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Fate and removal of typical pharmaceuticals and personal care products by three different treatment processes

Yu-jie He, Wei Chen, Xiao-ying Zheng *, Xing-nan Wang, Xi Huang

Key Laboratory of Integrated Regulation and Resource Development on Shallow Lakes, Ministry of Education, Environment College, Hohai University, Nanjing 210098, PR China

HIGHLIGHTS

- We investigated 8 kinds of PPCPs in each unit at 2 WWTPs with different processes.
- Agilent 1290–6460 HPLC–MS/MS was firstly utilized to detect estrogens.
- More hydrophobic estrogens such as EE2 and E2 had a higher removal efficiency.
- The OD system was less efficient than A/O and A/A/O-MBR processes in estrogen removal.
- The estrogen removal in anaerobic units was less efficient than that under aerobic conditions.

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ABSTRACT

The presence and distribution of typical of pharmaceuticals and personal care products (PPCPs), which comprise two types of polycyclic musks (PCMs) including Galaxolide (HHCB) and Tonalide (AHTN) as well as six types of estrogens containing estrone (E1), 17β-estradiol (E2), estriol (E3), 17α-ethynylestradiol (EE2), diethylstilbestrol (DES), and bisphenol A (BPA), were investigated at two wastewater treatment plants (WWTPs) in Jiangsu, China. Only raw wastewater was treated in WWTP A while WWTP B was serving an urban-industrialized area. In the influent, the concentrations of EE2 (2193–4437 ng L^{-1}), E2 (1126–1170 ng L^{-1}), and DES (268–421 ng L^{-1}) were generally higher than the previously reported values, whereas the concentrations of HHCB (306–316 ng L^{-1}), E1 (29–129 ng L^{-1}), E3 (53 ng L^{-1}), and BPA (26–176 ng L^{-1}) were much lower than those reported in other previous studies. In addition, AHTN was not detected in either WWTP and E3 was not found in WWTP B. The detected processes including anaerobic/oxic process (A/O), combined orbal oxidation ditch process (C-orbal OD) and anaerobic/anoxic/anoxic/oxic membrane biological reactor (A/A/A/O-MBR) showed higher removal efficiencies for HHCB (67–71%) and EE2 (87%) than those in other previous studies. Besides, the total hydraulic retention time (HRT) ranged between 6.7 and 20.0 h, sludge retention time (SRT) ranged between 8 and 23 d, and water temperature ranged from 24.8 to 28.2 °C. The removal efficiencies for estrogens in biological processes were related to the following factors: the level of hydrophobic estrogens, the type of removal process (C-orbal OD was consistently less efficient in removing estrogens than A/O and A/A/A/O-MBR), and a high SRT or HRT (A/A/A/O-MBR with higher SRT and HRT showed higher and more stable removal of hydrophobic estrogens).

1. Introduction

Recent years have witnessed increasing concerns about the potential harmful consequences of exposure to micropollutants. Various non-governmental and governmental organizations such as EPA, EU, WHO, and the International Program of Chemical Safety (IPCS) are exploring problems resulting from micropollutants and setting up directives to protect and further improve the quality of water resources (Esplugas et al., 2007). Pharmaceuticals and personal care products (PPCPs), which are a group of compounds that include pharmaceutical drugs, ingredients in cosmetics, food supplements, and other personal care products such as spices, cosmetics, and their respective metabolites and transformation products (Ratola et al., 2012), are considered as such emerging microcompounds. Despite their low concentrations, PPCPs are more likely to reach and possibly accumulate in the aquatic environment because of their intrinsic properties such as high polarity and persistence (Sipma et al., 2010). Briefly, PPCPs are characterized by four prominent features. First, they consist of a wide range of compounds whose adsorption behaviors vary with each other; moreover, their behaviors are often controlled by interactions with specific functional groups or complicated external factors such as temperature, concentration and the existence of some chemical substance, resulting in difficulty in predicting their transition (Kibbey et al., 2007). Second, although their distribution is detected by the application of sophisticated modern analytical techniques,

* Corresponding author. Tel./fax: +86 25 83786707.
E-mail address: zhxyqq@hhu.edu.cn (X. Zheng).

