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pH significantly affects removal of trace antibiotics in chlorination of municipal wastewater

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ABSTRACT

The effect of pH on chlorination behaviors of 12 antibiotics, including β-lactams, sulfonamides, fluoroquinolones, tetracyclines, macrolides, and others at environmentally relevant concentrations was systematically examined in the effluent matrix of activated sludge process. The removal of most antibiotics (except cefalexin and tetracycline) significantly depended on pH in the range of 5.5–8.5. The elimination rates of ciprofloxacin, norfloxacin, anhydro-erythromycin, and roxithromycin increased while that of sulfamethoxazole decreased significantly with the increase of pH. Sulfadiazine, ofloxacin, and trimethoprim exhibited the highest reactivity with free available chlorine under the pH of 6–7, 7, and 7.5, respectively. Not only the free available chlorine species (HOCl and OCl^-), but also the antibiotics species (cationic, neutral and anionic) affected the overall reaction rate. Anionic antibiotic species are usually much more reactive (1–3 orders of magnitude greater) than cationic antibiotic species toward free available chlorine. Although OCl^- is a weaker oxidant than HOCl, chlorination of sulfadiazine, sulfamethoxazole, ciprofloxacin, norfloxacin, and trimethoprim with OCl^- became significant at pH > 7.5. The observed kinetics rate constants calculated from species-specific rate constants could accurately ($0.91 < R^2 < 0.99$) predict the antibiotic removal in chlorination of activated sludge effluent with similar DOC and ammonia concentration to this study at a given pH value.

1. Introduction

In recent years, there has been growing interest on the occurrence, fate and potential toxicity of antibiotics in the environment all over the world (Xiao et al., 2008), although the antibiotics residue in the environment is at subinhibitory concentration, usually at ng/L to μg/L in water and μg/kg to mg/kg in soil and sludge. One antibiotic, erythromycin has been selected to the Drinking Water Contaminant Candidate List formulated by U.S. Environmental Protection Agency (USEPA, 2010).

Current wastewater treatment processes were not specifically designed to remove antibiotics (Hu et al., 2010). Antibiotics have been frequently detected in effluent and sludge from municipal wastewater treatment plants (WWTPs) (Golet et al., 2003; Li and Zhang, 2011). Therefore, WWTPs are considered to be one of the dominant point pollution sources and principal transfer pathways for human-use antibiotics into environment (Gulkowska et al., 2008). Considering the adverse effects of antibiotics, thorough understanding of the fate of antibiotics in the wastewater treatment processes is necessary for optimizing process operations to remove these emerging micropollutants of concern effectively (Hu et al., 2010). Generally, conventional biological treatment processes cannot eliminate antibiotics effectively (Adams et al., 2002; Zhang and Li, 2011). Disinfection process as the final barrier

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in WWTPs appears to result in significant removal of trace antibiotics (Hollender et al., 2009; Li and Zhang, 2011). Previous studies reported that ozonation could remove multiple classes of antibiotics in secondary effluent effectively (Hollender et al., 2009; Radjenović et al., 2009; Dodd et al., 2010; Rodayan et al., 2010). Compared to ozonation, UV irradiation was less effective and usually required 4.5–68.7 min to obtain a removal efficiency of 90% (Kim et al., 2009). Chlorination was commonly used as the disinfection process in WWTPs globally due to its low cost (Dodd et al., 2005; Qiang et al., 2006; Wang et al., 2010a). Although free available chlorine (FAC) was effective in eliminating antibiotics such as sulfonamides, carbadox, and trimethoprim from distilled and surface waters (Adams et al., 2002; Chamberlain and Adams, 2006), the removal behavior of antibiotics obtained based on the above less polluted water matrixes could not be applied directly to wastewater due to the vast difference in water characteristics, such as dissolved organic carbon (DOC) content and ammonia concentration, etc. (Yargeau and Leclair, 2008). Dodd and Huang (2004, 2007), Dodd et al. (2005) and Wang et al. (2010a) mainly focused on the transformation products and reaction kinetics between FAC and trimethoprim, sulfamethoxazole, ciprofloxacin, enrofloxacin as well as tetracyclines in reagent water (18.2 MΩ cm at 25 °C) systems. Additional experiments were conducted in real municipal wastewater water matrixes to assess the field-applicability of kinetic results obtained from reagent water systems in the laboratory. Nevertheless, significant bias occurred when predicting the trimethoprim removal rate in chlorination of the wastewater (Dodd and Huang, 2007). Similar bias on the prediction of elimination of ciprofloxacin and enrofloxacin in chlorination due to the matrix effect was also reported by Wang et al. (2010b) and Dodd et al. (2005).

