Received: 5 May 2023 | Revised: 27 October 2023 | Accepted: 9 November 2023
DOI: 10.1002/wer.10953

RESEARCH ARTICLE

water
ENVIRONMENT RESEARCH

Removal of emerging micropollutants from nanofiltration retentate of municipal wastewater within biological fixed-bed reactors under nitrifying and denitrifying conditions

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Funding information
Hamburg Wasser: Company of municipal Wastewater Treatment

Abstract

Municipal water resource recovery facilities are not designed to eliminate micropollutants, leading to many pollutants entering the aquatic environment. Within this study, as part of the project *MicroStop*, the biological treatment of nanofiltration effluent (retentate) under pure aerobic (without nitrification) as well as nitrifying and denitrifying conditions has been investigated for micropollutant elimination. A potential of further biotransformation under increased hydraulic retention time (HRT) of 14 days was shown. Under both HRT of 7 and 14 days, eliminations below LOQ were achieved in the aerated bioreactor for gabapentin, iomeprol, and metoprolol, reaching > 95%, > 69 to > 92%, and > 72%, respectively. The reduction of diclofenac was positively influenced by longer HRT leading to an elimination of up to 67%. Sulfamethoxazole was reduced under denitrification, but accumulated under aeration, resulting in fluctuating results and an overall elimination of 78% under 14 days HRT.

Practitioner Points

- The micropollutant elimination in fixed-bed bioreactors of highly concentrated nanofiltration retentate was studied.
- Pure aerobic (without nitrification), nitrifying, and denitrifying conditions were investigated under hydraulic retention times (HRT) of 7 and 14 days.
- Higher initial pollutant concentrations enhanced the biological degradability in attached growth for substances being moderately degradable in activated sludge systems.
- 4A potential of further biological micropollutant elimination was shown for gabapentin, iomeprol, metoprolol, and diclofenac.

KEYWORDS

denitrification, fixed-bed bioreactor, micropollutants, *MicroStop*, municipal wastewater, nanofiltration retentate treatment, nitrification

INTRODUCTION

Conventional mechanical-biological processes within municipal water resource recovery facilities are not designed for the elimination of micropollutants, such as pharmaceuticals, pesticides, sweeteners and hormones, and thus represent a main source of pollution in surface waters (Hillenbrand et al., 2015; Joss et al., 2006). Micropollutants can have a negative impact on the environment, animals, and humans, even at low concentrations it can lead to feminization of fish and threaten drinking water resources (Abegglen et al., 2012; Athing et al., 2018; Parrott & Blunt, 2005). Thus, a source-oriented reduction of micropollutants, as well as end-of-pipe measures, are needed with one being the expansion of municipal water resource recovery facilities by a fourth treatment step (Hillenbrand et al., 2015). Two known processes are ozonation and activated carbon adsorption, both of which were implemented on an industrial scale with the disadvantage of an additional post-treatment step required for each (Abegglen et al., 2012). Therefore, the project *MicroStop* started in 2017 to investigate an alternative water resource recovery facility concept, which aims to eliminate micropollutants between nutrients and multi-resistant germs by a biological treatment step (Büning et al., 2020). As a continuation of the project, this study further investigates the effect of different process conditions (with/without nitrogen removal, hydraulic retention time [HRT]) on the micropollutant elimination potential within biological fixed-bed reactors. While the effect of nitrogen removal on micropollutant elimination has been investigated within activated sludge as well as biofilm carriers (Clara et al., 2005; Falås et al., 2012; Wellbrock et al., 2019), the use of highly concentrated retentate from a nanofiltration process as feed stock with nitrogen removal in fixed-bed reactors (FBRs) is an innovative approach.

Biological elimination of micropollutants

The biodegradability of micropollutants varies widely with elimination rates from 0 to 100% (Abegglen et al., 2012). Nevertheless, biotransformation is an important elimination mechanism for micropollutants (Suarez et al., 2010; Tran et al., 2018). It can occur both through metabolism and co-metabolism with co-metabolism predominating (Margot, 2015; Xu et al., 2016). Co-

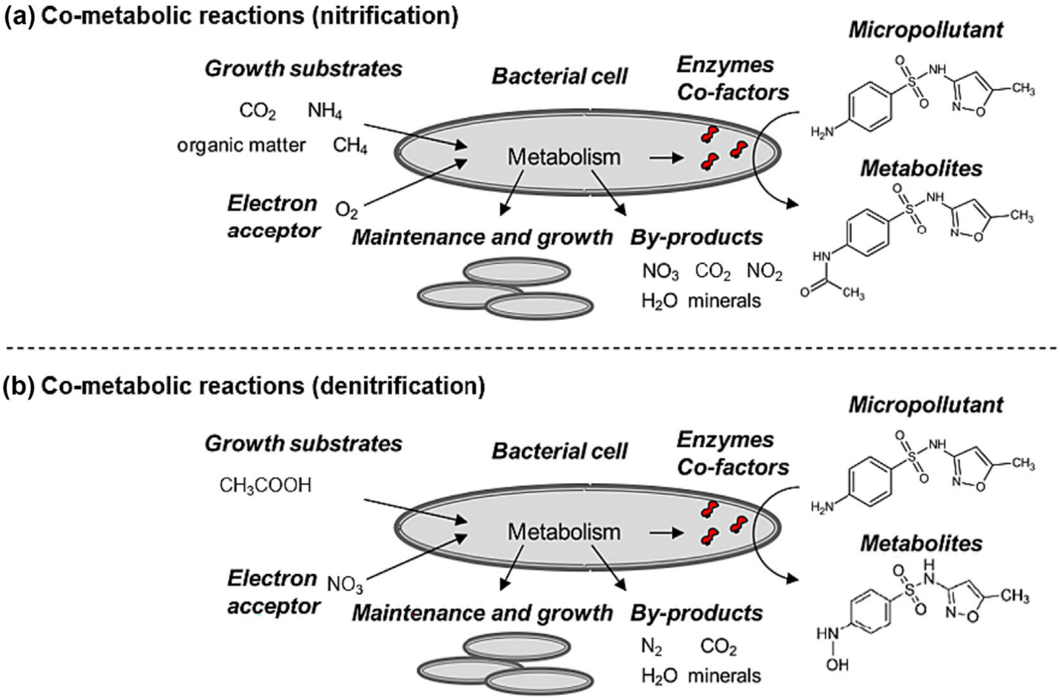

FIGURE 1-1 Biotransformation mechanisms for micropollutants (e.g., sulfamethoxazole) under co-metabolism in aerobic and nitrifying conditions (a) and under denitrification (b) (modified from Margot, 2015; L. Zhang et al., 2020).

