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Chlorination of bensulfuron-methyl: Kinetics, reaction factors and disinfection by-product formation

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ABSTRACT

The kinetics of bensulfuron-methyl chlorination were studied at pH 4–9 at room temperature (25 ± 1 °C), which can be described well by a second-order kinetic model, first-order in chlorine and first-order in bensulfuron-methyl concentrations. Bensulfuron-methyl reacted very rapidly with aqueous chlorine with the maximum reaction rate constant at pH 6 and minimum at pH 9. The superior reactions were the reactions between HOCl and ionized/nonionized bensulfuron-methyl. The reaction factors including bromide and ammonium concentrations as well as temperature were also evaluated. It was found that bromide accelerated the chlorination of bensulfuron-methyl and the reaction rate increased linearly with the increase of bromide concentration. In contrast, the presence of ammonium inhibited the degradation of bensulfuron-methyl due to its quick conversion of chlorine to chloramines. Bensulfuron-methyl chlorination is an endothermic reaction with the activation energy being estimated as 13.74 kJ/mol using the Arrhenius equation. Four volatile disinfection by-products (DBPs) were identified after bensulfuron-methyl chlorination, including chloroform, dichloroacetonitrile, 1,1,1-trichloroacetone and nitrotrichloromethane. Trihalomethanes were the dominant species with a maximum reached at pH 8, which could cause potential risks to public health during bensulfuron-methyl chlorination, especially with the presence of bromide because the concentration and species of brominated DBPs increased with increasing bromide concentration.

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1. Introduction

Many different types of herbicides have been widely applied in most countries to destroy weeds in farmland, orchard, flower nursery and grassland as well as safeguard agricultural production [1]. In recent years, great attention has been paid to these pesticides due to their carcinogenicity and wide spread in the environment, which can cause potential risk to human health [1]. Methyl α-[(4,6-dimethoxypyrimidin-2-ylcarbamoyl) sulfamoylmethyl]-o-toluat, also known as bensulfuron-methyl, is a systemic sulfonylurea herbicide used for the control of annual and perennial weeds in rice [2]. Bensulfuron-methyl is one of the most used herbicides to control weeds in the paddy soils of California, Japan and many regions of the World [3]. Pareja et al. [4] investigated the occurrence of pesticides in 59 water samples collected in paddy fields located in Spain, and bensulfuron-methyl was detected at 10–33 ng/L. Although bensulfuron-methyl is generally considered to be a new type of effective and safe herbicide, wide and high dose

application makes bensulfuron-methyl and its residues one of the main organic pollutants in paddy soil [5]. Bensulfuron-methyl is stable under neutral and alkaline conditions with the half-life of 143 d at pH 7 [6], but its hydrolysis rate increases with the decrease of pH [7]. The accumulated bensulfuron-methyl in soil could leach out into water sources and react with the applied oxidant(s) as well as bromide in source water during drinking water treatment processes and form various disinfection by-products (DBPs), which might be toxic or carcinogenic to human beings. Therefore, it is rational and crucial to investigate the control and fate of bensulfuron-methyl in source waters to ensure drinking water safety.

Chlorine is an effective and inexpensive disinfectant widely used in drinking water disinfection process, in which hypochlorous acid (HOCl) is produced and then dissociated to hypochlorite (OCl⁻) rapidly [8]. Two key factors determining the ratio of HOCl to OCl⁻ in water are pH and temperature [9]. The dissolved organic matters in raw water would be oxidized by HOCl and OCl⁻ during chlorination, and various DBPs will be formed, such as trihalomethanes (THMs), haloacetic acids and nitrogenous DBPs [10]. Many studies have focused on the chlorination of specific emerging compounds including insecticide [11], phenols [12,13], endocrine disruptors [14], antibacterials [15], cyanobacteria produced toxins [16,17] and herbicides

[18,20]. The reactivity of organic chemicals with chlorine is sensitive to water matrixes including pH, temperature and the presence of bromine and ammonia and is deviated greatly due to the variety of chemical structures [18]. Some literature regarding the chlorination of herbicides such as diuron, isoproturon [18] and chlortoluron [19,20] have been published already. However, to the authors' best knowledge, no literature regarding the reaction mechanisms and DBP formation of bensulfuron-methyl during chlorination could be found, which would provide valuable theoretical basis for the strategies regarding the removal and control of bensulfuron-methyl as well as its DBPs.

The objectives of this study were (1) to investigate the kinetics of bensulfuron-methyl chlorination at pH 4–9, (2) to study the effect of reaction factors including pH, bromide concentration, ammonium concentration and temperature on the degradation of bensulfuron-methyl during chlorination, and (3) to assess the formation of volatile DBPs during the chlorination of bensulfuron-methyl as a function of reaction time and solution pH.

2. Materials and methods

2.1. Chemicals and analytical methods

Bensulfuron-methyl (99%), analytical grade of NaOCl, NH$_4$Cl, Na$_2$SO$_3$, Na$_2$CO$_3$, NaHCO$_3$, NaBr, KH$_2$PO$_4$, NaOH, and H$_2$SO$_4$ were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). DBP standard solutions including chloroform (CF), trichloroethylene, dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), 1,3-dichloroacetone, trichloronitromethane (TCNM), trichloroethane, 1,1,1-trichloroacetone (1,1,1-TCP), tetrachloromethane, tetrachloroethylene, bromodichloromethane (BDCM), dibromochloromethane (DBCM), dibromoethane, bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), dibromoethane and bromoform (TBM)) were purchased from Sigma–Aldrich (USA). HPLC grade methanol and methyl *tert*-butyl ether (MTBE) were purchased from J.T. Baker (USA). All solutions were prepared with Milli-Q water.

