



Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Degradation kinetics and DBP formation during chlorination of metribuzin

Chen-Yan Hu^a, Ai-Ping Li^a, Yi-Li Lin^{b,*}, Xiao Ling^a, Ming Cheng^a

^a College of Environmental and Chemical Engineering, Shanghai University of Electric Power, Shanghai 200090, PR China

^b Department of Safety, Health and Environmental Engineering, National Kaohsiung First University of Science and Technology, Kaohsiung 824, Taiwan, ROC

ARTICLE INFO

Article history:

Received 6 April 2017

Revised 26 June 2017

Accepted 5 July 2017

Available online xxx

Keywords:

Metribuzin

Chlorination

Kinetic model

Rate constant

Disinfection by-product

Water treatment

ABSTRACT

A common nitrogen-containing herbicide, metribuzin, was studied for the effect of pH, bromide and ammonium concentrations as well as temperature on its degradation kinetics and disinfection by-product (DBP) formation during chlorination. Metribuzin chlorination can be well described by a second-order kinetic model, and the rate constants of the acid-catalyzed and HOCl oxidizing charged metribuzin (metribuzin⁺) were calculated as $7.72 (\pm 0.90) \times 10^8 \text{ M}^{-2} \text{ min}^{-1}$ and $8.22 (\pm 4.00) \times 10^3 \text{ M}^{-1} \text{ min}^{-1}$, respectively. Metribuzin degradation rate increased with increasing bromide concentration or decreasing ammonium concentration. A kinetic model of metribuzin chlorination in the presence of bromide and ammonium, respectively, was developed in this study, and the rate constant for the reaction of HOBr and metribuzin⁺ was calculated as $2.44 (\pm 2.30) \times 10^5 \text{ M}^{-1} \text{ min}^{-1}$. Moreover, the formation and distribution of chlorinated DBPs were analyzed. Chloroform was the major volatile degradation product with the molar yield of 0.86% under the circumneutral condition, and its formation increased gradually with the increase of reaction time and pH. However, the formation of dichloroacetone, 1,1-dichloro-2-propanone, 1,1-trichloro-2-propanone and trichloronitromethane climbed up and then declined with increasing reaction time and pH. The formation of brominated DBPs increased with increasing bromide to chlorine molar ratio, especially for dibromochloromethane. The rate constants of metribuzin chlorination increased with increasing temperature, and the activation energy was estimated as $22.83 \text{ kJ mol}^{-1}$. In sum, special attention should be paid during metribuzin chlorination at alkaline conditions, especially in the presence of bromide, which would cause the formation of more toxic brominated DBPs than their chlorinated analogs.

© 2017 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

Metribuzin [1, 2, 4-Triazin-5(4H)-one, 4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-(9Cl)], one of the nitrogen-containing herbicides in the family of triazine herbicides, is registered for the control of annual broadleaf weeds and grassy weeds. Approximately 2.7 million pounds of metribuzin was used for the year 1992 in the United States [1] and 100,000–500,000 kg of metribuzin was used in 1986 in Canada [2]. Therefore, metribuzin ranks among the top 200 agricultural pesticides used in USA [3] and has been monitored under the Safe Drinking Water Act in USA [4]. The United States Geological Survey (USGS) analyzed 59 significant watersheds and aquifers over ten years and reported the maximum concentration of 3.70 and $25.1 \mu\text{g L}^{-1}$ in surface and ground water,

respectively [5]. The maximum concentration of metribuzin in the effluents of rural waste water treatment plant in Germany was reported as $1.2 \mu\text{g L}^{-1}$ between the years of 1996 and 1997 [6], while $300 \mu\text{g L}^{-1}$ of metribuzin was reported in a well in Ontario surveyed from 1981–1985 [7]. Metribuzin can only moderately adsorb to soil with high clay or organic content and slightly bioaccumulate according to its organic carbon partition coefficient ($K_{oc} = 60$) [8]. The half-life of metribuzin in soil and pond water is 2.5–4 months and 7 days, respectively [9,10]. However, once the leached out metribuzin enters the source water, it cannot be removed through traditional water treatment processes, including coagulation, sedimentation and filtration [8]. Therefore, it is crucial to control its application and understand its reaction mechanisms in the following disinfection process as well as disinfection by-products (DBP) formation to ensure the supply of safe drinking water.