metabolism, as shown in Figure 1-1, was especially observed by ammonia oxidizing bacteria because of their non-substrate specific enzyme ammonia monooxygenase (AMO) (Xu et al., 2016).

The biodegradability can further be influenced by sludge age as well as redox conditions. An increased sludge age can significantly increase the elimination of micropollutants (Clara et al., 2005; Ternes et al., 2006), as it allows slow-growing bacteria to become better established for a more specific substrate degradation (Abegglen et al., 2012). By implementing attached growth instead of suspended growth, higher biomass concentrations can be achieved and slow-growing bacteria can establish (Guo et al., 2012). Further, for some compounds, no difference is seen between aerobic and anoxic conditions, while others are only reduced under either condition (Suarez et al., 2010). A parameter to additionally describe biological degradability is the degradation constant k_{biol} (Joss et al., 2006).

In this study, the term biodegradability refers to biotransformation and is used for the reduction of investigated substance, as it cannot be further stated whether a full mineralization or a transformation to metabolites and by-products took place.

MicroStop concept

All relevant treatment steps in the alternative water resource recovery facility concept under project *MicroStop* are shown as flow chart in Figure 1-2. The concept includes an increased particular matter and carbon removal by flocculation within the primary clarifier for more energy-efficiency and combinability with processes such as POWERSTEP (Powerstep, 2019). This process is not considered for micropollutant elimination because of its low potential for many micropollutants with the exception of musk fragrances (Acero et al., 2016; Luo et al., 2014; Sterkele & Gujer, 2009; Suarez et al., 2009). The increased energy demands by the nanofiltration process can be covered by the energy generated from removed carbon within primary sludge, leading to a process with reasonable costs.

Main concept is the combination of biological FBRs with a downstream nanofiltration, focusing on the high potential for micropollutant reduction. Scope is the biodegradation of micropollutants while achieving sufficient nitrification and denitrification after increased carbon extraction within bioreactors. The downstream nanofiltration retains pollutants with > 80 to > 95% as well as wastewater substances (Acero et al., 2016; Büning et al., 2020; Ge et al., 2017), also leading to a higher phosphorus retention (Abegglen et al., 2012). The retentate is recycled back to induce thresholds for micropollutant degradation and achieve adaptation of microorganisms to the food supply. The permeate can be discharged into the receiving water or is available for direct and indirect use. Non-degradable pollutants which accumulate through retentate recirculation can be eliminated by further concentrate treatment such as ozonation.

MATERIAL AND METHODS

Wastewater and retentate generation

Within this study, the secondary effluent of a municipal wastewater treatment plant (conventional set-up) was sampled for generating highly concentrated retentate, further called concentrate. The corresponding wastewater of 700 L was reduced to 30 L by using a nanofiltration pilot plant located in the laboratories of Institute of Wastewater Management and Water Protection (AWW) at Hamburg University of Technology (TUHH). The spiral-wound membrane NF270–2540 from Dow FILMTEC™ was run at 450–460 L/h and 5 bar. While the permeate was led out of the system, the retentate was recycled back to retain a high micropollutant concentration within the concentrate. For comparable concentrate qualities, an UV-absorbance increase at 254 nm (SAC_{254})

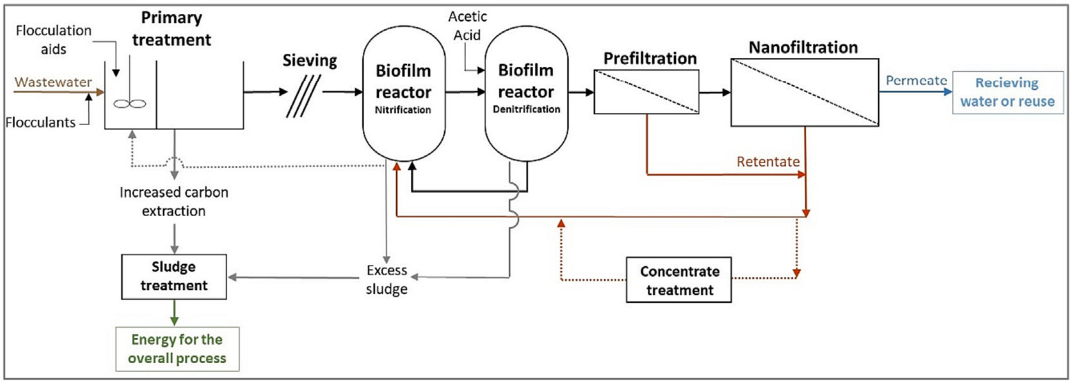

FIGURE 1-2 Flow chart of water resource recovery facility concept MicroStop (modified from Büning et al., 2020).

by factor 10 was tackled. Within this study, two different batches of concentrate, called Conc-1 and Conc-2, based on two different wastewater batches sampled, were used to avoid degradation of micropollutants (e.g., Gabapentin and Iomeprol) during storage, which was observed within pretests. Conc-1 was generated in August resulting in 210 ± 8.7 mg/L TOC, 1.7 ± 0.46 mg/L NH_4-N, 8.7 ± 0.72 mg/L NO_3-N, and 1.1 ± 0.14 mg/L PO_4-P. NO_2-N was neglectable low, pH was at 8.1 ± 0.06, and conductivity was 4.0 ± 0.03 mS/cm. Conc-2 was generated half a year later in February, showing the characteristics of 190 ± 5.3 mg/L TOC, 1.1 ± 0.33 mg/L NH_4-N, 18 ± 0.92 mg/L NO_3-N, and 1.8 ± 0.06 mg/L PO_4-P with a pH of 8.0 ± 0.06 and a conductivity of 4.1 ± 0.02 mS/cm.

