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Different removal behaviours of multiple trace antibiotics in municipal wastewater chlorination

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ABSTRACT

The chlorination behaviours of 12 antibiotics belonging to six classes at environmentally relevant concentrations were systematically examined under typical conditions relevant to municipal wastewater chlorination. Cefotaxime, cefalexin, ampicillin and tetracycline were completely removed under all three initial free chlorine dosages (5 mg/L, 10 mg/L, and 15 mg/L). The removal efficiencies of sulphamethoxazole, sulphadiazine, roxithromycin, anhydro-erythromycin, ofloxacin, and trimethoprim were closely correlated to the residual free chlorine concentration, and no further significant mass removal was observed after the residual free chlorine concentration decreased to less than ~0.75 mg/L. Ammonia plays a critical role during chlorination because of its competition with antibiotics for free chlorine to form combined chlorine, which reacts slowly with these antibiotics. Except for norfloxacin and ciprofloxacin, the removal behaviours of the 10 other target antibiotics under ammonia nitrogen concentrations ranging from 2 to 15 mg/L were characterised by a rapid initial removal rate upon contact with free chlorine during the first 5 s–1 min (depending on the specific antibiotic and ammonia nitrogen concentration) and then a much slower removal rate. Free chlorine was responsible for the reaction with antibiotics during the rapid stage (first 5 s–1 min), whereas combined chlorine reacted with antibiotics in the subsequent slow stage. Combined chlorine can remove norfloxacin and ciprofloxacin at a relatively faster rate. The presence of suspended solids at 30 mg/L slightly decreased the antibiotic removal rate. The kinetic rate constants decreased by 2.1–13.9%, while the half-lives increased by 2.0–15.0% compared to those of a 0 mg/L suspended solid for the target antibiotics.

1. Introduction

Recently, the occurrence, fate and potential toxic effects of antibiotics have gained the attention of environmental researchers throughout the world (Xiao et al., 2008). Although the antibiotic concentration in the environment is at a subinhibitory level, usually at ng/L to μg/L in water and μg/kg to mg/kg in soil and sludge, it might still result in an increased selection pressure for the development and spread of antibiotic resistant bacteria and resistance genes, which is regarded as one of the three greatest threats to human health by the World Health Organization (Martínez, 2008; Kummerer, 2009;

Abbreviations and notations: AMP, ampicillin; CC, combined chlorine; CIP, ciprofloxacin; CLX, cefalexin; CTX, cefotaxime; ACN, acetonitrile; DOC, dissolved organic carbon; ERY-H_2O, anhydro-erythromycin; FC, free chlorine; NOR, norfloxacin; OFL, ofloxacin; ROX, roxithromycin; SDZ, sulphadiazine; SMX, sulphamethoxazole; SS, suspended solid; TC, tetracycline; TMP, trimethoprim; UPLC–MS/MS, ultra-performance liquid chromatography–tandem mass spectrometry; WWTPs, municipal wastewater treatment plants.

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Davies and Davies, 2010; Wise, 2011; Oberlé et al., 2012). The problem becomes much more serious when the pathogens possess antibiotic resistance because this leads to an increase in the morbidity and mortality as well as in the cost of treatment (Levy, 2001; Andersson and Hughes, 2010). In addition, as the reuse of treated wastewater increases, the opportunity for antibiotics to be introduced into drinking water systems has escalated, and human exposure to these antibiotics has also increased (Kim and Aga, 2007). Currently, people are becoming more and more concerned about the potential toxic effects of antibiotics; thus, erythromycin, one type of macrolide antibiotic, has been added into the Drinking Water Contaminant Candidate List established by the U.S. Environmental Protection Agency (USEPA, 2010).