It was reported that not only the FAC species (HOCl and OCl^-), but also the speciation of antibiotics (cationic, neutral and anionic) could affect the overall chlorination rate (Qiang et al., 2006). The percentage distribution of both FAC and antibiotics species is predominantly dependent on pH. However, very limited studies on chlorination of antibiotics have been conducted to investigate the effect of pH values in real municipal wastewater matrixes. Thus, the chlorination behaviors of multiple classes of antibiotics, including β-lactams, sulfonamides, fluoroquinolones, tetracyclines, macrolides, and others at environmentally relevant concentrations were systematically examined in this study for the first time under different pH values relevant to municipal wastewater treatment. Particular emphasis was placed on (1) determining the chlorination effectiveness and kinetics of 12 antibiotics with FAC under different pHs; (2) calculating and validating the species-specific kinetics constants between FAC species and antibiotics species.

2. Materials and methods

2.1. Chemicals and standards

The standards of 12 antibiotics, including 3 β-lactams: ampicillin (AMP), cefotaxime (CTX) and cefalexin (CLX); 2 sulfonamides: sulfamethoxazole (SMX) and sulfadiazine (SDZ); 3 fluoroquinolones: norfloxacin (NOR), ciprofloxacin (CIP) and ofloxacin (OFL), 1 tetracyclines: tetracycline (TC), 2 macrolides: roxithromycin (ROX) and erythromycin (ERY), and 1 others: trimethoprim (TMP) were all purchased from Sigma–Aldrich. All the standards were of the highest purity available (≥95%). Anhydro-erythromycin (ERY-H_2O), the major degradation product of ERY was generated according to the method described by McArdell et al. (2003). NaClO was obtained from Fisher Scientific at ~12% solution concentration. Free chlorine stock solution was diluted to 1000 mg/L as Cl_2 and standardized iodometrically (Clesceri et al., 1998). Other chemicals, such as acetonitrile, ultrapure water, formic acid, ascorbic acid, sodium hydroxide, sulphonic acid solution, and 0.2 μm cellulose nitrate membrane were the same as those reported previously (Li et al., 2009).

2.2. Analytical methods

Free chlorine and total chlorine were measured using the Hach Method 8021 and 8167 with a DR/2400 portable spectrophotometer, respectively (Hach Co., Loveland, CO). Ammonia, nitrite, and nitrate were detected according to the Standard Methods (Clesceri et al., 1998). The dissolved organic carbon (DOC) was measured using a total organic carbon analyzer (TOC-VCPH, Shimadzu, Japan). Acquity ultra performance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS, Waters) was applied to analyze antibiotics using the positive electrospray ionization multiple reaction monitoring mode. The detailed information on UPLC–MS/MS was described in the previous study (Li et al., 2009).

2.3. Municipal wastewater sample

Grab effluent samples were collected after the secondary sedimentation tank but prior to disinfection contact tank of Stanley WWTPs in Hong Kong which utilized anoxic-aerobic activated sludge process combined with chlorination process. Important characteristics of the wastewater sample are: pH 6.7, ammonia-N 0.62 mg/L, nitrite-N 0.20 mg/L, nitrate-N 4.1 mg/L, suspended solid (SS) 6 mg/L and dissolved organic carbon (DOC) 5.5 mg/L. About 5 L secondary effluent samples were vacuum-filtered through 0.45 μm cellulose nitrate membrane upon arrival to the laboratory, stored at −20 °C freezer for the following batch experiments use.

2.4. Batch chlorination experiments

Experiments were conducted using a 200 mL glass beaker with 150 mL secondary effluent filtrate at 22 ± 1 °C. The antibiotics were spiked with an aqueous stock solution mixture containing 10 mg/L of each antibiotic to obtain a final environmentally relevant concentration of 10 μg/L. The mixing was supplied by the magnetic stirrer at 150 rpm. Reaction was initiated by adding appropriate volumes of free chlorine stock solution. With regard to the wastewater quality of this study and the typical chlorine dosage values, 15 mg/L was selected as the initial FAC dosage for the following experiments (Metcalf and Eddy, 2004). Five milliliter samples were taken at 5 s, 10 s, 20 s, 30 s, 1 min, 2 min, 3 min, 5 min, 10 min, 15 min, 30 min and 60 min and immediately quenched with