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many details remain to be improved for investigating their specific properties. Third, Some PPCPs can be degraded during wastewater treatment in which the efficiencies of PPCP removal could be highly variable within and between facilities due to general operating conditions, technology used, and microbial community composition (Hedgespeth et al., 2012). Finally, they may affect water quality and potentially influence drinking water supplies, the ecosystem, and human health (Boleda et al., 2011) in ways that remain poorly understood. The effluent from wastewater treatment plants (WWTPs) is one of the most important sources of PPCPs (e.g., pharmaceuticals, personal care products, endocrine disruptors and illicit drugs) released into receiving water systems (Hedgespeth et al., 2012; Kasprzyk-Horderna et al., 2009; Grover et al., 2009; Yang et al., 2011). Thus, an emerging task that WWTPs must perform is to act as a barrier for PPCPs and prevent the emission of potentially harmful substances into the aqueous environment (Yu et al., 2013).

Polycyclic musks (PCMs) and estrogens, which are two types of representative PPCPs, are selected as the target compounds to be detected in this study. PCMs currently constitute the largest group of synthetic musks among which Galaxolide (HHCB) and Tonalide (AHTN) are the main representative compounds ranked by utilization rate (Zeng et al., 2007; Shek et al., 2008). The key structural feature of the above two musks is an indane or tetraline skeleton, which can be highly substituted by methyl groups (Ricking et al., 2003). Studies examining the toxicity of PCMs have reported a range of harmful effects. For instance, fish collected from areas all over Europe showed concentrations in the range of 0.1–1.5 μg/g wet wt. AHTN and HHCB (Schnell et al., 2009). Meanwhile, various types of estrogens, along with PCMs, have also become a public health concern because of their detrimental interference with human natural endocrine regulation (Zhang et al., 2012). Exposure of freshwater or estuarine fish to estrogens may result in the alteration of their sexual function (Labadie and Hill, 2007). For example, 4 ng L^{-1} of 17α-ethynylestradiol (EE2) can prevent male fathead minnows from developing normal secondary sexual characteristics (Länge et al., 2011). The natural estrogens, 17β-estradiol (E2) and its main metabolites estrone (E1) and estriol (E3), along with the synthetic estrogens such as EE2, contribute to a large extent to the estrogenicity of WWTP effluent (Xu et al., 2012). Considering that only a few studies were previously conducted on diethylstilbestrol (DES) in the wastewater treatment field and that bisphenol A (BPA) was especially widespread to an extreme degree in China (Zoeller et al., 2005), these two estrogens were also investigated in this study.

In specific area of China, few studies are focus on the efficacies of different units within a specific WWTP or how various WWTP treatment technologies compare in terms of removal of PPCPs. However, this information is important to decide appropriate steps for minimizing risk from PPCP emissions into the environment. In addition, given that most of the related researches on PPCPs have only focused on the preliminary influent and effluent at WWTPs in China, this study was conducted to illustrate the removal of PPCPs in different units at different plants using different treatment processes. Two WWTPs, located in Yangtze River and Taihu Lake, were chosen as the specific cases. In this study, HPLC–MS/MS (Agilent 1290–6460 system) was firstly used to detect the six estrogens. There was considerable ambiguity regarding the removal mechanism. Thus, this study was expected to provide greater insight into the development of wastewater treatment technologies for PPCP removal.

