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Biotransformation of trace organic compounds by activated sludge from a biological nutrient removal treatment system

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HIGHLIGHTS

- Simultaneous removal of a suite of TOrCs in BNR treatment was investigated at the bench-scale.
- Biodegradation of TOrCs was modeled using pseudo-first order kinetics.
- Most TOrCs showed highest removal within the aerobic zone.
- Biotransformation of some TOrCs occurred in anoxic and anaerobic zones.

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ABSTRACT

The removal of trace organic compounds (TOrCs) and their biotransformation rates, k_b (L g_{SS}^{-1} h^{-1}) was investigated across different redox zones in a biological nutrient removal (BNR) system using an OECD batch test. Biodegradation kinetics of fourteen TOrCs with initial concentration of 1–36 μg L^{-1} in activated sludge were monitored over the course of 24 h. Degradation kinetic behavior for the TOrCs fell into four groupings: Group 1 (atenolol) was biotransformed (0.018–0.22 L g_{SS}^{-1} h^{-1}) under anaerobic, anoxic, and aerobic conditions. Group 2 (meprobamate and trimethoprim) biotransformed (0.01–0.21 L g_{SS}^{-1} h^{-1}) under anoxic and aerobic conditions, Group 3 (DEET, gemfibrozil and triclosan) only biotransformed (0.034–0.26 L g_{SS}^{-1} h^{-1}) under aerobic conditions, and Group 4 (carbamazepine, primidone, sucralose and TCEP) exhibited little to no biotransformation (<0.001 L g_{SS}^{-1} h^{-1}) under any redox conditions. BNR treatment did not provide a barrier against Group 4 compounds.

1. Introduction

Biological nutrient removal (BNR) treatment, which utilizes an anaerobic/anoxic/oxic (A^2O) design configuration, has emerged as a cost effective process for reducing nitrogen (N) and phosphorus (P) from wastewater. Since the focus to date of BNR has been on nutrient reduction, few studies have investigated the fate of trace organic compounds (TOrCs), such as pharmaceuticals, personal care product ingredients, endocrine disrupting compounds, and pesticides in BNR systems, compared to conventional activated sludge (CAS) treatment. Knowledge on the fate of TOrCs during BNR is thus limited.

The presence of TOrCs in sewage impacted water bodies at concentrations up to μg L^{-1} have raised significant concerns regarding their potential detrimental effects on human and other biota (Phan et al., 2014). Treatment plant operators, regulatory agencies and the public are concerned about the discharges of such TOrCs and are interested in the removal of these compounds during wastewater treatment processes. CAS systems typically include an aeration tank where biochemical oxygen demand (BOD) and ammonia are reduced by aerobic biomass, and the biomass is separated from the treated water in a secondary clarifier.

The 3-stage A^2O BNR process not only removes BOD and total suspended solids (TSS), but also removes N and P by activated sludge in anaerobic, anoxic, and aerobic regimes. Although, BNR systems were not specifically designed to remove TOrCs, microorganisms in the activated sludge can play a major role in the removal of TOrCs. As a result of biological reactions, an organic compound may undergo alterations (biotransformation; sometimes called primary biodegradation), and sometimes to the point of complete mineralization (ultimate biodegradation). In order for these reactions to occur, an organism must exist that has the

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necessary enzymes to bring about the transformation and the chemical must be accessible to the organism. The biotransformation rate constant, which can be expressed as a half-life, is deemed the most critical and uncertain parameter in predicting the fate of an organic compound in a water resource recovery facility, particularly for compounds that are not volatile and have a low sorption potential. This uncertainty stems from biotransformation being dependent upon many factors including temperature, diversity of microorganisms, degree of acclimation, chemical substrate concentration, type of chemical structure, accessibility of macro- and micro-nutrients, and the method employed to measure biotransformation (Clark et al., 1995; Khan and Ongerth, 2004).

There is evidence that differing redox conditions in BNR systems are important for increasing diversity among microbial populations and transforming the properties of activated sludge that control the sorption and/or biotransformation of TOrCs (Phan et al., 2014). Microbial propagation (e.g., Proteobacteria and Bacteroidetes species) is robust under aerobic conditions because substrate oxidation by oxygen provides a maximum amount of free energy for microbial metabolism, when compared to alternate electron acceptors (e.g., nitrate or sulfate) in limited or no oxygen conditions (Phan et al., 2016; Semblante et al., 2014). The cycling of sludge between anaerobic/anoxic/aerobic zones is thus critical because it creates unique niches for sharing facultative bacteria and associated enzymes secreted within these three zones for TOrC degradation (Gómez-Silván et al., 2014; Phan et al., 2016). For instance, biological transformation and removal of TOrCs, e.g., estrogenic compounds, were attributed to the reduction and oxidation of functional moieties (e.g., ketone and hydroxyl groups) within the anoxic or aerobic regimes of a biological treatment system (Shi et al., 2013). Compared to CAS systems, BNR treatment was shown to significantly reduce the presence of estrogenic compounds in treated wastewater (Parker et al., 2014). Studies (Phan et al., 2014; Suarez et al., 2010) investigating the removal of TOrCs under different redox regimes report higher removal and biotransformation in aerobic than in anoxic or anaerobic conditions. The contributions of anaerobic and anoxic zones to TOrC removal and associated biotransformation pathways within these zones are not yet fully understood.

