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Characterizing the removal routes of seven pharmaceuticals in the activated sludge process

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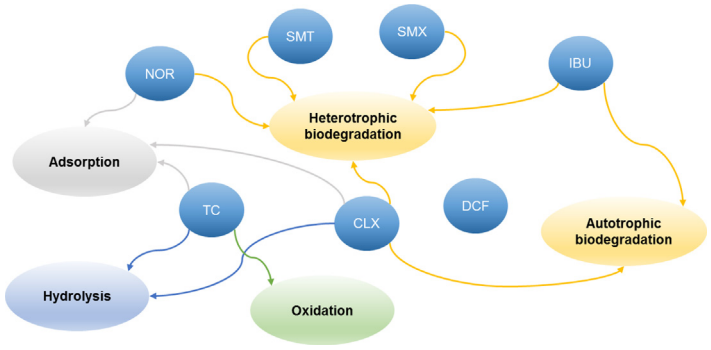
HIGHLIGHTS

- Biodegradation routes were divided into three processes.
- Nitrification played an important role in the removal of CLX and IBU.
- COD degradation was the major removal route of CLX, IBU, NOR, SMT and SMX.
- Adsorption and biodegradation via COD degradation were the major removal routes.

GRAPHICAL ABSTRACT



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ABSTRACT

The removal routes of pharmaceuticals especially biodegradation routes in the activated sludge process are still unclear. Some studies indicated pharmaceuticals were mainly removed via nitrification process (autotrophic biodegradation), while others suggested pharmaceuticals were mainly removed via COD degradation process (heterotrophic biodegradation). These unclear problems limited the improvements of pharmaceuticals removal. In this study, in order to elucidate three biodegradation routes (nitrification, COD degradation, or both nitrification and COD degradation), autotrophic and heterotrophic reactors were individually developed to separate nitrification and COD degradation form the activated sludge process (mix-trophic process including nitrification and COD degradation). Furthermore, the pharmaceuticals removal routes of adsorption, hydrolysis, and oxidation were also studied. Among six degradable pharmaceuticals, heterotrophic biodegradation and adsorption were the major removal routes. Two sulfonamides of five antibiotics were predominantly removed by COD degradation process, while nitrification and adsorption had no contributions. Adsorption, hydrolysis, nitrification, and COD degradation were the main elimination routes of cefalexin. COD degradation and adsorption were the dominant removal routes of norfloxacin. Tetracycline was mainly removed by the adsorption route, and hydrolysis and oxidation also played a role. For two drugs, ibuprofen was removed mainly via nitrification and COD degradation, and no adsorption occurred. Diclofenac could not be removed at all and was persistent in the aerobic conditions. Kinetic studies showed that biodegradation of the two sulfonamides, cefalexin, norfloxacin, and ibuprofen followed first-order kinetics rather than zero-order or second-order kinetics.

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1. Introduction

Anthropogenic pharmaceuticals are widely distributed in the environment. Pharmaceuticals are directly discharged into wastewater and are eventually discharged into natural water bodies such as rivers, lakes and oceans from wastewater treatment plants. Although pharmaceutical residues in the water environment are at trace levels, usually at the ng or μg per liter level, their potential ecological risks are attracting increasing attention (Li and Zhang, 2010; Luo et al., 2018a; Xiao et al., 2017; Yang et al., 2017; Ye et al., 2017; Zhu et al., 2017a; Zhu et al., 2017b). In addition, the spread and aggregation of antibiotic-resistant genes poses a potential worldwide risk on water ecosystem and human health (Kumarasamy et al., 2010; Polesel et al., 2016; Zhu et al., 2013). Wastewater treatment plants, as the collection sites for various types of pharmaceuticals, are suitable to control pharmaceuticals.