Current municipal wastewater treatment processes were initially designed to remove organic matter and/or nutrients (nitrogen and phosphorus) instead of micropollutants such as antibiotics (Hu et al., 2010; Michael et al., 2013). Because municipal wastewater treatment plants (WWTPs) cannot completely remove antibiotics (Golet et al., 2003; Watkinson et al., 2007; Li et al., 2009), WWTPs become the hotspots for the release of human-use antibiotics into the environment (Gulkowska et al., 2008; Michael et al., 2013). To enhance the removal of these micropollutants via treatment process optimisation, it is essential to thoroughly understand the fate of antibiotics in each individual wastewater treatment process (Hu et al., 2010). In general, conventional biological treatment processes cannot effectively remove antibiotics (Adams et al., 2002; Zhang and Li, 2011; Michael et al., 2013). The disinfection of treated wastewater with chlorine, ozone or UV in WWTPs appears to lead to a significant removal of trace antibiotics (Hollender et al., 2009). Previous studies demonstrated that ozonation is a promising approach to effectively remove multiple classes of antibiotics in secondary effluent (Hollender et al., 2009; Radjenović et al., 2009; Dodd et al., 2010; Rodayan et al., 2010). Nevertheless, the high cost of equipment and the energy required have limited the practical application of ozonation in large-scale WWTPs (Homem and Santos, 2011). In comparison to ozonation, UV irradiation has proven to be less effective and usually requires a dosage 20–100 times higher than the typical disinfection dosage for wastewater effluent to obtain a removal efficiency of 90% (Kim et al., 2009; Katsoyiannis et al., 2011). Although the formation of numerous chlorinated disinfection by-products (DBPs) including volatile or semivolatile/neutral/hydrophobic and nonvolatile/polar/hydrophilic organic compounds caused public concerns, chlorination was still commonly used as the disinfection process in WWTPs globally for decades because of its low cost (Zhang and Minear, 2002; Dodd et al., 2005; Qiang et al., 2006; Wang et al., 2011; Watson et al., 2012). Previous studies investigated the removal behaviours of multiple antibiotics (sulphonamides, carbadox, trimethoprim, fluoroquinolones, and β-lactams) during the chlorination of distilled and surface waters, which simulated the drinking water treatment, using free chlorine (FC) or chlorine dioxide as a disinfectant (Adams et al., 2002; Chamberlain and Adams, 2006; Navalon et al., 2008; Wang et al., 2010, 2011, 2012). Although FC and chlorine dioxide are effective in removing most of these antibiotics from distilled and surface waters, the findings obtained from the above-mentioned less-polluted water matrixes cannot be applied directly to predict the antibiotic removal in wastewater chlorination because of the vast difference in water characteristics, i.e., the dissolved organic carbon (DOC) content and ammonia concentration. Otherwise, significant bias occurs when predicting the loss rate of antibiotics during the chlorination of the wastewater matrix (Dodd et al., 2005; Dodd and Huang, 2007; Yargeau and Leclair, 2008; Wang et al., 2010, 2011, 2012). Our previous study investigated the importance of the pH effect on antibiotic removal and calculated the species-specific kinetics constants between FC species and antibiotics species in the wastewater chlorination process under a specific FC dosage, ammonia concentration and suspended solid (SS) concentration. The results indicated that slight pH value fluctuations markedly affect the removal efficiencies of many antibiotics (Li and Zhang, 2012).

However, to date, very few studies have been conducted on the chlorination of antibiotics under conditions relevant to the chlorination of municipal wastewater, such as different FC dosages and ammonia and SS concentrations, which are important parameters affecting antibiotic removal. Therefore, the chlorination behaviours of 12 antibiotics, including two sulphonamides, three β-lactams, two macrolides, three fluoroquinolones, one tetracycline, and one other antibiotic, at environmentally relevant concentrations were systematically investigated in the secondary effluent matrix. This study focused on (1) determining the chlorination effectiveness of the above frequently used antibiotics under different FC dosages and ammonia and SS concentrations and (2) investigating the kinetics of antibiotics removal by chlorination in relation to the FC and SS concentrations.

2. Material and methods

2.1. *Chemicals and standards*

Twelve antibiotic standards, including two sulphonamides: sulphamethoxazole (SMX) and sulphadiazine (SDZ); three β-lactams: ampicillin (AMP), cefotaxime (CTX), and cefalexin (CLX); two macrolides: roxithromycin (ROX) and erythromycin (ERY); three fluoroquinolones: norfloxacin (NOR), ciprofloxacin (CIP), and ofloxacin (OFL); one tetracycline: tetracycline (TC); and one other antibiotic: trimethoprim (TMP), were obtained from Sigma–Aldrich. The standard purity was the highest commercially available (≥95%). Anhydro-erythromycin (ERY-H_2O), the major metabolite of ERY, was obtained based on the method suggested by McArdell et al. (2003). NaClO was purchased from Fisher Scientific at ~12% (available chlorine, w/w) solution concentration. The FC stock solution was diluted to 1000 mg/L as Cl_2 and standardised iodometrically (Clesceri et al., 1998). Other chemicals and materials, including ultrapure water, acetonitrile, ascorbic acid, formic acid, sulphonic acid solution, sodium hydroxide, and 0.2 μm cellulose nitrate membranes, were the same as those described previously (Li et al., 2009).

2.2. *Analytical method*

The analytical methods of FC, total chlorine, ammonia, nitrite, nitrate, and dissolved organic carbon (DOC) were reported in a