



Transformation and fate of natural estrogens and their conjugates in wastewater treatment plants: Influence of operational parameters and removal pathways



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ABSTRACT

Natural estrogens (NEs) discharged from wastewater treatment plants (WWTPs) have drawn great attention because of their potential risks to aquatic ecosystems. However, neglect of the conjugated natural estrogens (C-NEs) has caused large discrepancies among different studies on the removal of NEs in WWTPs. The present work investigated the transformation and fate of three NEs and six corresponding C-NEs along wastewater treatment processes. The removal efficiencies of the target estrogens (i.e., NEs and C-NEs) and their correlations with the operational parameters were determined over a twelve-month monitoring period at a typical WWTP adopting a combined bio-treatment process (i.e., anaerobic/anoxic/oxic process followed by a moving-bed biofilm reactor). The concentration variations of the target estrogens along the treatment processes were examined to differentiate the transformation and fate of NEs and C-NEs. Moreover, lab-scale experiments were conducted to clarify the removal pathways of C-NEs in the bio-treatment process. Results indicate that both NEs and C-NEs could pass through the treatment processes, thus being frequently detected in the effluent and excess sludge. The aqueous removal efficiencies of NEs and C-NEs were significantly correlated with the sludge retention time and temperature, respectively. C-NEs were more persistent than NEs, so considerably high conjugated ratios (13.5–100.0%) were detected in the effluent. Sulfate conjugates presented a lower adsorption affinity to sludge and a slower hydrolysis rate than glucuronide conjugates, which makes the former more recalcitrant to biodegradation. This study highlights the challenge on the elimination of NEs, particularly their conjugates, by wastewater treatment processes.

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1. Introduction

Since the 1990s, the occurrence of endocrine disrupting chemicals (EDCs) in the environment has induced great challenges to the safety of aquatic ecosystems and received increasing attention (Schwarzenbach et al., 2006; Ternes et al., 1999). Among the EDCs, natural estrogens (NEs), including estrone (E1), 17 β -estradiol (E2) and estriol (E3), were the most studied because of their strong estrogenic potencies (Liu et al., 2015). Human and animal excretions constituted the main sources of NEs in the environment, while the occurrence of NEs in municipal wastewater is primarily attributed to human excretions. The occurrence and behavior of

NEs in wastewater treatment plants (WWTPs) has been extensively investigated around the world (Hamid and Eskicioglu, 2012; Liu et al., 2009; Nie et al., 2012), but the reported NE removal efficiencies in different WWTPs are largely variable. An important reason for the inconsistencies is that the operational parameters, including temperature, hydraulic retention time (HRT) and sludge retention time (SRT), varied greatly among the different studies. However, studies that discussed the influence of operational parameters on the NE removal also showed significant discrepancies (Clara et al., 2005; Hashimoto et al., 2007; Liu et al., 2015; Nakada et al., 2006). It is particularly difficult to isolate the influence of one operational parameter, as the treatment processes and other operational parameters differed across these studies. Therefore, focusing only on one WWTP and statistically analyzing its long-term monitoring data may clarify the effects of different

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operational parameters.

Another reason behind the variations in the NE removal efficiencies found in previous studies is the neglect of conjugated natural estrogens (C-NEs). NEs are predominantly excreted from human and animal bodies in their conjugated forms, so C-NEs can constitute a notable proportion in the influent of WWTPs (Johnson and Williams, 2004). C-NEs can be deconjugated into their corresponding NEs by arylsulfatase and β -glucuronidase derived from microorganisms which are abundant in WWTPs (Dray et al., 1972; Liu et al., 2015), thus leading to an inaccurate estimation on the removal efficiencies of NEs. However, limited research has been conducted on the transformation and fate of C-NEs in full-scale WWTPs, probably due to a lack of easily applicable methods for simultaneous detection of both NEs and C-NEs in complicated matrices (Zhu et al., 2015). The C-NE removal pathways in biotreatment processes have been proposed as follows: the conjugates are first deconjugated into their corresponding NEs and then biodegraded (Gomes et al., 2009; Liu et al., 2015). However, Kumar et al. (2012) found that C-NEs were not converted stoichiometrically to their corresponding NEs in raw sewage, so other metabolites may be formed. Additionally, batch studies on the removal of C-NEs usually focused on the concentration variations of the NEs and C-NEs (D'Ascenzo et al., 2003; Gomes et al., 2009; Kumar et al., 2012), while the contributions of enzymatic hydrolysis, biodegradation and sludge adsorption have not yet been separately identified. Thus, the removal pathways of C-NEs in wastewater treatment processes need to be further clarified.

This work aimed to elucidate the transformation and fate of three NEs and six C-NEs in WWTPs. A typical WWTP was selected for long-term (twelve-month) monitoring, which adopted an anaerobic/anoxic/oxic process followed by a moving-bed biofilm reactor (A/A/O-MBBR) as biotreatment. The aqueous removal efficiencies of target estrogens were determined and further correlated with the operational parameters of the WWTP. The difference in the transformation and fate of NEs and C-NEs was clarified by monitoring their concentration variations along the treatment processes. In particular, the removal pathways of C-NEs in the biotreatment were explored by lab-scale tests under well controlled conditions.

