



Occurrence and removal of estrogens in Brazilian wastewater treatment plants



Germana P. Pessoa^a, Neyliane C. de Souza^b, Carla B. Vidal^a, Joana A.C. Alves^a, Paulo Igor M. Firmino^a, Ronaldo F. Nascimento^c, André B. dos Santos^{a,*}

^a Department of Hydraulic and Environmental Engineering, Federal University of Ceará, Rua do Contorno, S/N Campus do Pici, Bl. 713, CEP: 60455-900, Fortaleza, CE, Brazil

^b Department Sanitary and Environmental Engineering, State University of Paraíba, Rua Juvêncio Arruda, S/N, Campus Universitário, Bodocongó, CEP: 58109-790, Campina Grande, PB, Brazil

^c Department of Analytical Chemistry and Physical Chemistry, Federal University of Ceará, Rua do Contorno, S/N Campus do Pici, Bl. 940, CEP: 60451-970, Fortaleza, CE, Brazil

HIGHLIGHTS

- The occurrence of four endocrine disrupting chemicals was evaluated.
- The removal efficiency of four hormones in low-cost plants was examined.
- Estrogen occurrence showed a wide variation in influent and effluent samples.
- Estrone showed the highest occurrence in the influent and the effluent samples.
- WSP treatment was observed to be less effective for removing estrogens.

ARTICLE INFO

Article history:

Received 11 February 2014

Received in revised form 2 May 2014

Accepted 2 May 2014

Available online xxxx

Editor: D. Barcelo

Keywords:

Endocrine disrupting chemical

Hormone

Occurrence

Removal

Wastewater treatment plant

ABSTRACT

This paper evaluated the occurrence and removal efficiency of four estrogenic hormones in five biological wastewater treatment plants (WWTPs), located in the State of Ceará, Brazil. The five WWTPs comprised: two systems consisted of one facultative pond followed by two maturation ponds, one facultative pond, one activated sludge (AS) system followed by a chlorination step, and one upflow anaerobic sludge blanket (UASB) reactor followed by a chlorination step. Estrogen occurrence showed a wide variation among the analyzed influent and effluent samples. Estrone (E1) showed the highest occurrence in the influent (76%), whereas both 17 β -estradiol (E2) and 17 α -ethynylestradiol (EE2) presented a 52% occurrence, and the compound 17 β -estradiol 17-acetate (E2-17A), a 32% one. The occurrence in the effluent samples was 48% for E1, 28% for E2, 12% for E2-17A, and 40% for EE2. The highest concentrations of E1 and EE2 hormones in the influent were 3050 and 3180 ng L⁻¹, respectively, whereas E2 and E2-17A had maximum concentrations of 776 and 2300 ng L⁻¹, respectively. The lowest efficiencies for the removal of estrogenic hormones were found in WWTP consisted of waste stabilization ponds, ranging from 54 to 79.9%. The high-rate systems (AS and UASB), which have chlorination as post-treatment, presented removal efficiencies of approximately 95%.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Endocrine disrupting chemicals (EDCs) are a heterogeneous group of substances characterized by their potential to interfere with endocrine system functions in wildlife and humans (Sanfilippo et al., 2010). The presence of these contaminants in aquatic environment and their potential effects on living organisms have become a growing concern in recent years, which requires identification, analysis and characterization of risks in different environmental matrices (Dolar et al., 2012).

Estrogenic hormones excreted by humans are emerging contaminants which can reach the aquatic environment via wastewaters

release. The presence of such micropollutants in surface waters poses various questions concerning their degradation and their potential adverse effects on the sexual and reproductive systems in wildlife, fish and humans (Chang et al., 2011; Gabet-Giraud et al., 2010; Jobling et al., 1998; Purdom et al., 1994).