Biological fixed-bed reactors

Biological FBRs were used in three experimental phases. In the first phase (phase 1), two FBRs were run under pure aerobic conditions (without nitrification) as preparation for phases 2 and 3. In the second phase (phase 2), nitrification was introduced in Reactor 1 (R1) and denitrification in Reactor 2 (R2) to individually investigate the two processes. In the third phase (phase 3), the HRT was increased in comparison to phase 2 to the same HRT used in phase 1.

Experimental set-up

For all experimental phases, R1 and R2 were identically built. The reactor was built from polyvinyl chloride (PVC) with an inner diameter of 0.1 m. Connections at the reactor were made of PVC tubes, pipes, and valves. Reactors were run in upflow with a recirculation pump (Totton NDP 14/2 centrifugal pump) leading to a continuous upflow speed of 120 L/h and an upflow velocity of 15 m/h. The inlet of reactor was at the bottom, and the fluid was led out of the reactor at the top after passing the fixed bed to be recycled back. The fixed-bed consisted of round expanded clay beads (Liapor GmbH & Co.KG; 8 4/8) of 4–8 mm particle size with a fixed-bed heights of 1.17 m for R1 and 1.16 m for R2. The specific surface of particles was 900 m^2/m^3 (Ramaswami et al., 2018). For phase 1, both reactors were connected to an air supply of 10–20 L/h to achieve sufficient aeration. The fluid was recycled back over a recirculation tank serving as fluid buffer at the bottom of the reactors, where an overflow flask was connected. During phase 1, the overall reactor height was 1.34 and 1.36 m for R1 and R2, respectively. The outlet of reactor was not flooded within this phase. To achieve anoxic conditions in R2 during phases 2 and 3 of this study, the recirculation tanks and overflow flasks were removed and replaced by additional volume at the top of the reactors. This led to an overall height of 1.6 m for both reactors, and fluid outlet of the end of fixed bed being flooded. The fixed bed itself stayed untouched. For a sufficient oxygen supply, R1 was connected to the air supply with a more precisely adjustable flow rate of 0.6–2.0 L/h, whereas the previous air supply of R2 was disconnected. During phase 1, the overall reactor fluid was 3.3 L in the reactor and 2.1–2.2 L in recirculation flask for R1, and 3.45 L in the reactor and 2.1–2.2 L in recirculation flask for R2. For both phases 2 and 3, where both reactors were run as one overall process (nitrification and denitrification), because of sampling, R1 was run with 5.95 L and R2 with 5.75 L. The flow charts of both reactor setups are shown in Figure 2-1.

Experimental procedure

Description of experimental procedure is carried out per experimental phase 1, and phases 2 and 3 combined.

Phase 1 – identical feed under pure aerobic conditions

Within this experimental phase, the reactors were identically fed with Conc-1 in a rhythm of 500 mL in the first week, 500 mL in the second week, 1000 mL in the third week, and no additional feeding in the fourth week. Experimental data for micropollutant elimination were generated within 2-week experiments according to preceding research (Büning et al., 2020). The experimental phase was run over 140 days including a start-up phase of 4 weeks. Overall, four 2-week experiments run in weeks 5–6, 9–10, 12–13, and 16–17. Samples were taken before and after feeding from recirculation tank for water analytics.

Phases 2 and 3 – nitrifying and denitrifying conditions

The experimental phases (2 and 3) of nitrification and denitrification were conducted over 216 days. During phase 2, reactors were fed twice per week. This part included the establishment phase for nitrifying and denitrifying conditions in R1 and R2, respectively, as well as process optimization and investigations on micropollutant removal. HRT was 7 days overall, resulting in 3–4 days per nitrification and denitrification as a compromise between resources, micropollutant reduction, and nitrogen removal within this feasibility study. After 102 days as phase 3, the HRT was doubled to 14 days overall (for comparison to phase 1) and 7 days per nitrification and denitrification each to increase micropollutant removal efficiency. Reactors were fed once per week. Experiments were run in cycles, which started with the feed of R1 as start in nitrification, included the switch

