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Fate of selected emerging micropollutants during mesophilic, thermophilic and temperature co-phased anaerobic digestion of sewage sludge

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HIGHLIGHTS

- Two single-stage and a two-stage thermophilic/mesophilic AD systems were used.
- Removal efficiency of synthetic EDCs and NSAIDs was investigated.
- NSAIDs were highly removed during sludge AD, EDCs removal was moderate.
- The use of thermophilic/mesophilic system slightly enhanced removal of EDCs.
- Biotransformation of NP_1EO and NP was affected by digesters' temperature.

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ABSTRACT

The removal of endocrine disrupting compounds (EDCs) and non-steroidal anti-inflammatory drugs (NSAIDs) was studied in three lab-scale anaerobic digestion (AD) systems; a single-stage mesophilic, a single-stage thermophilic and a two-stage thermophilic/mesophilic. All micropollutants underwent microbial degradation. High removal efficiency (>80%) was calculated for diclofenac, ibuprofen, naproxen and ketoprofen; whereas triclosan, bisphenol A and the sum of nonylphenol (NP), nonylphenol monoethoxylate (NP_1EO) and nonylphenol diethoxylate were moderately removed (40–80%). NSAIDs removal was not affected by the type of AD system used; whereas slightly higher EDCs removal was observed in two-stage system. In this system, most microcontaminants were removed in thermophilic digester. Biotransformation of NP_1EO and NP was affected by the temperature applied to bioreactors. Under mesophilic conditions, higher removal of NP_1EO and accumulation of NP was noticed; whereas the opposite was observed under thermophilic conditions. For most analytes, higher specific removal rates were calculated under thermophilic conditions and 20 days SRT.

1. Introduction

Anaerobic digestion (AD) is currently one of the most widely adopted treatment processes for sludge produced in wastewater treatment plants (WWTPs). The application of single stage mesophilic AD results to efficient sludge stabilization and biogas production (Appels et al., 2008; Cao and Pawlowski, 2012). Single stage thermophilic AD and two-stage thermophilic/mesophilic AD are also used worldwide to assure safer sludge disposal and better operational stability, respectively (Chen et al., 2008; Ge et al., 2010; Rubio-Loza and Noyola, 2010).

Nowadays, almost 10 million tons of dry sludge are produced in EU27 and more than half of this amount is spread to the land for agricultural purposes (Kelessidis and Stasinakis, 2012). Recent studies have indicated the occurrence of several emerging organic micropollutants such as endocrine disrupting compounds (EDCs) and non-steroidal anti-inflammatory drugs (NSAIDs) in sludge at concentrations ranging between few $\mu g\ kg^{-1}$ to some $mg\ kg^{-1}$ DS (Stasinakis, 2012; Narumiya et al., 2013; Stasinakis et al., 2013). Among the EDCs commonly detected in sludge, the non-polar and highly lipophilic nonylphenol (NP), nonylphenol monoethoxylate

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(NP_1EO) and nonylphenol diethoxylate (NP_2EO) as well as triclosan (TCS) and bisphenol A (BPA) are of critical environmental concern due to their high concentrations and toxicological properties. On the other hand, diclofenac (DCF), naproxen (NPX), ketoprofen (KFN) and ibuprofen (IBF) are a group of NSAIDs with worldwide high consumption due to their analgesic and antipyretic effects. Despite the often detection of the aforementioned compounds in sludge samples, so far, little work has been conducted to systematically track their removal in sludge AD. Relevant information usually originates from the monitoring of full-scale anaerobic digesters (Narumiya et al., 2013; Samaras et al., 2013), while there is no study comparing emerging contaminants' removal in parallel mesophilic, thermophilic and two-stage AD systems.

Specifically, according to monitoring studies, NP_1EO and NP_2EO are partially removed during sludge AD, whereas in many cases concentrations of NP in digested sludge are higher comparing to raw sludge (González et al., 2010; Samaras et al., 2013). NP_1EO and NP_2EO seem to be biodegraded to some extent during AD, while contradictory results have been presented for NP by a number of authors (Hernandez-Raquet et al., 2007; Chang et al., 2005; Paterakis et al., 2012). Regarding BPA and TCS, in a recent monitoring study a mean removal rate lower than 40%, was observed for both compounds in a mesophilic full-scale anaerobic digester (Samaras et al., 2013). To the best of our knowledge, no lab-scale experiments have been performed to investigate the fate of these micropollutants during sludge AD. Regarding the removal of target NSAIDs in full-scale anaerobic digesters, Samaras et al. (2013) reported that IBF and NPX were removed at a rate higher than 80% and Narumiya et al. (2013) reported a removal of KFN and DCF between 30% to 40%. Carballa et al. (2006), using mesophilic lab-scale anaerobic digesters, reported removals ranging between 40% to 87% for IBF, DCF and NPX.

