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Sorption and biodegradation of six pharmaceutically active compounds under four different redox conditions

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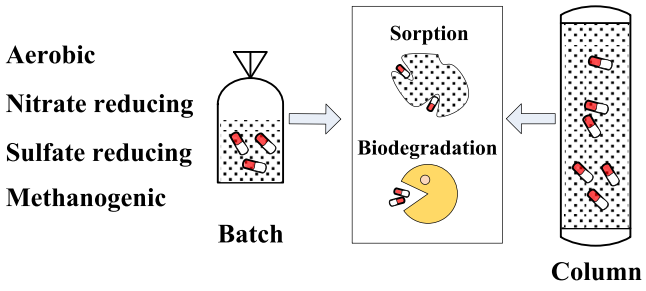
HIGHLIGHTS

- Redox conditions influence sorption and biodegradation of PhACs.
- Lowest sorption of PhACs was found under nitrate reducing conditions.
- Caffeine effectively biodegraded under all tested redox conditions.
- Enrichment of biomass accelerates biodegradation of PhACs.

GRAPHICAL ABSTRACT



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ABSTRACT

This study explored the removal of six pharmaceutically active compounds (PhACs) in lab-scale experiments with sediments under four redox conditions, namely aerobic, nitrate reducing, sulfate reducing, and methanogenic conditions using batch and column set-ups. Redox conditions were found to influence PhAC removal by sorption and biodegradation. The most optimal PhAC removal was observed at the outer ranges of the redox spectrum, i.e. either aerobic or deep anaerobic (sulfate reducing and methanogenic conditions), whereas nitrate reducing conditions were found least effective for PhACs biodegradation and sorption. For instance, sorption coefficient K_d values for metoprolol in column experiments were 90, 65, 42 and 11 L/kg for sulfate reducing, methanogenic, aerobic and nitrate reducing conditions, respectively. For the same conditions K_d values for propranolol were 101, 94, 55 and 55 L/kg, respectively. As expected, biodegradation efficiencies were highest under aerobic conditions, showing >99% removal of caffeine and naproxen, but no removal for propranolol and carbamazepine. The adaptive capacity of sediment was demonstrated by pre-exposure to PhACs leading to improved PhAC biodegradation. The results of this study indicate the necessity to combine diverse redox conditions, including aerobic conditions, for maximizing PhAC removal by sorption and biodegradation. Furthermore, our findings stress the need for additional treatment measures as recalcitrant PhACs are not effectively removed under any redox condition.

1. Introduction

Pharmaceutically active compounds (PhACs) were developed to target specific human physiological pathways (Mei Fun Choong et al., 2006). After consumption, residual PhACs or/and their metabolites are excreted from human bodies into sewage systems. Conventional wastewater treatment plants (WWTPs) are not specifically designed for removing PhACs (Santos et al., 2005). Therefore, PhACs that are not completely removed are discharged to the aquatic environment and may even reach drinking water intakes (Carballa et al., 2004). In this context, efficient post-treatment technologies for removing PhACs are needed and emerging.

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Biological technologies are robust and attractive as post-treatment processes. However, processes involved in biotechnological systems are more complex and require a proper understanding to come to a robust design and operation. In most biological technologies, both sorption and biodegradation play an important role in removing organic contaminants. It is well known that organic matter (OM), temperature and pH affect sorption of organic contaminants (Meng et al., 2014), however the effect of redox conditions (electron acceptors availability) on sorption behaviour of organic contaminants is less known. For inorganic contaminants like heavy metals it is known that redox conditions affect their sorption behaviour (Calmano et al., 1993; Chuan et al., 1996). Redox conditions strongly influence the biological removal of organic contaminants as specific electron acceptors select for specific microbial communities with different targeted functions (Faulwetter et al., 2009). For example, transformation of sulfamethoxazole was reported to strongly depend on the occurrence of nitrate reducing conditions and be sensitive to the concentration of nitrate (Banzhaf et al., 2012).

Although redox condition is identified as one of the controlling factors for biodegrading PhACs, the reported dependencies of removal processes on redox conditions vary significantly for specific PhACs for various reasons. Firstly, most of the previous works only study the removal efficiencies of PhACs under oxic and anoxic conditions without identifying the dominant terminal electron acceptor (Zwiener and Frimmel, 2003; Xue et al., 2010). Secondly, results reported for PhACs biodegradation in terms of redox effects are often contradictory. For example, sulfamethoxazole (SMX) was proven to be more rapidly eliminated under anoxic conditions than under aerobic conditions in bank filtration in the work of Heberer et al. (2008), while Baumgarten et al. (2011) concluded that SMX was more rapidly removed under aerobic conditions compared to anoxic conditions. Conkle et al. (2012) concluded that degradation of carbamazepine (CBZ) was enhanced under aerobic conditions as compared to anaerobic conditions in sediment collected from three types of wetlands; in contrast, Hai et al. (2011) reported that CBZ showed degradation only in an anoxic environment instead of under oxic conditions in a membrane bioreactor. Furthermore, the various studies that report the effects of redox conditions on PhAC removal are difficult to compare as they use different reactor setups, different concentrations and different compounds.