An Agilent 1260 infinity high performance liquid chromatography (HPLC) system equipped with a C18 chromatographic column (4.6 mm × 250 mm, 3.5 μm) and a UV detector was used to analyze the concentration of bensulfuron-methyl at the wavelength 240 nm. The mobile phase consisted of 70%/30% (v/v) methanol and pure water at a flow-rate of 0.70 mL/min. The injection volume was 5 μL. The pH was measured with a regularly calibrated pH-meter (Sartorius, Germany). At least two replicates of each measurement were carried out and more replicates were executed in cases in which the variation between the two measurements exceeded 10%.

After the chlorination of bensulfuron-methyl, 10 mL samples were extracted with 2 mL MTBE with 4 min vigorous mixing and 3 min still separation. An aliquot of the supernatant was withdrawn for the analysis of DBP formation using a GC-2010 (Shimadzu) equipped with a RTX-5 column (30 m × 0.25 mm, 0.25 μm thickness). Helium was used as the carrier gas at the flow-rate of 0.94 mL/min. The GC temperature program was set as follows: injector temperature of 200 °C, column initial temperature of 37 °C held for 10 min, increased to 50 °C with the gradient of 5 °C/min and held for 5 min and then increased to 260 °C with the gradient of 30 °C /min and held for 10 min.

2.2. Experimental procedures

All experiments were performed in a 100 mL batch reactor made of brown glass at controlled room temperature (25 ± 1 °C). Typical experiments were initiated by adding an aliquot of a stock chlorine solution to the reactor containing bensulfuron-methyl solution (1 mg/L, 2.4 μM) buffered with 10 mM monopotassium at pH 7. In the experiments of kinetic study, chlorine dose was in excess to ensure the chlorination reaction happened under pseudo first-order conditions. The solutions were buffered using 10 mM monopotassium phosphate buffer for pH 4–8 because the commonly used acetate buffer will react with bensulfuron-methyl and interfere with the analytical results. The solutions were buffered using 10 mM sodium bicarbonate for pH 9. Small volumes of H$_2$SO$_4$ (0.18 M) and NaOH (1 M) were used to adjust solution pH to the desired value. Variation of solution pH during the experiments was negligible. At different reaction time, 1 mL of solution was withdrawn and added to a HPLC vial containing 100 μL Na$_2$SO$_3$ (1 M) to quench the reaction. The samples were stored in the dark at 4 °C and analyzed using HPLC within 10 min.

The kinetic experiments were carried out at pH 4–9 and were monitored until more than 50% of bensulfuron-methyl was degraded. The effect of bromine concentration (ranged from 0.1 to 0.6 μM) and ammonium (ranged from 1 to 4 μM) was evaluated at pH 7, chlorine dose of 4.86 μM buffered with monopotassium phosphate. The effect of temperature on the reaction rate constant was determined at 20, 25, 30, and 35 °C at pH 7. For the measurement of volatile DBPs, experiments were conducted in duplicate under headspace-free conditions in 45-mL glass screw-cap vials. For the experiments of DBP formation as a function of pH, triplicate samples were performed to ensure the data quality in this study. A chlorine dose of 1 mg/L was added into a bensulfuron-methyl solution, which was buffered at pH 7 using 10 mM monopotassium phosphate.

2.3. Kinetic modeling

The kinetic models for bensulfuron-methyl chlorination without and in the presence of bromide were developed in Sections 3.2 and 3.3, respectively, and the corresponding rate constants were simulated with Matlab 7.10.0 (R2010a) using the function of *nlinfit* with nonlinear least squares fitting of the experimental data.

3. Results and discussion

3.1. Effect of applied chlorine doses on the degradation of bensulfuron-methyl

It has been reported that chlorination of various organic matter follows a second-order overall reaction, first-order in chlorine concentration and first-order in organic matter concentration [1,20,21]. Fig. 1 shows the effect of applied chlorine dose on bensulfuron-methyl degradation and illustrates the plot of ln([bensulfuron-methyl]$_{T, 0}$/[bensulfuron-methyl]$_{T, t}$) as a function of reaction time, in which [bensulfuron-methyl]$_{T, 0}$ is the initial concentration of bensulfuron-methyl and [bensulfuron-methyl]$_{T, t}$ is the concentration of bensulfuron-methyl at different reaction time. Good linear fit of the experimental data in Fig. 1 indicates pseudo-first order reaction kinetics of bensulfuron-methyl degradation with the slopes as the pseudo-first-order rate constants (k_{obs}). As the concentration of chlorine increased from 2.4 to 24.3 μM, the degradation rate of bensulfuron-methyl increased due to the increasing formation of hypochlorous acid in water acting as a strong oxidant. The upper-right figure in Fig. 1 shows that the k_{obs} is first-order related to chlorine concentration. Accordingly, the reaction of bensulfuron-methyl chlorination follows the second-order kinetics with k_{app} as the apparent second-order rate constant. The relation between k_{app} and k_{obs} can be described as follows:

$$\frac{-d[\text{bensulfuron} - \text{methyl}]_T}{dt}$$
$$= k_{app}[\text{HOCl}]_T[\text{bensulfuron} - \text{methyl}]_T$$
$$= k_{obs}[\text{bensulfuron} - \text{methyl}]_T \qquad (1)$$