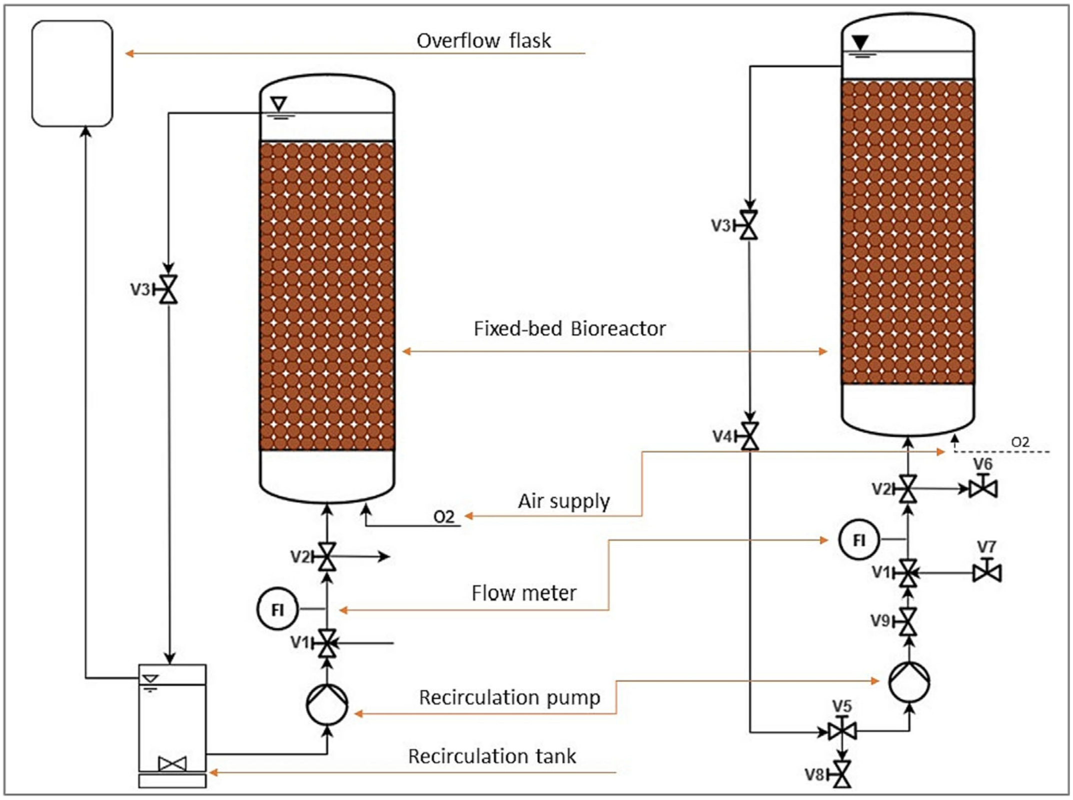

FIGURE 2-1 Flow chart of reactor setup, left: phase 1 under pure aerobic conditions with identical reactor operation, right: phase 2 and phase 3 for nitrification and denitrification with optional air supply.

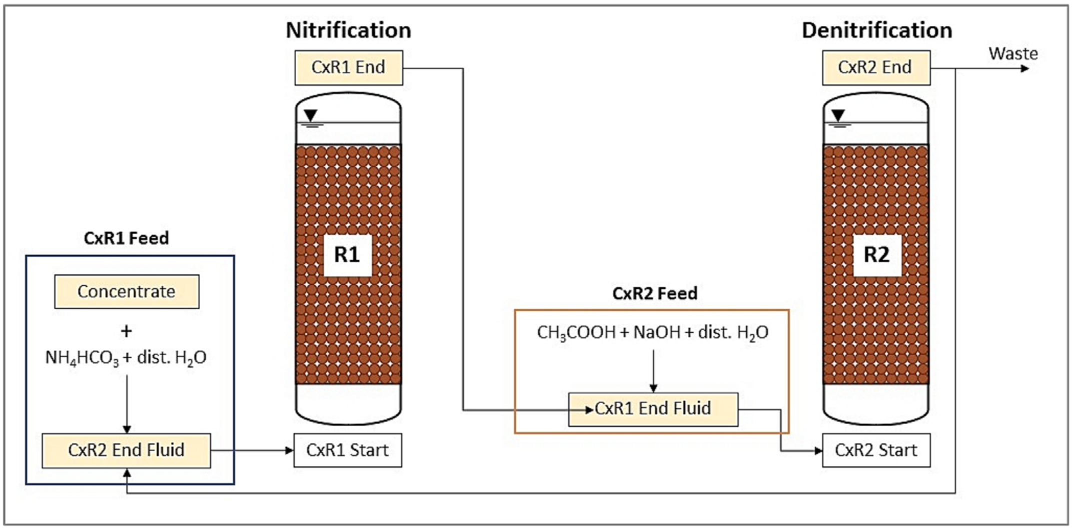

FIGURE 2-2 Scheme of one cycle including nitrification and denitrification.

from R1 to R2, as end of nitrification and start of denitrification and ended with the end of denitrification in R2 after 1 week or 2 weeks, for phases 2 and 3, respectively. While the reactor fluid was continuously recirculated within each reactor, the nitrification and denitrification were run discontinuously. Figure 2-2 visually shows one experimental cycle with composition of reactor feed. After denitrification, most of R2 fluid is recycled back to R1, while a part was disposed. Feeding twice per week included Cycle 1 (C1) to Cycle 29 (C29), whereas feeding once per week was performed for Cycle 30 (C30) to Cycle 44 (C44).

For R1 feed, Conc-2 was added to the reactor fluid of R2. For nitrification, ammonium bicarbonate

($NH_4HCO_3 \geq 98\%$, Carl Roth 7094.1) was added to reach a concentration of 60 mg/L NH_4-N within the entire reactor volume based on average concentration measured for primary clarifier effluents within *MicroStop*. With start of phase 3, from Cycle 30 the concentration was increased to 120 mg/L NH_4-N to keep the amount fed per week constant. For R2, acetic acid ($CH_3COOH \geq 95.9\%$, Carl Roth X895.1) was added as carbon source. From Cycle 23, sodium hydroxide (NaOH, VWR Chemicals 28248.298) as 1 M and from C31 as 2 M was additional added for pH adjustments because of increased need in CH_3COOH.

Composition of R1 and R2 feed are given in Table 1. For each manual feeding, reactors were emptied, feed was prepared, and added back to corresponding reactor by an external feed pump. Samples were taken for reactor end and reactor feed on feeding days as well as for concentrate. Additionally, twice per week, intermediate samples were taken for nitrogen parameters. Further half-an hour after feeding and recirculation pumps started, parameters (as described in Section 2.3) were measured at the top of the reactors.

Methods of analysis

Before and after feeding as well as trice per week in between feeds, common parameters such as pH, temperature, dissolved oxygen (DO), redox-potential, and electrical conductivity were measured directly within the fluid tanks or at the top of the reactor. For water analytics, samples TOC (as NPOC), NH_4-N, NO_3-N, NO_2-N, PO_4-P, and SAC_{254} were measured. Micropollutant analysis was performed by the Central lab at TUHH according to method M03.026 with LC-MSMS (liquid chromatography with mass spectrometry coupling) in Sciex Qtrap 5500 (Stahl & Frerichs, 2019). This method covers a sum of 13 micropollutants, which are shown with their physical and chemical properties in Table 2. These micropollutants were selected in preceding studies based on their persistence, ecotoxicity, and poor elimination in municipal water resource recovery facilities (Büning et al., 2020). For substances not detected, the limit of quantification (LOQ) is considered.

