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Influence of feed characteristics on the removal of micropollutants during the anaerobic digestion of contaminated sludge

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ABSTRACT

The removal of 13 polycyclic aromatic hydrocarbons, 7 polychlorobiphenyls and nonylphenol was measured during the continuous anaerobic digestion of five different sludge samples. The reactors were fed with one of the following: primary/secondary sludge (PS/SS), thermally treated PS, cellulose-added SS, or SS augmented with dissolved and colloidal matter (DCM). These various feeding conditions induced variable levels of micropollutant bioavailability (assumed to limit their biodegradation) and overall metabolism (supposed to be linked to micropollutant metabolism throughout co-metabolism). On the one hand, overall metabolism was higher with secondary sludge than with primary and the same was observed for micropollutant removal. However, when overall metabolism was enhanced thanks to cellulose addition, a negative influence on micropollutant removal was observed. This suggests that either the co-metabolic synergy would be linked to a specific metabolism or co-metabolism was not the limiting factor in this case. On the other hand, micropollutant bioavailability was presumably diminished by thermal treatment and increased by DCM addition. In both cases, micropollutant removal was reduced. These results suggest that neither overall metabolism nor bioavailability would absolutely limit micropollutant removal. Each phenomenon might alternatively predominate depending on the feed characteristics.

1. Introduction

Organic micropollutants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorobiphenyls (PCBs) can be removed efficiently from wastewater: for example, 75% of PCBs are removed at a WasteWater Treatment Plant (WWTP) in Greece [1] and at a WWTP in Paris, France, 76% and 98% of PCBs and PAHs, respectively [2]. However, biodegradation only accounts for a small part of this removal. In fact, since PAHs and PCBs present very low water solubility and are highly hydrophobic, these properties favour their sorption to organic matter. As a consequence, sorption onto the solid effluent (sludge) has been demonstrated to be the main removal mechanism for PAHs and PCBs [1–4]. Thus, their concentration in sludge reaches 0.001–10 $\mu g_{PAH}/g_{DM}$ [2,5,6] and 0.01–1 $\mu g_{PCB}/g_{DM}$ [1,2,6], depending on the influent and the characteristics of the WWTP.

Nonylphenol (NP) is produced within WWTP as a byproduct of the aerobic/anoxic biodegradation of long-chain ethoxylated nonylphenols [7,8]. Due to its recalcitrance and hydrophobicity, NP accumulates in the biological process and is removed from wastewater through sorption to residual matter and subsequent clarification [9,10]. NP occurs in sludge at a typical concentration of about 100 $\mu g_{NP}/g_{DM}$ [11,12].

Before its final disposal, sludge has to be stabilized. Among the available solutions, anaerobic digestion followed by spreading is the most sustainable option [13]. In addition, the anaerobic consortia involved in this bioprocess have been shown to partially remove PAHs [14–16], PCBs [17–19] and NP [20,21]. However, the comparison of published data reveals considerable variation in the anaerobic removal of micropollutants. Indeed, PCB removal ranged from 12% [19] to 98% [18] in continuous mode while NP removal varied from 0% in continuous mode [22] to 40% in batch mode when operated with same retention times [21]. This variability highlights a lack of understanding of the mechanisms which determine micropollutant removal. Nonetheless, several operational parameters have been shown to influence their removal, such as retention time [18,23] and temperature [15,18,23,24]. In addition to these operating conditions, the microbial population, bioavailability and co-metabolism were also found to influence

Abbreviations: BSA, bovine serum albumin; COD, chemical oxygen demand; CSS, composite sludge prepared from SS and cellulose; DCM, dissolved and colloidal matter; DM, dry matter; Glu, glucose; NP, nonylphenol; OC, organic carbon; OM, organic matter; PAH, polycyclic aromatic hydrocarbon; PCB, polychlorobiphenyl; PEEM, petroleum ether extractible matter; PS, primary sludge; SS, secondary sludge; TTPS, thermally treated primary sludge; VFA, volatile fatty acid.

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micropollutant removal. For example, an adapted inoculum is favourable [15], suggesting that the abundance of micropollutant-degrading microorganisms is a crucial factor. Moreover, the poor bioavailability of micropollutants is usually assumed to limit their biodegradation [19,25]. Thus, when they are transferred to the aqueous phase thanks to surfactants, removal rates are higher [21]. PAHs, PCBs and NP are recalcitrant compounds and their biodegradation is only likely to occur thanks to co-metabolism and syntrophic interaction in conjunction with overall metabolism and the structure of the microbial population. Thus, an additional readily biodegradable carbon source can enhance micropollutant removal [14,21], probably because it stimulates the overall metabolism. Finally, the anaerobic biodegradation of micropollutants is influenced by their physico-chemical properties [23,25,26].

In this study, the removal by anaerobic digestion of PAHs, PCBs and NP was measured for different feed characteristics, in fixed operating conditions (retention time, temperature, inoculum, chemical oxygen demand and micropollutant load). The feed characteristics varied according to sludge origin, thermal treatment and the preparation of sludge composites obtained by mixing with cellulose or sludge supernatant. The objective was to identify both key parameters of the feed sludge along with the properties of the micropollutants which condition their removal and might help to predict their fate.

2. Material and methods

2.1. Chemicals

All solvents were purchased from J.T. Baker. The compounds studied are listed in Table 1. PAH and PCB powders were obtained from Dr Ehrenstorfer GmbH. Each compound was separately dissolved in dichloromethane at 1 g/L. The pure 4-nonylphenol (NP) isomer mixture was purchased from Interchim. It was diluted in hexane to obtain 40 g/L. The spiking mix was prepared from these individual concentrated solutions to the final concentration of 100 mg/L, except for indeno(1,2,3,c,d)pyrene (20 mg/L) and nonylphenol (2 g/L).