The occurrence of estrogens in wastewaters and surface waters has been investigated in numerous studies (Chang et al., 2011; Coleman et al., 2010; Gabet-Giraud et al., 2010; Lundstrom et al., 2010; Radjenovic et al., 2009), in which both natural (estrone and 17 β -estradiol) and synthetic (17 α -ethynylestradiol) varieties were identified as the main compounds responsible for estrogenic activities in wastewater treatment plants (WWTPs). Many studies have also reported that the elimination of some EDCs in WWTP can be ineffective (Carballa et al., 2004; Dolar et al., 2012; Moon et al., 2008), as a result,

* Corresponding author. Tel.: +55 85 33669490.

E-mail address: andre23@ufc.br (A.B. dos Santos).

they are found in surface water, groundwater, and even drinking water (Al-Odaini et al., 2010; Rahman et al., 2009). Therefore, it is important to develop reliable wastewater treatment technologies which can efficiently remove these emerging contaminants at trace level concentrations.

Estrogen removal in WWTPs is a very complex procedure since it depends on numerous design aspects (sludge age, hydraulic retention time (HRT), organic loading rate (OLR), etc.), environmental conditions (sunlight, temperature, pH, toxic compounds, etc.), type of sludge and operational conditions (Clara et al., 2005). There are several studies worldwide which have assessed the behavior of micropollutants in WWTPs. However, most of them refer to activated sludge systems, which are most commonly used in development countries (Andersen et al., 2003; Baronti et al., 2000; Carballa et al., 2004; Fernandez-Fontaina et al., 2012; Joss et al., 2006; Kanda and Churchley, 2008). In contrast, there are only a few published reports on the concentrations or removal of EDCs in Brazilian WWTPs (Brandt et al., 2013; Froehner et al., 2010; Queiroz et al., 2012; Ternes et al., 1999b), especially those which uses waste stabilization ponds (WSP) technology.

In the state of Ceará, biological processes are widely used, being 62% of these wastewater treatment systems consisted of stabilization ponds (Brandão, 2000). Because of the great applicability, low capital and operational costs of WSP in hot-climate developing countries, such as Brazil, it is important to evaluate the micropollutants removal efficiency of these systems (Coleman et al., 2010) and compare them with the systems commonly used in other countries, such as activated sludge systems and anaerobic reactors (Carballa et al., 2007; Czajka and Londry, 2006; Paterakis et al., 2012).

It is also important to determine the concentrations and fate of estrogenic compounds in Brazilian WWTPs since there are limited studies on these compounds in wastewater systems, receiving bodies (water and sediments) and drinking water (Jardim (Jardim et al., 2012; Montagner and Jardim, 2011; Moreira et al., 2009, 2011; Sodré et al., 2010a, 2010b)). Despite the significant increase in research on the subject, the occurrence of several micropollutants in environmental matrices has not been established yet for many countries, mainly due to the difficulties and costs associated with the chemical analyses (Virukyte et al., 2010). In fact, in Brazil, there are only a small number of studies reporting the occurrence of a few compounds.

Therefore, the main objective of this paper was to determine the occurrence and removal of four EDCs in five Brazilian real scale WWTPs (specially low costs treatment technologies), i.e. three waste stabilization ponds systems, an activated sludge system followed by a chlorination step and a UASB reactor also followed by a chlorination step. This would provide important insights into the technology which can most effectively remove these compounds and, therefore, help to guide current environmental legislations. The paper does not focus on either removal mechanisms, which are well reported in literature and depend on the treatment technology, or estrogenic activity, which was out of the scope of the present investigation.

2. Materials and methods

2.1. Reagents and material

Solid-phase extraction (SPE) was carried out by using 200 mg Oasis® HLB cartridges (Waters, Milford, MA, USA) and HPLC-grade methanol purchased from Sigma-Aldrich (St. Louis, MO, USA). HPLC-grade water was produced using a Milli-Q purification system (Millipore, Bedford, MA, USA). Standards for estrone (E1, 99% purity), 17 β -estradiol (E2, 98% purity), 17 α -ethynylestradiol (EE2, 99.4% purity) and 17 β -estradiol 17-acetate (E2-17A, 98.8% purity) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The stock EDC standard solutions, at a concentration of 1000 ng mL⁻¹, and the appropriate working standard solutions were prepared in methanol and stored in amber glass bottles at 4 °C.

