiocarb (Mesurol, 3,5-dimethyl-4-(methylthio) phenyl methylcarbamate) (MC), one N-methylcarbamate pesticide used as insecticide, acaricide, molluscicide and bird repellent, is frequently applied worldwide in agriculture practices [1–6]. In recent years, MC has attracted increasing attention because of its toxic effects on animals and humans [1–4,7]. It has been detected in surface and ground waters of many countries (e.g. the United States, Australia, Greece, Mexico, Spain) at concentration levels from

ng L^{-1} to $\mu\text{g L}^{-1}$ [8–12]. The World Health Organization has classified MC as a highly hazardous pesticide [13]. For some aquatic invertebrates that are commonly regarded as bioindicators of water environment contamination, the LC_{50} or EC_{50} (acute) values of MC were found to be within a low range of 1.6–19 $\mu\text{g L}^{-1}$ [14]. The U.S. Environmental Protection Agency declares that the acute benchmark of MC for aquatic invertebrates is 3.5 $\mu\text{g L}^{-1}$ [15], and the health-based screening level is 40 $\mu\text{g L}^{-1}$ [16]. Considering the potential adverse effects of MC to public health, it is imperative to investigate its transformation and fate during water treatment.

According to the Joint Meeting of Pesticide Residues (JMPR) report published in 1999 [17], MC metabolizes mainly into methiocarb sulfoxide (MCX), methiocarb sulfone (MCN), methiocarb

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phenol (MCP), methiocarb sulfoxide phenol (MCXP), methiocarb sulfone phenol (MCNP), and N-hydroxymethyl methiocarb sulfoxide in plants, animals and soils. In aqueous environment, MC can be degraded to MCX or lose its carbamate group to yield MCP. In addition, the oxidation of MC by ClO_2 mainly produces MCX and MCN [7]. Based on the oral LD_{50} values in rats, MCX is more toxic while MCN, MCP, MCXP and MCNP are less toxic than MC [18]. MCX is on the Priority List of Transformation Products in Great British Drinking Water Supplies based on a comprehensive evaluation of the usage, toxicity, byproducts formation, mobility, and persistence of pesticides [6]. The toxicity of the MC solution was also found to increase after ClO_2 treatment [7]. Thus, the micropollution of drinking water sources by MC will pose a serious threat to public health, and equally important, the concentration levels of MC degradation byproducts should also be concerned with.

Free chlorine is a most commonly-used chemical disinfectant in water treatment plants [19,20]. It is cheap, stable and effective against a broad spectrum of pathogens including bacteria and viruses. Hence, it still acts as a primary disinfectant in many countries despite the formation of harmful chlorinated disinfection byproducts. Free chlorine is known to react with numerous pesticides. For example, organophosphate pesticides could react with free chlorine to produce stable oxons or oxidation analogues [21,22]. Isoproturon was also found to be degraded by free chlorine [23,24]. Moreover, some carbamate pesticides could react with free chlorine to produce sulfoxides or sulfones [25,26]. However, the transformation and fate of MC during chlorination of drinking water are still unknown.

The objectives of this study were to determine the kinetics of MC reacting with free chlorine, propose the degradation pathways based on identified byproducts, and assess the toxicity variation of MC solution after chlorination. The results would elucidate the transformation and fate of MC during water disinfection with free chlorine, thus providing useful information regarding the safety of drinking water in the case of MC micropollution.

2. Materials and methods

2.1. Chemicals

MC (98.5%) was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany), and MCX (98.2%), MCN (94.4%), and L-methionine (MN, $\geq 98\%$) from Sigma–Aldrich (St. Louis, MO, USA). Methanol, acetone, and acetonitrile (HPLC grade) were obtained from Fisher Scientific (Fair Lawn, NJ, USA). Free chlorine (NaOCl) solution (available chlorine $\geq 5\%$) of analytical grade was obtained from Beijing Modern Oriental Fine Chemistry Company (Beijing, China). All other chemicals were of at least analytical grade and used without further purification.

