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Role of methanogenesis on the biotransformation of organic micropollutants during anaerobic digestion

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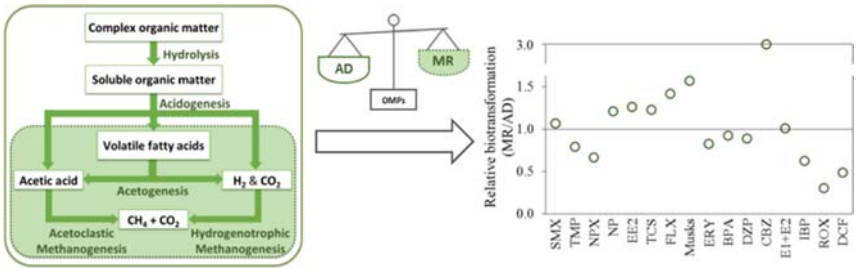
HIGHLIGHTS

- Organic micropollutant (OMP) removal during anaerobic digestion is still a black-box.
- The fate of 20 OMPs during the methanogenic step of anaerobic digestion was assessed.
- All OMPs underwent biotransformation during methanogenesis, but to different extents.
- The organic loading rate and the OMP partitioning did not affect biotransformation.
- Methanogenesis is a main contributor to OMP biotransformation in anaerobic digestion.

GRAPHICAL ABSTRACT



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ABSTRACT

Several studies showed that some organic micropollutants (OMPs) are biotransformed during anaerobic digestion (AD). Yet, most of them aim at reporting removal efficiencies instead of understanding the biotransformation process. Indeed, how each of the main AD stages (i.e., hydrolysis, acidogenesis, and methanogenesis) contribute to OMP biotransformation remains unknown. This study focuses on investigating the role of methanogenesis, the most characteristic step of AD, to OMP removal. More specifically, the sorption and the biotransformation of 20 OMPs by methanogenic biomass were analyzed determining their concentrations in both liquid and solid phases. Sorption onto methanogenic biomass displayed a similar behavior as reported for digested sludge. Most of the OMPs were biotransformed to a medium extent (35–70%) and only sulfamethoxazole was completely removed. Comparing these results with those reported for the complete AD process, methanogenesis was proven to play a key role, accounting for more than 50% of the OMP biotransformation (except for roxithromycin) during AD. An increase in the organic loading rate from 1 to 2 g COD/L d, typical loads employed in sewage sludge anaerobic digesters, did not exert a clear cometabolic effect on the OMPs biotransformation. It is hypothesized that biotransformation occurs in both liquid and solid phases because no link between the partition coefficient (*Kd*) and the overall biotransformation efficiency was found. These findings allow a better understanding of the OMPs fate under anaerobic conditions, which is necessary to design efficient biological mitigation strategies.

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1. Introduction

The increasing presence of organic micropollutants (OMPs), such as pharmaceuticals, hormones, pesticides, household, and industrial chemicals in the environment is an issue of emerging concern due to their potential harm to ecosystems and public health (Luo et al., 2014). Indeed, research in this field and particularly dealing with the removal of pharmaceuticals in sewage treatment plants (STPs) (Qian et al., 2015) has experienced an exponential growth since the late 1990s (Daughton, 2016). Yet, studies dealing with OMPs fate in the sludge line of STPs are still very limited and no clear mitigation strategies are proposed.

Anaerobic digestion (AD), the main stabilization process of sewage sludge, has a limited biological capacity to remove OMPs (Stasinakis, 2012). Therefore, residual OMP concentrations can routinely be detected in digested sludge at levels above 1 mg/kg (Golet et al., 2003; Gonzalez-Gil et al., 2016; Langdon et al., 2011). A wide variety of OMPs was also found at lower concentrations (Petrie et al., 2015; Stasinakis, 2012), favoring the potential appearance of negative synergistic effects on the environment (Petrie et al., 2015). The capacity of OMP biotransformation of the anaerobic process should be maximized to fulfill the upcoming legislation limits of OMPs in biosolids (Inglezakis et al., 2014) pursuing a safe application of sludge in agricultural fields (Chen et al., 2014). To achieve this, it is essential to move from merely monitoring the removal efficiencies to understanding the factors influencing the fate of OMPs during AD.

Some authors suggest that the two main mechanisms affecting the fate of OMPs, sorption, and biotransformation, could be interrelated because sorption could modify the biotransformation rates and the bioavailability of OMPs during AD (Barret et al., 2010b). The partition coefficient (*Kd*) is suitable to predict the distribution between phases and quantify the sorption of OMPs in solid matrices (Carballa et al., 2008). However, the concentrations of OMPs in the solid phase of digested sludge have been rarely measured (Petrie et al., 2015), leading to little information about their *Kd* values and the sorption role during AD.