Methods of evaluation

For evaluation of results, elimination ratios are calculated by the difference of end concentration c_E in correlation to start concentration c_S given in percent, as shown in Equation (1). Results are given as average with 95% confidence level unless otherwise stated.

$$E\,[\%] = \left(\frac{c_S - c_E}{c_S}\right) \cdot 100\% = \left(1 - \frac{c_E}{c_S}\right) \cdot 100\% \qquad (1)$$

RESULTS AND DISCUSSION

Water characteristics

Water characteristics are shown in Table 3. For phase 1, an overall average of R1 and R2 is given. The pH was higher than optimum (6.5–7.5), although being in biological acceptable range of 6–9 (Metcalf & Eddy Inc. et al., 2014). NH_4-N, NO_2-N, and PO_4-P were present in negligible low concentrations so neither nitrification nor phosphorus removal took place. With DO being saturated in the bioreactor fluid, no denitrification took place, resulting in a NO_3-N concentration of 44 mg/L that needed to be reduced within the first weeks of experimental phase 2 with the denitrification establishment. TOC was reduced in low rates by 8.8 ± 3.4% and SAC_{254} by 7.2 ± 3.6% because of hardly degradable organic substances from the effluent of the secondary clarifier being

TABLE 1 Reactor feed composition during nitrification and denitrification.

	C1–C29 (as phase 2)		C30–C44 (as phase 3)	
Composition – reactor feed	**R1**	**R2**	**R1**	**R2**
Reactor fluid (mL)	5300 (from R2)	5700 (from R1)	4700 (from R2)	5700 (from R1)
Concentrate (mL)	600	-	1200	-
Deionized water with $NH_4HCO_3/CH_3COOH + NaOH$ (mL)	50	50	50	50
Overall volume (mL)	5950	5750	5950	5750
Recirculation from R2 to R1 (%)	89		79	

TABLE 2 Selected micropollutants with their physical and chemical properties (data from ChemSpider databank by The Royal Society of Chemistry, n.d.), LOQ, and initial concentrations with 95% confidence level.

Type	Active substances with abbreviation	Classification	Molecular weight (g/mol)	Chemical structure	Log K_{OW} (−)	LOQ (µg/L)[a]	Initial concentrations (µg/L)[b]
Pharmaceuticals	Bezafibrate (BEZ)	Lipid-lowering agents	361.8	$C_{19}H_{20}ClNO_4$	3.46	0.1|0.2	< LOQ – 0.32
	Carbamazepine (CMP)	Anti-epileptic drug	236.3	$C_{15}H_{12}N_2O$	2.67	0.1|0.2	2.6 ± 0.24
	Carbamazepine 10,11-epoxide (CMP-10,11)	CMP metabolite	252.3	$C_{15}H_{12}N_2O_2$	-	0.1|0.2	0.45 ± 0.05
	Diclofenac (DIC)	Anti-inflammatory drug	296.1	$C_{14}H_{11}Cl_2NO_2$	4.06	0.2|0.5|1	5.6 ± 0.82[c] 4.9 ± 1.2[d] 6.8 ± 0.27[e]
	Gabapentin (GBP)	Anti-epileptic drug	171.2	$C_9H_{17}NO_2$	1.19	0.2|0.5	5.7 ± 0.92[c] 8.9 ± 0.57[d] 16 ± 1.5[e]
	Ibuprofen (IBU)	Anti-inflammatory drug	206.3	$C_{13}H_{18}O_2$	3.72	5	< LOQ
	Iomeprol (IOM)	X-ray contrast agent	777.1	$C_{17}H_{22}I_3N_3O_8$	−3.08	1|2|5	8.5 ± 2.4[c] 25 ± 4.8[d] < LOQ – 39[f]
	Metoprolol (MET)	Betablocker	267.4	$C_{15}H_{25}NO_3$	1.79	0.1	0.61 ± 0.27
	Sulfamethoxazole (SMX)	Antibiotic drug	253.3	$C_{10}H_{11}N_3O_3S$	0.89	0.1	0.96 ± 0.22
Artificial sweetener	Cyclamate (CYC)	Artificial sweetener	178.2	$C_6H_{12}NSO_3$	0.98	0.1|0.2	< LOQ – 0.26
Pesticide	Mecoprop (MEC)	Herbicide	214.6	$C_{10}H_{11}ClO_3$	2.84	0.1|0.2|0.5	< LOQ
	Terbutryn (TER)	Biocide	241.4	$C_{10}H_{19}N_5S$	1.28	0.01|0.02|0.05|0.2	< LOQ
	Triclosan (TRI)	Biocide	289.5	$C_{12}H_7Cl_3O_2$	5.17	0.2|0.5|1	< LOQ

Note: LOQ, limit of quantification.

[a] LOQ values vary based on sample batches handed in and corresponding quality control.

[b] Combined for standard deviation < 1 µg/L over all three phases.

[c] Phase 1.

[d] Phase 2.

[e] Phase 3.

[f] Varying data because of degradation of IOM within concentrate.

TABLE 3 Water characteristics of reactor fluids averaged for phase 1 and per nitrification/denitrification feed and end for phases 2 and 3 with 95% confidence level.