2. Materials and methods

2.1. Chemicals

NE (E1, E2, and E3) standards were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany; purity > 99.0%). Sodium salts of six C-NEs, including estrone 3- β -D-glucuronide (E1-3G), β -estradiol 3- β -D-glucuronide (E2-3G), β -estradiol 17- β -D-glucuronide (E2-17G), estrone 3-sulfate (E1-3S), β -estradiol 3-sulfate (E2-3S), and estriol 3-sulfate (E3-3S), were purchased from Sigma-Aldrich (Shanghai, China; purity > 95%). Two internal standards, E2-d₂ ($\geq 98\%$) and E2-3S-d₄ (50% Tris), were supplied by CDN Isotopes (Quebec, Canada). The major physicochemical properties of the target estrogens and internal standards are listed in Table S1. The stock solutions of the target estrogens and internal standards were individually prepared by dissolving each compound in methanol at a concentration of 1000 mg L⁻¹ and then stored at -20 °C in a refrigerator.

Methanol, methyl *t*-butyl ether, acetonitrile, dichloromethane, ammonia (25% aqueous solution, by weight) and acetone, all of high-performance liquid chromatography grade, were obtained from Fisher Scientific (Geel, Belgium). Na₂EDTA-McIlvaine buffer was prepared by dissolving 21.00 g citric acid monohydrate, 17.75 g Na₂HPO₄, and 60.50 g Na₂EDTA·2H₂O in 1.625 L of ultrapure water, with pH adjusted to 4.00 \pm 0.05. β -Glucuronidase from *Helix*

pomatia (containing 100,000 U mL⁻¹ glucuronidase activity and 5000 U mL⁻¹ sulfatase activity), saccharic acid 1,4-lactone monohydrate (SA, an inhibitor for β -glucuronidase), STX 64 (an inhibitor for sulfatase), D-glucuronic acid sodium, glucuronide phenolphthalein and NaN₃, were all purchased from Sigma-Aldrich (Shanghai, China). Ultrapure water was produced from a Milli-Q system (Advantage A10, Millipore, USA).

2.2. Sample collection

The selected WWTP is located in Wuxi City, Jiangsu Province, East China, which serves 820,000 inhabitants and operates with a flow rate of 100,000 m³ d⁻¹. The treatment processes comprise a screen and a horizontal-flow grit chamber as the primary treatment, an A/A/O-MBBR combined biotreatment process as the secondary treatment, and rotary fiber disc filters and UV disinfection as the tertiary treatment. A twelve-month monitoring investigation was conducted from July 2014 to June 2015. The influent, effluent and excess sludge samples were collected every month, and concurrently the real-time operational parameters, including HRT, SRT and temperature, were recorded (Table S2). During the sampling periods, major characteristic parameters of the influent and effluent (Table S3) were analyzed to confirm the normal operation of the WWTP. Additionally, flow-proportional (24 h) composite samples were collected using automatic samplers (SD900, Hach, Loveland, USA) from each treatment unit along the treatment processes in July 2015, with the sampling points illustrated in Fig. 1. All the acquired samples were subjected to pretreatment and extraction (detailed in Section 2.3) on site, and the resulting solid phase extraction (SPE) cartridges were stored in ice boxes and transported to our laboratory for analysis.

2.3. Analytical methods and quality control

The extraction and detection of the target estrogens in the wastewater and sludge samples followed the methods developed in our previous study (Zhu et al., 2015). In brief, SPE was applied to concentrate the target estrogens and purify the interfering matrix in the wastewater samples with an Oasis HLB cartridge coupled with a Sep-pak C18 cartridge (500 mg/6 mL both, Waters, USA). For the sludge samples, ultrasonic solvent extraction was first adopted to extract the target estrogens from the sludge before the SPE procedure. Subsequently, the target estrogens were separated using an Agilent 1290 ultra-performance liquid chromatography equipped with a Waters BEH-C18 column (100 mm \times 2.1 mm, 1.7 μ m), and detected by an Agilent 6420 Triple Quad mass spectrometer equipped with a negative electrospray ionization source in the multiple reaction monitoring mode. Quantification of the target estrogens was performed with the internal standard method for minimizing matrix effects. The recoveries were in the ranges of 61.2–122.4% and 59.7–106.2% for the wastewater and sludge, respectively; the limits of quantification (LOQs) ranged from 0.04 (E2-3S) to 1.4 ng L⁻¹ (E2-17G) and from 0.05 (E2-3S) to 1.9 ng g⁻¹ (E2) for the wastewater and sludge, respectively (Table S1). Calibration curves for the target estrogens were re-established every month. If any estrogen concentration was detected above the upper limit of the calibration range, then the sample was diluted and analyzed again. During sample analysis, ongoing quality control checks, including blank, duplicate of samples, and spiking recovery checks, were performed every 15 samples to ensure that all data were of good quality.

2.4. Lab-scale batch experiments

A series of lab-scale batch experiments were carried out to

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