The stock solutions of MC, MCX and MCN were individually prepared in acetone with a concentration of 250–300 mg L^{-1} . The calibration standards containing MC, MCX and MCN (0.25–10.0 μM) were prepared by mixing their stock solutions and then adding 0.1 M HCl 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 NaOH solution (1 mL, 2.0 M) for about 1 min, followed by acidifying with HCl solution (5 mL, 2.0 M) and diluting with ultrapure water to 100 mL. The completeness of hydrolysis was confirmed by the liquid chromatograph/photodiode array/mass spectrometer (LC/PDA/MS, Alliance 2695 HPLC and ZQ4000 MSD, Waters, USA) analysis. All reaction solutions were buffered with 10 mM phosphate in the studied pH range of 6.0–9.0. Ultrapure water, produced by a Milli-Q system (Advantage A10, Millipore, Billerica, MA) with a resistivity of 18.2 $\text{M}\Omega \text{ cm}$, was used to prepare the aqueous solutions.

2.2. Analysis

In competition kinetics experiments, MC and MN (a reference compound) were quantified by high performance liquid chromatography coupled with a diode array detector (HPLC/DAD, Agilent 1200, Wilmington, USA) at 200 nm. An Atlantis C18 column (150 mm \times 2.1 mm, 3 μm particle size) was used for organic separation at a constant temperature of 40 $^\circ\text{C}$ and an eluent flow rate of 0.2 mL min^{-1} . The eluent consisted of two mobile phases (methanol and water) with the following gradient program: started with 10% methanol for 3 min, linearly ramped to 75% methanol over 3 min and held for 8 min, then decreased to 10% methanol over 2 min and held for 9 min. The retention times of MN and MC were 3.9 and 15.6 min, respectively.

To identify and quantify MC degradation byproducts, LC/PDA/MS was employed in combination with an Atlantis C18 column (150 mm \times 2.1 mm, 3 μm particle size) at a constant temperature of 40 $^\circ\text{C}$ and an eluent flow rate of 0.2 mL min^{-1} . Acetonitrile and water were used as two mobile phases with the following gradient program: started with 20% acetonitrile for 3 min, linearly ramped to 60% acetonitrile over 5 min and held for 4 min, then decreased to 20% acetonitrile over 3 min and held for 10 min. The MS was operated in the positive ionization mode with an electrospray ionization source for byproducts identification under the following conditions: capillary voltage 3.5 kV, cone voltage 20 V, source temperature 120 $^\circ\text{C}$, and desolvation temperature 300 $^\circ\text{C}$. Nitrogen gas was used for both cone and desolvation at a flow rate of 50 and 300 L h^{-1} , respectively. The PDA was utilized to determine the concentrations of MC and its byproducts in an acquisition wavelength range of 209–211 nm. The limits of quantification, which gave a signal-to-noise ratio of 10, were determined to be about 0.03, 0.02, 0.03, 0.02, 0.01 and 0.01 μM for MC, MCN, MCNP, MCP, MCX and MCXP, respectively.

The concentration of free chlorine was measured with a Hach DR5000 UV/Vis spectrophotometer (Hach method 10070). The concentration of TOC was determined by use of a Phoenix 8000 TOC analyzer (Tekmar Dohrmann, USA). Solution pH and temperature were simultaneously measured by a Mettler Toledo Delta 320 pH meter.

2.3. Kinetics of MC oxidation by free chlorine

The reaction between MC and free chlorine proceeded so fast that its rate constant could not be determined by conventional methods. In this study, competition kinetics was adopted to determine the reaction rate constants in the pH range of 5.6–7.5 at 25 $^\circ\text{C}$. MN was selected as a reference compound because it has the same thioether functional group as MC and its reaction rate constant with free chlorine is already known (i.e., $k_{\text{MN},\text{HOCl}} = 8.7 \times 10^8 \text{ mol}^{-1} \text{ L s}^{-1}$) [27]. The experiments were carried out in a series of 40 mL glass vials containing an equal concentration (50 μM) of MC and MN. Different volumes of NaOCl stock solution were added into these vials to attain the desired concentrations (15–60 μM) under vigorously stirring condition. The residual concentrations of MC and MN were analyzed by HPLC/DAD immediately.

2.4. Byproducts formation along with MC degradation by free chlorine

The formation of byproducts during MC degradation by free chlorine was investigated in a series of 250 mL brown glass bottles to exclude potential light influence. To prevent MC from hydrolysis, the reaction solution of MC (10 μM , 100 mL) was freshly prepared by diluting 0.8 mL of its stock solution (in acetone) with ultrapure water containing 10 mM KH_2PO_4 (pH 4.7). After adjusting the pH to a desired value with NaOH solution (2.0 M), NaOCl solution (80 μL) was immediately spiked to initiate the reaction. Our preliminary experiment had shown that the presence of ace-

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