	Phase 1 – pure aerobic treatment	**Phase 2 – nitrification and denitrification HRT of 7 days**				**Phase 3 – nitrification and denitrification HRT of 14 days**			
	Average R1 & R2	Nitrification R1 feed	Nitrification R1 end	Denitrification R2 feed	Denitrification R2 end	Nitrification R1 feed	Nitrification R1 end	Denitrification R2 feed	Denitrification R2 end
pH [−] @ temp (°C)	8.4 ± 0.02 19 ± 0.32	8.0 ± 0.04 20 ± 0.70	7.9 ± 0.09 22 ± 0.71	6.2 ± 0.08 21 ± 0.69	7.8 ± 0.06 22 ± 0.79	8.1 ± 0.10 22 ± 1.0	7.9 ± 0.07 24 ± 1.2	5.5 ± 0.07 23 ± 1.0	7.7 ± 0.03 24 ± 1.2
DO (mg/L)	9.5 ± 0.07	5.8 ± 0.68	9.3 ± 0.15	8.7 ± 0.14	0.15 ± 0.05	5.3 ± 0.33	8.7 ± 0.22	8.1 ± 0.51	0.21 ± 0.10
Redox (mV)	−100 ± 1.2	−71 ± 1.4	−68 ± 4.7	26 ± 4.5	−61 ± 2.4	−79 ± 4.6	−61 ± 22	67 ± 5.1	−60 ± 0.55
Conductivity (mS/cm)	4.9 ± 0.15	5.2 ± 0.10	5.0 ± 0.10	5.0 ± 0.10	4.9 ± 0.12	4.9 ± 0.04	4.5 ± 0.02	4.6 ± 0.02	4.2 ± 0.01
TOC (NPOC) (mg/L)	110 ± 4.9	110 ± 4.7	110 ± 4.3	190 ± 7.7	110 ± 6.3	96 ± 4.1	76 ± 1.8	220 ± 10	73 ± 2.7
NH_4-N (mg/L)	0.14 ± 0.02	61 ± 0.92	< 0.10	0.18 ± 0.08	0.67 ± 0.23	120 ± 5.4	< 0.10	0.13 ± 0.06	1.5 ± 0.61
NO_2-N (mg/L)	0.01 ± 0.00	16 ± 5.5	< 0.01	0.03 ± 0.02	18 ± 6.2	0.05 ± 0.06	0.02 ± 0.01	< 0.01	0.06 ± 0.08
NO_3-N (mg/L)	44 ± 0.82	6.5 ± 1.3	87 ± 6.2	85 ± 5.9	4.5 ± 1.2	5.8 ± 0.33	120 ± 4.3	120 ± 6.2	1.9 ± 0.19
PO_4-P (mg/L)	0.13 ± 0.02	0.17 ± 0.05	0.11 ± 0.01	< 0.10	< 0.10	0.34 ± 0.02	< 0.01	< 0.10	< 0.10
SAC_{254} (1/m)	290 ± 15	320 ± 12	310 ± 14	-	300 ± 12	260 ± 11	220 ± 8.3	-	200 ± 8.8

Note: HRT, hydraulic retention time.

concentrated in fed Conc-1. In phases 2 and 3, pH for nitrification was around optimal range of 7.5 to 8.0 (Metcalf & Eddy Inc. et al., 2014), whereas in denitrification, the feed concentration was lower because of CH_3COOH addition. The pH increased drastically after fluid was added to > 7.0 and slowly increased further to 7.7 to 7.9. With 5.3–5.8 mg/L in R1 feed and an increase to fully saturated in R1 end, the DO of nitrification was above the limiting range of DO < 2.0 mg/L (Bever et al., 2002). Although for further optimization, a reduction of DO to 4 mg/L is recommended to reduce the process energy demand (Metcalf & Eddy Inc. et al., 2014). Within nitrification, low reduction ratios for TOC were achieved with 7.9 ± 2.4% for phase 2 and 20 ± 11% in phase 3 because of hardly degradable organic substances similar to phase 1. Within denitrification, the reduction ratios increased to 44 ± 3.7% in phase 2 and 67 ± 10% in phase 3 because of CH_3COOH added. SAC_{254} reduction was lower for denitrification than nitrification as CH_3COOH dosage has no influence on SAC_{254}. Within R1, the reduction resulted in 4.5 ± 0.9% in phase 2 and 13 ± 2.6% in phase 3, whereas in R2 in phase 2, a ratio of 2.0 ± 0.8% and in phase 3 of 7.4 ± 3.1% was observed. Full nitrification was achieved to below LOQ (0.1 mg/L NH_4-N) with > 99.8% and > 99.9% for phases 2 and 3, respectively. For denitrification, a nitrite-accumulation occurred within phase 2, which was eliminated with an increase of carbon source, leading to a full elimination and an increase of elimination ratio from 94% in phase 2 to 98% in phase 3.

Composition of concentrates Conc-1 and Conc-2

The average compositions of Conc-1 and Conc-2 can be seen in Table 4. Qualitatively, the four main substances are the same; in order from larger to smaller amount, they are IOM, GBP, DIC, and MET. While in Conc-1, on the fifth place, IBU was detected, it was below LOQ in Conc-2. Further, in order of percentage, CMP, SMX, and CMP-10,11 are following, with CMP-10,11 being only detected in low concentration of 0.5 μg/L in Conc-1 and 0.3 μg/L in Conc-2. These seven were the relevant substances in this study and are representing a minority of proposedly present micropollutants within the wastewater samples as a limited number could have been analyzed.

Overall elimination per experimental phase

As for concentrate, the pharmaceuticals CMP, CMP-10,11, DIC, GBP, IOM, MET, and SMX were detectable within the bioreactors throughout this study. BEZ and CYC were unregularly detected, often being below LOQ, and are separately discussed in Section 3.3.3. IBU was only detected within Conc-1 but below LOQ within the bioreactors. TER and TRI were not detected in the bioreactors, either being below LOQ or not present, whereas MEC was once detected in phase 1. Thus, no evaluation on pesticide removal can be carried out within this study. Overall elimination ratios for all three experimental phases are shown in Table 5.

Based on the results shown in Table 5, the micropollutants can be grouped into well (> 90% or permanently to below LOQ) to medium (> 20–90%) as well as low to non-biodegradable (< 20%) micropollutants in the sense of biotransformation similar to the ranking of biological degradation constant k_{biol} by Joss et al. (2006).

