Chemical Engineering Journal 219 (2013) 43–50

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Chlorination and bromination kinetics of emerging contaminants in aqueous systems

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HIGHLIGHTS

- Chlorination and bromination kinetics of emerging contaminants was investigated.
- Apparent rate constants were pH dependent and the primary oxidant species was HOCl.
- Chlorine was specially efficient for the removal of 3-Methylindole and Chlorophene.
- The additional presence of bromide enhanced slightly the chlorination of ECs.

ARTICLE INFO

Article history:
Received 25 October 2012
Received in revised form 20 December 2012
Accepted 26 December 2012
Available online 11 January 2013

Keywords:
Emerging contaminants
Chlorine and bromine
Apparent and intrinsic rate constants
Combined chlorination–bromination process

ABSTRACT

Second-order rate reaction constants of micropollutants with chlorine are essential for evaluating their removal efficiencies from water during chlorine disinfection. In this study, the reactions of five selected emerging contaminants with unavailable kinetic data (Benzotriazole, N,N-diethyl-m-toluamide or DEET, Chlorophene, 3-Methylindole, and Nortriptyline HCl) with chlorine and bromine have been investigated, and their apparent second-order rate constants have been determined as a function of the pH. For the chlorination process, the intrinsic rate constants for the elementary reactions of the ionized and neutral species were also evaluated. The sequence of reaction rates was Methylindole > Chlorophene > Nortriptyline HCl > Benzotriazole > DEET. The bromination of the selected emerging contaminants in ultra-pure water provided exactly the same sequence of reaction rates as in the chlorination process, although higher values of rate constants. The efficiency of the chlorination process for the degradation of these ECs when present in several aqueous systems (surface water from a public reservoir, and two effluents from municipal wastewater treatment plants) was investigated. During wastewater or drinking water treatment, chlorine is a good option for the degradation of Methylindole, and in a lower extent for Chlorophene and Nortriptyline. However, it is not a suitable oxidant for the abatement of Benzotriazole and DEET. Finally, chlorination in the presence of bromide revealed that low bromide concentrations enhanced slightly the degradation of the selected compounds during chlorine oxidation.

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1. Introduction

Chemical oxidants are commonly used in water treatments because of their potential for destruction of micropollutants. Some of the oxidation systems include UV radiation, ozonation, and advanced oxidation processes (AOPs), such as O_3/H_2O_2, UV/H_2O_2 or Fenton's reagent. Most of these AOPs have demonstrated high effectiveness in the degradation of organic compounds present in water systems which are oxidized to readily biodegradable and less toxic compounds [1]. Although less reactive than ozone, chlorine (Cl_2) as gaseous chlorine or hypochlorite has also been frequently used in water treatments [2,3]. Chlorine hydrolyzes in water and forms hypochlorous acid:

$$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+ \quad (1)$$

Moreover, hypochlorous acid is a weak acid that dissociates in aqueous solutions:

$$HOCl \iff ClO^- + H^+ \quad (2)$$

This equilibrium presents a dissociation constant $K_{HOCl} = 2.9 \times 10^{-8}$ ($pK_a = 7.54$ at 25 °C). In the pH range 6–9 (typical of water treatment conditions), hypochlorous acid and hypochlorite are the main chlorine species present [3]. Besides its low cost, the great advantage of chlorine is the reaction with numerous inorganic and organic micropollutants present in waters. However, its main

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http://dx.doi.org/10.1016/j.cej.2012.12.067