Chlorine is widely used in disinfection process in water treatment plants (WTPs) because it is an efficient, convenient and relatively cheap disinfectant, but it can react with organic matter

* Corresponding author.

E-mail addresses: yililin@nkfust.edu.tw, yililin@ntu.edu.tw (Y.-L. Lin).

<http://dx.doi.org/10.1016/j.jtice.2017.07.005>

1876-1070/© 2017 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

to form various harmful DBPs including trihalomethanes (THMs), haloacetic acids (HAAs), and other chorine derivatives such as chlorinated bisphenol A, which are more toxic than their parent compound [11–16]. Recently, many studies have focused on the chlorination of nitrogen-containing precursors, such as diuron, chlortoluron, dinoseb and bensulfuron-methyl that belong to nitrogen-containing herbicide and confirmed that these herbicides can form various nitrogenated disinfection by-products (N-DBPs) [17,18,27], such as nitrosodimethylamine (NDMA), trichloronitromethane (TCNM), dichloroacetonitrile (DCAN) and trichloroacetonitrile (TCAN). Metribuzin can also react with chlorine to form various N-DBPs during disinfection process in our preliminary study, and N-DBPs are known to be more toxic than their chlorinated analogs with high mutagenicity and carcinogenicity. To the authors' best knowledge, no study regarding the chlorination of metribuzin could be found in the literature. Therefore, it is important to identify the ultimate fate of metribuzin and its degradation disinfection by-products (DBPs) during chlorination in water treatment process.

The objectives of this study were (1) to study the degradation mechanics and kinetics of metribuzin during chlorination, (2) to study the effect of influencing factors on metribuzin degradation, including pH, bromide and ammonium concentrations as well as temperature, (3) to develop kinetic models for metribuzin chlorination at different influencing factors, and (4) to identify and characterize DBP formation during metribuzin chlorination.

2. Materials and methods

2.1. Chemicals and analytical methods

Metribuzin (>99%) and DBP standards including EPA 551A (bromodichloromethane (BDCM), bromoform (BF), carbon tetrachloride (CTC), chloroform (CF), dibromochloromethane (DBCM), 1,2-dibromoethane (EDB), trichloroethylene (TCE), tetrachloroethylene (PCE), 1,1,1-trichloroethane (TCA), 1,2-dibromo-3-chloropropane (DBCP)) and EPA 551B (bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), dichloroacetonitrile (DCAN), 1,1-dichloro-2-propanone (DCP), 1,1,1-trichloroacetone (TCP), trichloroacetonitrile (TCAN), trichloronitromethane (TCNM)) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received. NaOCl, Na₂S₂O₃, NaBr, NH₄Cl, KH₂PO₄, Na₂CO₃, CH₃COOH, CH₃COONa, NaOH, and HCl were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) without further purification. Stock solutions of chlorine were prepared by diluting a commercial NaOCl solution (1.31 M) in Milli-Q water. All solutions were prepared with Milli-Q water.

2.2. Experimental procedures

Metribuzin degradation experiments were performed in a 200 mL batch reactor equipped with a dispenser at room temperature (25 ± 1 °C). The experiments were initiated by adding an aliquot of a concentrated chlorine solution to the reactor containing metribuzin solution (4.67 μM in all cases) buffered using 10 mM acetate for pH 4–5, 10 mM phosphate for pH 5–8, and 10 mM carbonate for pH 8–10. Small volumes of H₂SO₄ (1 M) and NaOH (1 M) were used to adjust solution pH to the desired values. Variation of solution pH during the experiments was negligible. At different reaction time, 1 mL of the solution was rapidly transferred into a high performance liquid chromatogram (HPLC) vial containing 10 μL Na₂S₂O₃ solutions (63.2 mM) to quench the reaction, which was then analyzed using HPLC as soon as possible.