The objective of this study was to investigate the simultaneous removal of a suite of TOrCs by activated sludge from differing redox zones within a BNR treatment system using the OECD Test No. 314 method, which uses environmentally relevant concentrations (ng L^{-1} to μg L^{-1}). The novelty of this study is that it brings further insight to the removal rates of TOrCs within anaerobic and anoxic zones of a BNR treatment system. The current study also seeks to add to the growing database of biotransformation rate constants and compare biotransformation in anaerobic, anoxic and aerobic regimes within a BNR treatment system.

2. Material and methods

2.1. TOrCs and reagents

Certified standard solutions for each target trace organic compound (Table 1) and potassium nitrate were purchased from Sigma-Aldrich. Trace analysis grade methanol was obtained from Burdick and Jackson (Muskegon, MI). Working stocks and calibration standards were prepared in methanol and stored at −4 °C until use.

2.2. Batch experiments with activated sludge

Biotransformation kinetics of TOrCs during aerobic, anoxic and anaerobic treatments were measured in batch bench-scale experiments according to OECD Test No. 314 (OECD, 2008), which follows a previously published procedure (Federle and Itrich, 1997). This method was used to determine the extent and kinetics of primary degradation of organic compounds whose route of entry into the environment begins with their discharge to wastewater. Fresh mixed-liquor activated sludge samples were collected from different redox zones (anaerobic, anoxic, and aerobic zones) of a 30 MGD BNR treatment facility in Nevada. The BNR facility consists of seven zones; three (3) anaerobic, three (3) anoxic, and one (1) aerobic zone (Fig. S1, Supplementary information). The BNR system is operated at a solids residence time (SRT) of 8 days, and a hydraulic residence time (HRT) of 5.5 h. Treatment in the BNR system is initiated in the first anaerobic zone where returned activated sludge

Table 1
TOrC classification, properties, and pseudo first order kinetic parameters under different redox regimes.

Contaminants	Log D_{ow}* at	Charge at pH 7/8.8	K_d (L g_{SS}^{-1})	k_b ± 95% CI (L g_{SS}^{-1} h^{-1})			Literature, k_b (L.g_{SS}^{-1}.h^{-1})	Removal (%) at 8 h (anoxic) and 12 h (anaerobic and anoxic)
Groups	pH 7, 8.8	*(pK_{as})		Anaerobic	Anoxic	Aerobic	Anoxic, aerobic	Anaerobic, anoxic, aerobic
Atenolol	−1.94, −0.39	Positive (9.67, 14.08)	0.035[a]	0.018 ± 0.03	0.071 ± 0.07	0.22 ± 0.22	n.d, 0.06[d]	48, 89, 99
Trimethoprim	1.06, 1.42	Positive/Neutral (−0.90, 7.16)	0	c.n.d	0.009 ± 0.01	0.21 ± 0.50	n.d, 0.006[e]	7, 17, 99
Meprobamate	1.09	Neutral (15.17, 15.63)	0	<0.001	0.017 ± 0.05	0.043 ± 0.05	n.d, <0.004[h]	0, 34, 83
Gemfibrozil	1.75, 0.87	Negative (4.42)	0.045[a]	<0.001	<0.001	0.26 ± 0.99	0.26[g]	0, 0, 99
Ibuprofen	1.62, 0.33	Negative (4.85)	0[c]	c.n.d	c.n.d	c.n.d	~0.06[e], 0.83[e]	0, 0, ⩾81
Naproxen	−0.51, 0.18	Negative (4.19)	0.024[b]	c.n.d	c.n.d	c.n.d	<0.008[e], 0.37[e]	0, 0, ⩾71
DEET	1.83	Neutral (−0.95)	0.042[a]	<0.001	<0.001	0.041 ± 0.06	n.d, 0.24[h]	0, 0, 85
Triclosan	4.94, 3.95	Neutral/Negative (7.68)	3.61[h]	<0.001	<0.001	0.034 ± 0.58	n.d, 0.054[h]	59, 69, 99
Carbamazepine	2.81	Neutral (15.96)	0.036[a]	<0.001	<0.001	<0.001	<0.001[e], <0.003[e]	0, 0, 0
Primidone	0.96	Neutral (11.50, 11.62)	0.007[d]	<0.001	<0.001	<0.001	n.d., <0.001[f]	0, 0, 0
Sucralose	−0.27	Neutral (11.91, 12.50)	0	<0.001	<0.001	<0.001		0, 4, 0
Fluoxetine	1.38, 2.88	Positive (9.80)	3.40[h]	<0.001	<0.001	<0.001	~0.21[e], 0.37[e]	95, 96, 95
Triclocarban	4.89	Neutral (11.42, 15.94)	4.00[d]	<0.001	<0.001	<0.001		96, 96, 97
TCEP	2.14	Neutral	0.03[a]	<0.001	<0.001	<0.001	n.d, <0.004[h]	0, 0, 0

* Source: ChemAxon (2014), c.n.d: could not be determined, n.d: not determined in cited study.
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[f] Abegglen et al. (2009).
[g] Joss et al. (2006).
[h] Salveson et al. (2012).