Well to medium biodegradable micropollutants

GBP, IOM, and MET are well biodegradable both with and without nitrification, as all three substances were reduced to below LOQ. GBP showed no significant difference in dependency of reactor conditions (pure aerobic and nitrification) with all results showing an elimination of > 95% up to > 98%. A minor increase in elimination can be seen at an increase of HRT, which is more likely referring to the higher start concentration than the HRT itself. The literature available on GBP is scarce with the mentioned biodegradability varying strongly. Non-significant removal was stated under aerobic and anoxic conditions with HRT < 24 h by Falås et al. (2013). Similar results were shown by Abegglen

TABLE 4 Average concentration of micropollutants analyzed within Conc-1 and Conc-2.

Micropollutant concentration (μg/L)													
	BEZ	**CMP**	**CMP-10,11**	**CYC**	**DIC**	**GBP**	**IBU**	**IOM**	**MEC**	**MET**	**SMX**	**TER**	**TRI**
Conc-1 (*n* = 3)	0.7	5.2	0.5	0.4	32	47	6.3	60	0.6	12	3.8	0.1	< LOQ
Conc-2 (*n* = 5)	1.4	3.8	0.3	0.2	23	72	< LOQ	170	0.1	9.6	2.4	0.04	< LOQ

Note: LOQ, LOQ, limit of quantification.

TABLE 5 Average overall elimination ratios of micropollutants detected throughout this study under pure aerobic, and under nitrification and denitrification for an HRT of 7 days and 14 days with 95% confidence level.

Micropollutant	Phase 1 – pure aerobic treatment HRT of 14 days Ø of R1 and R2 (µg/L) (n = 8)	Phase 2 – nitrification and denitrification HRT of 7 days Ø of R1 and R2 (µg/L) (n = 8)	Phase 3 – nitrification and denitrification HRT of 14 days Ø of R1 and R2 (µg/L) (n = 6)
Carbamazepine (CMP)	4.9 ± 17	23 ± 21	17 ± 11
CMP 10,11-epoxide (CMP-10,11)	−28 ± 20	19 ± 19	13 ± 12
Diclofenac (DIC)	67 ± 15	47 ± 14	66 ± 6.1
Gabapentin (GBP)	> 96 ± 0.7	> 95 ± 1.1	> 98 ± 1.0
Iomeprol (IOM)	> 69 ± 10	> 92 ± 2.0	-
Metoprolol (MET)	> 72 ± 14	>72 ± 7.9	> 76 ± 1.7
Sulfamethoxazole (SMX)	−1.2 ± 23	−42 ± 180	78 ± 7.7

Note: HRT, hydraulic retention time.

et al. (2012), Herrmann et al. (2015), and Margot (2015). In contrast, Wellbrock et al. (2019) observed an elimination ratio of 86% in activated sludge systems and Yu et al. (2006) an even higher elimination ratio of > 99%. GBP is a substitute drug for CMP. With only one amid group present and no nitrogen heterocyclic aromatic groups, in comparison to CMP (see Section 3.3.2), there might be less resistance by the chemical structure. GBP shows hydrophilic characteristics with a log $K_{\mathrm{OW}} < 2.5$, and a reduction by sorption is expected to be low (Rogers, 1996). Results of this study support a high potential of biotransformation of GBP by specific microorganisms, which is remarkably higher than absorbance on PAC with < 12% or an elimination by ozone with 38–39% (Abegglen et al., 2012; Margot, 2015). Further studies on biotransformation and possible metabolites are needed.

MET was eliminated with > 72% up to > 76% in all three phases. The average initial concentration of 0.62 µg/L was close to the LOQ of 0.1 µg/L. A small increase in elimination ratio in phase 3 can rather be explained with an increase in initial concentration than the increase in HRT. Elimination ratios observed in this study are rather high in comparison to literature, where values < 25% are stated (Abegglen et al., 2012; Behera et al., 2011; Margot, 2015; Sturm et al., 2022), with Burzio et al. (2022) even showing an accumulation. In contrast, Wellbrock et al. (2019) observed a MET average elimination of 75% in activated sludge systems with higher initial concentrations, and further studies stated elimination in ranges of 30% to 80% (Jelic et al., 2011; Luo et al., 2014; Verlicchi et al., 2012). With an elimination of 71–88%, AOP and ozone processes showed slightly higher reduction (Abegglen et al., 2012; Margot, 2015; Sturm et al., 2022). Considering the production of H_2O_2 or ozone at the recovery facilities, their safety risks, and energy demands (Abegglen et al., 2012; Sturm et al., 2022), the biological elimination in fixed-bed reactors has the advantages of lower energy and space demand as well as lower safety hazards for employees. Based on log K_{OW}, sorption should not be relevant for MET (Rogers, 1996), though it was proven to be reduced by adsorption on PAC with ranges of 62–95% in several studies in dependency of used dosage, waste water quality, and DOC levels (Abegglen et al., 2012; Evers et al., 2022; Gidstedt et al., 2022; Margot, 2015). Adsorption of > 99% was observed on GAC by Sturm et al. (2022). Activated carbon processes have the disadvantage of high-energy demand and reduced elimination ratios with increasing MP load (Sturm et al., 2022). Therefore, it is further to be investigated whether higher biological elimination ratios are possible with an increase of initial concentration in fixed-bed reactors to achieve reduction ratios that are comparable to adsorption processes.