Based on the above, the objective of this study was to investigate the removal efficiency of five synthetic EDCs (NP, NP_1EO, NP_2EO, TCS, BPA) and four NSAIDs (DCF, NPX, IBF, KFN) in lab-scale anaerobic digesters, operating under single-stage and two-stage thermophilic and mesophilic anaerobic conditions. For this reason, three systems were used; a single-stage mesophilic, a single-stage thermophilic and a two-stage thermophilic/mesophilic. All systems operated at the same total sludge residence time (SRT: 20 days), their operation was divided in two phases and lasted 466 days. AD performance stability was monitored on a frequent basis by measuring total suspended solids (TSS), volatile suspended solids (VSS), total COD (COD_t), VFAs concentration, as well as biogas production and alkalinity. The removal efficiency and specific removal rates of target analytes were estimated in all bioreactors.

2. Methods

2.1. Analytical standards and reagents

Analytical standards of IBF, NPX, DFC, KFN, TCS, NP, NP_1EO and NP_2EO were supplied by Dr. Ehrenstorfer (Germany). BPA was purchased by Fluka (Switzerland); whereas the deuterated [$^2H_{16}$] bisphenol A (BPA d-16) and meclofenamic acid were purchased from Sigma–Aldrich (USA). Stock and working solutions of individual compounds were prepared in methanol at 1000 mg L^{-1} and kept at −18 °C. Methanol (MeOH) and ethyl acetate were of HPLC grade (Merck, Germany) and they were used as received. Bis(trimethylsilyl)trifluoroacetamide (BSTFA), BSTFA + 1% trimethyl chlorosilane (TMCS) solution and pyridine, used for silylation, were purchased by Supelco (USA) and Carlo Erba-SDS (France), respectively. The solid phase extraction (SPE) cartridges used for samples' clean-up were silica-based bonded C18 (Sep-Pak, 6 ml, 500 mg) and they were supplied by Waters (Ireland). HPLC grade water was prepared in the laboratory using a MilliQ/MilliRO Millipore system (USA). Ultra-pure HCl (32%), used for samples' acidification, was purchased by Merck (Germany). All the abbreviations used in this study can be found in Table S1.

2.2. Lab-scale anaerobic digesters

Four laboratory-scale continuously stirred anaerobic digesters (CSTRs) were used in this study (Fig. 1). Two of them were operated at the mesophilic temperature range (M_1 and M_2) and two at the thermophilic temperature range (T_1 and T_2). Each reactor was made of 5 mm thick steel cylinders, had an internal diameter of 100 mm, a total volume of 4 L and an operating liquid volume of 3 L. Sealing of the reactors was achieved by bolted O-ring mounted plexiglass stoppers. Three ports were installed in each digester for feeding, sample collection and biogas venting. Mixing was provided by steel stirrers, while feeding and decanting were carried out by calibrated peristaltic pumps. In order to provide optimum conditions for each process, the mesophilic anaerobic digesters were operated at 37 ± 0.5 °C, while the thermophilic at 55 ± 0.5 °C. In both cases, temperatures were kept constant using appropriate water baths.

2.3. Inoculation and experimental set-up

All reactors were initially seeded with an anaerobic inoculum obtained from a full-scale mesophilic anaerobic digester operated in Athens WWTP. Then, they were flushed with N_2 in order to remove oxygen and achieve anaerobic conditions. The substrate used for reactors' feeding was a mixture of primary sludge and secondary sludge (50:50 volume ratio), obtained from University Campus WWTP and municipal WWTP, respectively. During feed events, approximately a volume of 150 ml of mixed sludge was pumped to the system using peristaltic pumps. The operational sequence was identical in all reactors and included feeding for 10 min at a flow rate of 15 ml min^{-1} on a daily basis. The characteristics of raw sludge are presented in Table 1.

The operation of anaerobic digesters was divided into two phases. In the first phase (Phase I, 333 days), all four digesters operated continuously as single-stage systems, at SRT of 20 days and without spiking of the target analytes. In the second phase (Phase II, 133 days), the digesters T_2 and M_2 were connected in series and operated as a two-stage (dual) system (thermophilic/mesophilic) at SRT of 8 and 12 days, respectively. The remaining two digesters (T_1 and M_1) continued to operate in a single mode at a SRT of 20 days in order to compare and control both processes (Fig. 1). During Phase II and after an acclimation period of four SRT, target compounds were added into all systems. This was accomplished by adding daily a methanolic aliquot of micropollutants to the feeding substrate, in order to achieve an environmental relevant concentration of target compounds in raw sludge (2–4 μg g^{-1}).

2.4. Analytical methodology

To monitor the performance of the anaerobic processes, raw and digested sludge samples were periodically taken from all bioreactors during both experimental phases. Routine analyses, such as COD_t, soluble COD (COD_s), total solids (TS), volatile solids (VS), TSS, VSS, pH, VFAs and alkalinity, were carried out in accordance to Standard Methods (APHA, 2005) on a weekly basis. Moreover, daily biogas production was quantified by saline water displacement, while biogas composition was determined by a gas analyzer (Model GA 94A).