The removal of pharmaceuticals in wastewater treatment plants (WWTPs) has attracted increasing attention in recent years (Coutu et al., 2013; Kruglova et al., 2014; Xu et al., 2016; Zheng et al., 2019). To date, numerous efforts have been made to study the removal processes of pharmaceuticals in WWTPs (Luo et al., 2017; Luo et al., 2018b; Luo et al., 2018c). To address this question, many studies have focused on understanding the biotic and abiotic factors that control the removal of pharmaceuticals in the activated sludge process (Ahmed et al., 2015; Kim et al., 2005; Muter et al., 2017). The type of process (aerobic, anoxic or anaerobic process) and the effects of parameters (sludge residence time, dissolved oxygen, physicochemical properties, pH and temperature) on pharmaceutical removal processes have been investigated extensively (Cai et al., 2018; Cheng et al., 2018; Ejhed et al., 2018; Kim et al., 2005; Li and Zhang, 2012; Marx et al., 2015), which showed significant effects on the removal of pharmaceuticals. In addition, the intermediate metabolites of pharmaceuticals were studied on the laboratory scale (Senta et al., 2017). It was reported that biodegradation and adsorption were the major removal routes for 11 antibiotics in the activated sludge process (Li and Zhang, 2010). For many pharmaceuticals in WWTPs, physicochemical elimination processes are of minor importance and their overall removal is largely governed by biodegradation (de Castro et al., 2018; Falas et al., 2016; Zorita et al., 2009), and the design and operation of biological treatment can influence the overall removal of pharmaceuticals (Kirk et al., 2002). However, up to now information on the removal routes of pharmaceuticals in WWTPs is still limited. Many studies investigated the effects of biodegradation on pharmaceuticals removal using allylthiourea to inhibit the nitrification process (Kocamemi and Cecen, 2009; Suarez et al., 2010; Zhou and Oleszkiewicz, 2010). Some studies indicated pharmaceuticals were mainly removed by nitrification process (Kim et al., 2005; Kocamemi and Cecen, 2009; Suarez et al., 2010), while other studies showed pharmaceuticals were mainly removed by COD degradation process (Ren et al., 2007; Shi et al., 2004; Zhou and Oleszkiewicz, 2010). These conflicting results limited improvements in removal efficiency of pharmaceuticals in WWTPs. Therefore, it is critically important to investigate the removal routes of pharmaceuticals especially biodegradation routes in the activated sludge process. The processes of nitrification and COD degradation occurred simultaneously in the activated sludge system. Thus, it is difficult to distinguish pharmaceuticals biodegradation routes (nitrification or COD degradation). In this work, autotrophic (nitrification), heterotrophic (COD degradation), and mix-trophic (both nitrification and COD degradation) reactors were individually developed to distinguish nitrification and COD degradation processes from the activated sludge process.

In this study, we aimed to investigate the removal routes of pharmaceuticals in the activated sludge system. Seven pharmaceuticals including five antibiotics (sulfamethazine (SMT), sulfamethoxazole (SMX), cephalexin (CLX), norfloxacin (NOR), and tetracycline (TC)), and two antipyretic, analgesic and anti-inflammatory drugs (ibuprofen (IBU) and diclofenac (DCF)) were selected to study the removal routes of pharmaceuticals. Six removal routes of pharmaceuticals (biodegradation via nitrification, biodegradation via COD degradation, biodegradation via both nitrification and COD degradation, adsorption, chemical oxidation by oxygen, and hydrolysis) were examined in this study. Autotrophic, heterotrophic, and mix-trophic reactors were developed to distinguish the removal routes of biodegradation, that is, biodegradation via autotrophic process, biodegradation via heterotrophic process, and biodegradation via mix-trophic process. In addition, the kinetics of biodegradation routes were studied.

2. Materials and methods

2.1. Target pharmaceuticals

According to our experimental results of Xiaojiahe WWTP (Chongqing, China) (data not shown), seven pharmaceuticals including five typical antibiotics and two antipyretic, analgesic and anti-inflammatory drugs (ibuprofen and diclofenac) were detected. Five typical antibiotics included four classes: two sulfonamides, sulfamethazine and sulfamethoxazole; one β-lactam, cefalexin; one fluoroquinolone, norfloxacin; and one tetracycline, tetracycline. Consequently, these seven pharmaceuticals were chosen to investigate the removal routes of pharmaceuticals in activated sludge system.

2.2. Experimental reactors and operations

As shown in Fig. 1, three bench-scale, Plexiglas reactors (autotrophic, heterotrophic and mix-trophic reactors) with a working volume of 4.2 L were established for investigating the removal routes of pharmaceuticals in the activated sludge system. Autotrophic, heterotrophic and mix-trophic reactors were operated with a sequential batch reactor model for 8 h: feeding time 20 min, reaction time 380 min, settling time 60 min, drainage time 20 min. All three reactors were operated at the same conditions except for the composition of synthetic influent. 0.36 g L^{-1} NH_4Cl in influent was used as energy and nitrogen source for autotrophic reactor, while heterotrophic reactor used 0.025 g L^{-1} KNO_3 and 0.25 g L^{-1} $C_2H_9NaO_5$ with 0.55 g L^{-1} $C_6H_{12}O_6 \cdot H_2O$ as nitrogen source and energy, respectively. For mix-trophic reactor, 0.36 g L^{-1} NH_4Cl, 0.25 g L^{-1} $C_2H_9NaO_5$, and 0.55 g L^{-1} $C_6H_{12}O_6 \cdot H_2O$ were used as substrates. 0.1 mL L^{-1} trace element was added into each influent of three reactors, and the composition of the trace element solution was used in a previous study (Xu et al., 2015). The detailed compositions of synthetic wastewater were summarized in Table S1. 2.0 mol L^{-1} NaOH and 2.0 mol L^{-1} HCl were used to adjust the influent

Fig. 1. Set up of autotrophic, heterotrophic and mix-trophic reactor.