2.2. Sample preparation

The first step of sample preparation involved performing wastewater filtrations under vacuum through 0.45 μ m glass-fiber filters to remove suspended particulate matter and avoid SPE cartridge clogging. The pH of each sample was then adjusted to 3.0 by addition of 50% (v/v) HCl, after which the analytes were extracted with a Speed Mate 12-port SPE vacuum manifold (Applied Separations, Allentown, PA, USA).

The SPE cartridges were initially preconditioned with 10 mL of methanol, and subsequently with 10 mL of Milli-Q water. The samples, typically 500 mL, were then loaded onto the cartridges at a flow rate lower than 2 mL min⁻¹. The cartridges were then dried for 30 min under vacuum and eluted with 4 mL of methanol. Extracts collected in amber glass flasks were dried in an oven at 45 °C. The dry residues were derivatized by the addition of N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) for 30 min at 60 °C. The derivatives were cooled to room temperature and resuspended in 500 μ L of methanol. The solutions were then transferred to sealed cap vials and analyzed by gas chromatography–mass spectrometry (GC/MS).

2.3. GC/MS analysis

EDC determinations were performed on a Focus GC instrument interfaced to a DSQ II mass spectrometer and controlled by the software XCalibur (Thermo Electron SA, Madrid, Spain). The GC instrument was equipped with a Supelco SLB™-5MS capillary column (silphenylene polymer, which is virtually equivalent in polarity to 5% diphenyl/95% methyl siloxane; 30 mm \times 0.25 mm I.D. \times 0.25 μ m film thickness), and helium (>99.999% purity) was used as the carrier gas at a flow rate of 1.2 mL min⁻¹.

The injection port temperature was maintained at 250 °C, and the oven temperature program varied as follows: ramp up to 150 °C from 50 °C (at a rate of 40 °C min⁻¹), ramp up to 270 °C at a rate of 40 °C min⁻¹ (held for 1 min), ramp up to 280 °C at a rate of 10 °C min⁻¹ (held for 5 min), and ramp up to 290 °C at a rate of 10 °C min⁻¹ (held for 1 min). Sample injection was performed in splitless mode using an injection volume of 1 μ L. The mass spectrometer was operated in electron positive impact ionization mode at 70 eV, with a full scanning range of 50–650 m/z, and ion source and transfer line temperatures of 290 °C. This method was developed from previous studies (Liu et al., 2004; Mol et al., 2000; Shimada et al., 2001; Tan et al., 2007; Ternes et al., 1999b).

2.4. Quality assurance and quality control

The validation of the optimized method, as well as the determination of recoveries and occurrences in the wastewater samples, was conducted according to Brazilian standard DOQ-CGCRE-008 (INMETRO, 2006). Linearity (*L*), limits of detection (LOD) and quantification (LOQ), recovery, and repeatability (*R*) were investigated. LOQ and LOD were calculated from the calibration curve and the spiked recoveries, whereas repeatability was determined from the relative standard deviation (RSD) of 10 replicated samples. Analysis of each wastewater sample was performed in triplicate and was accompanied by the analysis of one blank laboratory reagent. Recoveries were determined by the extraction, derivatization and analysis of two replicated spikes at an estimated detection limit (500 ng L⁻¹) for each target analyte.

2.5. Sample collection

Duplicate grab wastewater samples were collected between April 2010 and April 2012 from five full-scale WWTPs located in the State of Ceará, a semi-arid zone in Brazil. Additional details regarding these WWTPs are given in Table 1. For each WWTP, five influent and effluent samples were analyzed in order to determine the estrogens removal.

Download English Version:

<https://daneshyari.com/en/article/6329050>

Download Persian Version:

<https://daneshyari.com/article/6329050>

[Daneshyari.com](https://daneshyari.com)