The 10 mg/L standard solution of PAHs in acetonitrile, the 10 mg/L standard solutions of PCBs and of tetrachloronaphthalene (TCN) in hexane and the 100 mg/L of NP in hexane were all supplied by Dr Ehrenstorfer GmbH. For quantification, the standard solutions were diluted to obtain 6 calibration levels from 10 to 1000 μg/L in acetonitrile for PAHs, from 100 to 1000 μg/L in dichloromethane for PCBs and from 500 to 5000 μg/L in hexane for NP. Standards were stored at −20 °C.

Table 1
Physico-chemical characteristics of the PAHs, NP and PCB180.

Compound	$\log K_{ow}$	M	$\log H$	n5C	n6C	nCl	nOH
Fluorene	4.18	166	1.64	1	2	0	0
Phenanthrene	4.57	178	1.03	0	3	0	0
Anthracene	4.45	178	2.34	0	3	0	0
Fluoranthene	5.1	202	0.40	1	3	0	0
Pyrene	5.32	202	0.87	0	4	0	0
Benzo(a)anthracene	5.85	228	0.81	0	4	0	0
Chrysene	5.89	228	0.69	0	4	0	0
Benzo(b)fluoranthene	6.57	252	−1.15	1	4	0	0
Benzo(k)fluoranthene	6.84	252	−0.16	1	4	0	0
Benzo(a)pyrene	6.00	252	0.09	0	5	0	0
Dibenzo(a,h)anthracene	6.70	278	−0.08	0	5	0	0
Benzo(g,h,i)perylene	6.73	276	−0.61	0	6	0	0
Indeno(1,2,3,c,d)pyrene	6.60	276	−0.40	1	5	0	0
Nonylphenol	5.76	220	1.04	0	1	0	1
PCB28	5.66	257	1.57	0	2	3	0
PCB52	5.95	292	2.21	0	2	4	0
PCB101	6.38	327	1.71	0	2	5	0
PCB118	6.65	327	1.58	0	2	5	0
PCB138	7.19	364	1.33	0	2	6	0
PCB153	6.86	364	1.77	0	2	6	0
PCB180	7.15	399	1.60	0	2	7	0

M: molar mass (g/mol); H: Henry's law constant (Pa m^3/mol); n5C: number of five carbon rings; n6C: number of six carbon rings; nCl: number of chlorines; nOH: number of hydroxyl substitutions.

2.2. Sludge samples

The experiments were carried out using five different sludge samples. The primary sludge sample (PS) was collected at the outlet of the primary settling tank at a domestic WWTP treating 33 000 PE (Person Equivalent). A part of this sample was hydrolysed at 165 °C for 30 min in a Zipperclave reactor to obtain the thermally treated primary sludge sample (TTPS). The secondary sludge sample (SS) came from the biological aerobic unit of a domestic plant treating 250 000 PE with a very low sludge retention time (0.4 day). The CSS sample was obtained by mixing SS with cellulose particles (20 μm, Sigma–Aldrich) at a chemical oxygen demand (COD) proportion of 50:50.

Centrifugation of SS (10 000 × g, 20 min), followed by filtration at 1.2 μm (Whatman GF/C filter), was carried out to separate the particles from the supernatant, this latter containing the dissolved and colloidal matter (DCM). Finally, SS was diluted with its own supernatant at volumic proportions of 3:1 (sludge: supernatant) to provide the fifth sludge sample SupSS.

Prior to their direct use or to composite preparation, PS and SS were stored at −20 °C.

All these samples were then diluted with deionised water to obtain 24 ± 5 g_{COD}/L and spiked at 5 μg/g_{DM} for each PCB and PAH, except for indeno(1,2,3,c,d)pyrene (1 μg/g_{DM}), and for NP (100 μg/g_{DM}), so that the spiked concentrations were similar to actual contamination levels.

2.3. Experimental setup

The anaerobic digestion of PS, TTPS, SS, CSS and SupSS was performed in stirred lab-scale reactors of 5L. Temperature was regulated at 35 °C thanks to hot water circulation in the external jacket. The feed, stored at 4 °C, was pumped six times per day into the reactor straight after the pumping out of the digested sludge. This latter was collected in tanks at 4 °C. Hence, the reactors were operated with a retention time of 20 days and an organic load of 1.2 ± 0.2 g_{COD}/L/day. For the start-up, they were filled with methanogenic sludge coming from an anaerobic mesophilic reactor adapted to PAH-polluted sludge, and directly fed at the normal operating conditions. The reactors were run during 4–5 retention times.

The pH and the volumetric production of biogas were monitored on-line. Once a week, 7-day composite samples were taken from the feeding tank, the outlet tank and the gaseous phase. Removals were calculated when a steady state was achieved.

A sorbent cartridge (ORBO, Supelco) was placed at the gaseous outlet of the reactor fed with SupSS for 7 days, to quantify the volatilisation of micropollutants.

2.4. Analytical methods

The phase containing dissolved and colloidal matter was separated from the total sludge samples by centrifugation (10 000 × g, 20 min) followed by filtration at 1.2 μm. The dry matter (DM, g_{DM}/L) in total sludge and in the dissolved/colloidal phase was measured by weighing the sample after heating at 105 °C during 24 h. The proteins and carbohydrates in total sludge samples were analysed according to the Lowry [27] and anthrone [28] methods, respectively. The standard curves 20–100 mg/L were obtained with bovine