Thus, there is a significant knowledge gap on comparative effects of redox conditions on removal of PhACs in biotechnological systems. To get a more comprehensive understanding of the influence of selected redox conditions on specific PhACs removal via sorption and biodegradation, it is necessary to investigate this in defined experimental setups varying the applied redox conditions. Therefore, the objective of this study is to elucidate the influence of redox conditions on removal mechanisms of six PhACs applying four specific conditions of the wide redox spectrum. Batch and column systems were used for controlled biological tests under aerobic, nitrate reducing, sulfate reducing, and methanogenic conditions. The results of this study give insight into understanding the influence of redox conditions on PhACs removal in biotechnological systems.

2. Materials and methods

2.1. Chemicals and regents

PhACs metoprolol (MET), caffeine (CAF), propranolol (PRO), carbamazepine (CBZ), naproxen (NAP), ibuprofen (IBP) were purchased from Sigma-Aldrich (USA). Details of the PhAC stock solution, other chemicals used and physio-chemical properties of PhACs are given in Text S1 and Table S1 of the Supporting Information (SI).

2.2. Experimental setup

2.2.1. Sediment

Sediment of constructed wetlands (CWs) at WWTPs Hapert and Land van Cuijk (both in the Netherlands) was collected as a solid phase of the batch and column systems. In addition, the sediments contain microorganisms that serve as a natural inoculant of the biologically active laboratory systems. CWs at both facilities have received WWTP effluent for several years. Sediment dry matter (DM) and OM content were determined gravimetrically after drying at 105 °C following combustion at 550 °C.

The aerobic column was inoculated with upper layer sediment (0–5 cm) with an OM content of 6.2 g OM/kg DM. Sediment at a depth of 10–20 cm below the surface level with an OM content of 16.2 g OM/kg DM was collected to inoculate the anaerobic columns. A mixture of upper, deeper layer, and rhizosphere sediment was used for batch experiments containing 19 g OM/kg DM. Concentrations of the six PhACs varied from 0 to 777 ng/g in CW sediment (He et al., 2017).

2.2.2. Batch experiments

Four different media were used to enrich dominant bacteria in different redox conditions. Media were prepared according to previous works for aerobic (Table S2), nitrate reducing (Evans et al., 1991), sulfate reducing (Langenhoff, 1997), and methanogenic conditions (Holliger et al., 1993). The ionic strength of growth media was calculated by importing all media compositions except of trace elements in OLI Studio Analyzer 9.2 software. In each batch bottle, 120 mL medium was mixed with 15 g wet sediment as inoculum. Batches were spiked with a mixture of six PhACs at 1 mg/L each. For analytical reasons the spiking concentration is far above the environmental relevant concentrations of PhACs, as also been applied in previous works (Al-Khazrajy and Boxall, 2016; Jewell et al., 2016). The gas phase of each bottle was filled with either atmospheric air for aerobic conditions or CO_2/N_2 (20/80, v/v) for anaerobic conditions. Among the four redox conditions, no extra carbon source was added except for the PhACs. Abiotic controls contained 1.3 g/L of sodium azide in aerobic batch bottles and 0.3 g/L of mercury chloride in anaerobic bottles to supress microbial activity.

The aerobic batch experiment lasted for six weeks and the anaerobic batch lasted for three months. Samples of week 0 were collected the day after spiking to ensure a homogeneous distribution of PhACs. In order to determine the role of microbial adaptation, mixed PhACs were re-spiked three times in the aerobic batches (biotic and abiotic) for enrichment after week 6. No re-spiking of anaerobic batches was performed. Batch bottles were incubated on a shaker (120 rpm) at 20 °C. Batch bottles were incubated in the dark during the experiment to prevent photolysis. Compared to the spiked PhAC levels, the initial PhAC concentrations in the sediment were minute and thus desorption of the initial PhACs to the liquid phase is negligible. Sorption coefficient K_d was calculated from the abiotic controls as the ratio of the PhACs concentration in the sediment phase and in the water phase at equilibrium. The concentrations of sorbed PhACs were calculated from the measured water phase concentrations based on mass balance.

2.2.3. Column experiments

Column experiments were conducted in four continuous-fed upflow soil columns (Fig. 1). Identical to the batch experiments, aerobic, nitrate reducing, sulfate reducing and methanogenic conditions were tested. Cylindrical glass columns (0.23 L) were packed with sediment containing 292 g DM and 230 g DM for respectively aerobic and anaerobic experiments. Sediment was retained in the columns by sintered glass filters (pore size 40–100 μm). The packed