Biotransformation is likely to occur through cometabolism (Delgadillo-Mirquez et al., 2011; Fernandez-Fontaina et al., 2016; Fischer and Majewsky, 2014; Plósz et al., 2010), due to the low concentrations of OMPs in comparison with the main growth substrate. This biotransformation process is influenced by the physicochemical properties of the OMPs, the microbial diversity, the enzymatic activities, and the environmental and operational parameters. Most studies about AD have focused on evaluating the effect of temperature, sludge retention time (SRT) and organic loading rate (OLR) on the removal of OMPs (Barret et al., 2010a; Carballa et al., 2007; Gonzalez-Gil et al., 2016; Malmborg and Magnér, 2015; Paterakis et al., 2012; Samaras et al., 2014; Zhou et al., 2017), concluding that these parameters are only relevant for few compounds. Nonetheless, little is known about other factors, such as the microbial population composition and the cometabolism linked to specific enzymes, and their relative significance on the biotransformation of OMPs during AD.

How microbial diversity affects the transformation of OMP is difficult to determine as there is a huge variety of microorganisms involved in the multistep AD process. Based on their physiology, nutritional needs, growth kinetics and sensitivity to environmental conditions, they can be classified into two main groups: acid-forming and methane-forming microorganisms. The influence of each group on the fate of OMPs has not been addressed in depth, although there are a few evidences about the capacity of methanogens to biotransform some OMPs (Cetecioglu et al., 2016; Chang et al., 2005; Lahti and Oikari, 2011; Veetil et al., 2012).

The objective of this study is to ascertain the contribution of the methanogenic step to the removal of OMPs during the overall AD process, which is still considered a black-box in terms of OMPs fate. To this aim, the biotransformation capacity of methane-forming microorganisms was evaluated for a set of 20 OMPs with different physicochemical properties, paying special attention to the influence of the OLR and the phase partitioning.

2. Materials and methods

2.1. Selected organic micropollutants

The 20 selected OMPs present a wide variety of physicochemical characteristics and applications (Table S1) and an environmentally relevant occurrence in sewage sludge (Gonzalez-Gil et al., 2016; Paterakis et al., 2012; Stasinakis, 2012). They comprise three musk fragrances, galaxolide (HHCB), tonalide (AHTN) and celestolide (ADBI); three anti-inflammatories, ibuprofen (IBP), naproxen (NPX) and diclofenac (DCF); four antibiotics, sulfamethoxazole (SMX), trimethoprim (TMP), erythromycin (ERY) and roxithromycin (ROX); three neurodrugs, fluoxetine (FLX), carbamazepine (CBZ) and diazepam (DZP); four endocrine disrupting compounds from daily life products, bisphenol A (BPA), triclosan (TCS), 4-octylphenol (OP) and 4-nonylphenol (NP); and three hormones, estrone (E1), 17β-estradiol (E2) and 17α-ethinylestradiol (EE2).

2.2. Methanogenic reactors

Two continuously stirred (IKA RW20, 150 rpm) lab-scale methanogenic reactors with a total volume of 15 L (liquid volume of 14 L) were operated under mesophilic conditions (37 °C). Both reactors were inoculated with biomass (15–20 g VSS/L) from a nearby mesophilic sewage sludge digester and were operated semi-continuously by once-a-day manual feeding and withdrawal. The feeding consisted of a synthetic mixture of volatile fatty acids (VFA), acetic (HAc), propionic, and butyric acid in a ratio of 2:1:1 (COD basis) to limit the hydrolytic and acidogenic steps and to promote the symbiosis between acetogens and methanogens (Lin et al., 1986). Nitrogen (0.6 g NH_4Cl/L), phosphorous (0.4 g KH_2PO_4/L), and trace concentrations of boron and metals (Fe, Ca, Mg, Cr, Co, Cu, Mn, Mo, Ni, Se, Zn) were added to the synthetic mixture since they are required for the microbial growth (Angelidaki and Sanders, 2004). The pH of the feeding was adjusted to 6–7 with NaOH. $NaHCO_3$ (5–10 g/L) was added to provide sufficient alkalinity. A more detailed description of the feeding characteristics is provided in Table S3.

The operation of the first methanogenic reactor (MR1) lasted 130 d (Fig. S1). During the start-up (25 d), a moderate OLR (0.5 g COD/L d) and high hydraulic retention time (HRT) (20 d) were applied to adapt the inoculum to the new conditions. Subsequently, the OLR was increased to 2 g COD/L d and the HRT was reduced to 10 d according to Rubio-Loza and Noyola (2010). These conditions were maintained for more than 1 month but the reactor operation being unsteady, the OLR was reduced to 1 g COD/L d (HRT = 10 d) achieving steady-state for almost 2 months.

To increase the confidence of the results, a second independent reactor (MR2) was operated during 70 d (Fig. S1). The start-up period lasted 10 d with an HRT of 20–26 d and an OLR of 0.3–0.5 g COD/L d. Then, the HRT was switched to 10 d and the reactor was operating at an OLR of 1 g COD/L d for 1 month. To encourage the methanogenic activity the OLR was changed to 2 g COD/L d by increasing the COD concentration of the synthetic feeding and keeping the HRT at 10 d. In this case, steady-state operation was achieved for 1 month. The applied OLR values (1–2 g COD/L d) were selected to approach the typical operating range of industrial sewage sludge anaerobic digesters (Green and Perry, 1999).

Temperature and biogas production were monitored daily. The rest of conventional parameters (i.e., pH, alkalinity, VFA, COD, solid concentrations, and biogas composition) were analyzed twice a week to check the performance of both reactors.