2. Methods and materials

2.1. Sampling from WWTPs

WWTP A at Nanjing, with a capacity of 640,000 $m^3 d^{-1}$, utilizes the anaerobic/oxic process (A/O). The investigated processes of WWTP B at Wuxi are anaerobic/anoxic/anoxic/oxic membrane biological reactor (A/A/A/O-MBR, 50,000 $m^3 d^{-1}$, the fourth phase project) processes and the combined orbal oxidation ditch (C-orbal OD, 50,000 $m^3 d^{-1}$, the third phase project). An investigation revealed that the composition of influent was urban wastewater in WWTP A serving 1.6 million people, while 40% of the influent was industrial wastewater in WWTP B serving 330 thousand people for the two phases above. A_1–A_6, B_1–B_8, and C_1–C_2 in Fig. 1 are the sampling sites in the three different processes (A_4–A_5 and B_3–B_6 represent separate tanks). Effluent of the screening chamber and influent before the disinfection unit were considered as the influent and effluent sewage respectively in the two WWTPs. In addition, the influents were identical for the C-orbal OD and A/A/A/O-MBR processes in WWTP B. In particular, there were two anoxic units in the A/A/A/O-MBR process (Fig. 1b). The main characteristics of the two WWTPs can be seen in Table 1. In addition, mixed liquor suspended solids in both WWTPs were (in mg L^{-1}) 4122–4364 (aerobic units of A/O), 5484–5812 (aerobic units of C-orbal OD), 8556–8701 (aerobic units of A/A/A/O-MBR) and 12548–12867 (MBR) respectively.

Three analytical campaigns, were carried out once every ten days in July 2011, each time from 9 a.m. to the end of the collection. Considering the influence of HRT (6.7, 10 and 20.0 h in three different treatment processes), samples taken from detected units were obtained by mixing wastewater samples collected every hour (7, 10, and 20 hour samples for three treatment processes respectively). Additionally, the sample of each unit was collected from three different positions in order to obtain composite sample. The following detected concentrations were all in mean values. Water samples were collected in pre-cleaned amber-glass bottles (2.5 L) from planned sites. To eliminate biodegradation during sample storage and transportation, the samples were immediately delivered to the laboratory and stored at 4 °C in the dark until analysis. Samples were first filtered with 0.45-μm glass-fiber membranes within 24 h then pretreated by solid-phase extraction (SPE) for identification and quantification of organics immediately after preliminary filtration.

2.2. Apparatus

Identification and quantification of PCMs were performed with a DSQ II Single Quadrupole GC–MS apparatus (ThermoQuest, San Jose, CA, USA) equipped with a fused-silica TR-5MS capillary column (30 m × 0.25 mm id, 0.25-μm film thickness). For estrogens, HPLC–MS/MS analyses were carried out using an Agilent 1290–6460 system fitted with an Agilent ZORBAX Eclipse Plus RRHD C18 threaded column (2.1 mm × 50 mm id, particle size 1.8 μm). The MS/MS analyses were performed with a Micromass Quattro triple–quadrupole mass spectrometer equipped with a Z-spray electrospray interface. Organic compounds were concentrated from sewage samples through a vacuum 12-position extraction manifold (Supelco) equipped with an Oasis HLB cartridge (6 cm^3/500 mg, Waters, USA).

2.3. Chemicals and standard reagents

The reference standard samples of PCMs (HHCB, AHTN) and estrogens, i.e., E1, E2, E3, EE2, BPA, and DES, were purchased from Sigma-Aldrich (USA). All standard samples had an isotopic purity greater than 98% and were stored at 4 °C. The standard samples were dissolved in organic solvents (PCMs in methylene chloride and estrogens in methanol) to prepare the stock and working solutions that were also stored at 4 °C in the dark. Chromatographic grade solvents containing dichloromethane, N-hexane, ethyl acetate, methanol, and acetonitrile were supplied by Merck, Germany. All pieces of glassware were cleaned with surfactant, ultrapure water, and acetone.

2.4. Sample preparation

For the PCMs, 5 mL of methanol/methylene chloride (1:1, v/v) was used to condition the SPE cartridge. The cartridge was drained dry after flushing and then eluted with 5 mL of methanol. In this step, the