The kinetic experiments were carried out over a pH range between 4 and 10 at the molar ratio of chlorine to metribuzin as 20. The concentration of metribuzin was monitored until more than

50% of metribuzin was degraded. The effect of bromide and ammonium concentrations (0.467–9.34 μM and 2.33–46.7 μM, respectively) as well as reaction temperature (15, 20, 25, 30 and 35 °C) on metribuzin chlorination were evaluated at metribuzin concentration of 4.67 μM, pH 7 (using phosphate buffer) and chlorine concentration of 46.7 μM (as Cl₂). The studied concentrations of bromide and ammonium cover the ranges of those in ambient environment (9–135 μg L⁻¹ [19–22] and 110–5490 μg L⁻¹ [21,23,24], respectively) in China and USA.

The analysis of metribuzin degradation by-products and DBP formation experiments were conducted in duplicate under headspace-free conditions in 45 mL glass of screw-cap vials with PTFE-lined septa. A typical run of chlorine dosage as 1.26 mM was applied to metribuzin solutions (93.4 μM, at pH 5–10) in order to enhance DBP formation for quantification using acetate, phosphate or carbonate buffers (10 mM). At the designed reaction time, the reaction was quenched using NH₄Cl instead of Na₂S₂O₃ to avoid its interaction with the formed N-DBPs [25], and then the water samples were extracted using methyl tert-butyl ether (MTBE) for the analysis of DBPs.

2.3. Analytical methods

The degradation of metribuzin was analyzed using a Agilent 1200 infinity series HPLC system equipped with an autosampler, a Waters X Terra C18 column (250 mm × 4.6 mm, 5 μm, Waters, USA), and was detected using a UV detector at wavelength 285 nm. The mobile phase was consisted of methanol/Milli-Q water (70/30%, v/v) at the flow rate of 1 mL min⁻¹. The injection volume was 5 μL. Chlorine concentration was analyzed using the N, N-diethyl-p-phenylenediamine (DPD) colorimetric method [26]. Solution pH was measured with a regularly calibrated pH-meter (PB-10, Sartorius, USA). Bromide and ammonium concentrations were analyzed using an ion chromatography (IC, Dionex ICS-2000, USA).

In order to analyze the formation of volatile DBPs after metribuzin chlorination, water samples were pretreated using the liquid-liquid extraction method with MTBE. An aliquot of the extract was injected into a gas chromatography (GC-2010 Plus, Shimadzu, Japan) equipped with an electron capture detector and a RTX-5 fused silica capillary column (30 m × 0.25 mm id, 0.25 μm film thickness) for the qualification of the volatile DBPs according to the USEPA method 551.1 [25]. The temperature program was set as: injector temperature 200 °C, detector temperature 290 °C, and column temperature 37 °C (hold for 10 min), increasing to 50 °C (with the rate of 5 °C min⁻¹), increasing to 260 °C (with the rate of 30 °C min⁻¹) and holding for 10 min.

2.4. Kinetic modeling

The concentration of metribuzin during chlorination was simulated with Matlab 7.4.0 (R2007a). The values of the kinetic parameters in the following Sections 3.1–3.5 were calculated and optimized through non-linear least square fitting of the experimental data using the function `nlinfit`. The simultaneous ordinary differential equations derived from the substitution of the rate equations were solved by the function `ode45`. Function `nlparci` was employed to determine the 95% confidence interval of the estimated parameters.

3. Results and discussion

3.1. Reaction kinetics of metribuzin chlorination and DBP formation

Fig. 1 illustrates the correlation of $\ln([\text{Metribuzin}]_0/[\text{Metribuzin}]_t)$ as a function of reaction time at different chlorine concentrations (32.69–93.40 μM), 25 ± 1 °C and pH 7, in

Download English Version:

<https://daneshyari.com/en/article/7105154>

Download Persian Version:

<https://daneshyari.com/article/7105154>

[Daneshyari.com](https://daneshyari.com)