For IOM, no elimination ratio is calculated in phase 3 because of a reduced concentration in Conc-2 being fed to the reactors, leading to lower initial concentrations and a reduction of elimination ratio over time. As IOM was always reduced to below LOQ, it is ranked as well biodegradable. With elimination ratios of > 69% and > 92% in phases 1 and 2, respectively, results are at the upper end or higher in comparison to ranges stated by other studies, although literature is scarce. Biological elimination ranges of 4–32% are reported (Abegglen et al., 2012; Margot, 2015), whereas k_{biol} by Joss et al. (2006) falls in the range of 20–90%. Applying ozone with < 50% or adsorption on PAC with 50–54% only led to moderate elimination (Abegglen et al., 2012; Altmann et al., 2014; Margot, 2015). Margot (2015) further states a reduction of 76% by fungi. Results of this study show that increased initial concentration of IOM can enhance the biological degradability and further biotransformation potential for X-ray contrast agents. The effect of metabolites forming within biotransformation should be further investigated considering their degradation potential and toxicity.

DIC is often analyzed. Within this study, it can be rated as good to medium biodegradable with elimination ratios of 67, 47, and 66% for phases 1, 2, and 3, respectively. No full elimination took place with remaining average concentrations of 1.8 μg/L for phase 1, 2.6 μg/L for phase 2, and 2.3 μg/L for phase 3. With similar initial concentrations of 4.9 to 6.8 μg/L, an influence of HRT that can be seen as a higher elimination of 66% was achieved for both phases 1 and 3 with an HRT of 14 days in comparison to phase 2 (HRT = 7 days). Results obtained within this study are higher than the degradation rates of 0–40% (often < 20%) observed in many lab experiments as well as municipal water resource recovery facilities under different COD/N ratios and process conditions (Abegglen et al., 2012; Ahmadi et al., 2023; Burzio et al., 2022; Clara et al., 2005; Falås et al., 2013; Fernandez-Fontaina et al., 2016; Joss et al., 2006; Luo et al., 2014; Margot, 2015; Sturm et al., 2022; Suarez et al., 2009). Only a handful of studies show higher elimination ratios. Among them, Behera et al. (2011) observed 81% and Kruglova et al. (2014) 68% and 90%, whereas Jelic et al. (2011) showed varying results with one plant resulting in 60% elimination and two others in < 24%. Fernandez-Fontaina et al. (2012) showed a positive influence of sludge age with an increase from < 15% elimination to 70% under 150 days sludge retention time. This positive effect was also observed by Clara et al. (2005), suggesting an establishment of slow growing bacteria because of long sludge age also being the reason of enhanced reduction within this study. One cause for the incomplete degradation of DIC is the slow degradation kinetics; in particular, the two chlorine atoms (halogens) and aromatic amines in the chemical structure can hinder degradation by AMO within nitrification (Fernandez-Fontaina et al., 2016). Because of the slow degradation, increased HRT resulted in higher reduction rates. The effect of a slowed or stopped reduction with a specific end concentration was observed by Blair et al. (2015) for other substances than DIC. A similar effect was seen in this study, where a reduction to below 1.8 μg/L was not possible, leading to the assumption that an increased initial concentration, as shown in this study, is needed for an increase of biodegradability of DIC. With a log K_{OW} of 4, DIC is more likely adsorbed, although elimination ratios with PAC adsorption are only slightly higher with 45% to above 81% depending on dosage (Abegglen et al., 2012; Evers et al., 2022; Gidstedt et al., 2022; Margot, 2015). For GAC, 93% were achieved by Sturm et al. (2022). In comparison, higher elimination of 90–100% was reached with ozone or AOP processes (Abegglen et al., 2012; Altmann et al., 2014; Margot, 2015; Sturm et al., 2022). To achieve a full reduction of DIC, a combination with ozone or AOP as retentate treatment (as shown in Figure 1-2) could be proposed to reduce non-biologically transformed DIC and achieve a biotransformation of oxidation products when recycled back into the fixed-bed reactors.

Low to non-biodegradable micropollutants

CMP, its metabolite CMP-10,11, and SMX are ranked as low to non-biodegradable based on data shown in Table 5. For both CMP and CMP-10,11, fluctuating results were seen in phases 2 and 3 with a similar behavior; thus, no transformation of CMP to CMP-10,11 or vice versa was seen. In phase 1, CMP-10,11 accumulated whereas CMP was fluctuation < 5% removal. While no comparison data is available for CMP-10,11, an accumulating behavior for CMP was seen by Blair et al. (2015) and Burzio et al. (2022), most likely taking place because of a release from fecal particles or retransformation to parent compound (Blair et al., 2015). In phase 1, average initial (0.42 μg/L) and end concentrations (0.5 μg/L) of CMP-10,11 were close to LOQ (0.1 μg/L), leading to a rather small retransformation, whereas a fecal particle release is to be excluded as the concentrate was produced from secondary clarifier effluent. CMP is often stated as persistent with several researches showing no or low elimination ratios of < 20% for attached and suspended growth systems (Abegglen et al., 2012; Ahmadi et al., 2023; Burzio et al., 2022; Falås et al., 2013; Margot, 2015; Suarez et al., 2010). Within this study, average end CMP concentration of 2.1 ± 0.23 μg/L is 19% lower than initial concentration, thus being in range of literature. Less hydrophobic properties (log $K_{\mathrm{OW}} < 3$) and chemically stable pollutant structure are cause of persistency (Fernandez-Fontaina et al., 2016; Nakada et al., 2006). With PAC adsorption, reduction ratios of 50–86% can be achieved (Evers et al., 2022; Gidstedt et al., 2022), whereas ozone treatment is more promising with > 90 to 100% elimination (Abegglen et al., 2012; Altmann et al., 2014). As for DIC, an additional ozone step could be feasible for CMP (as shown in Section 1.2), as CMP metabolites with hydroxyl or carbonyl groups were shown to be biologically mineralized (Keen et al., 2012).

For SMX, a fluctuating behavior with positive and negative elimination ratios was also seen throughout the literature with −138% up to 93% showing no to well biological degradation (Abegglen et al., 2012; Burzio et al., 2022; Fernandez-Fontaina et al., 2016; Göbel et al., 2007; Sturm et al., 2022). Göbel et al. (2005) showed a re-/transformation from SMX to its main human metabolite N^4 –acetylsulfamethoxazole and vice-versa as the cause of fluctuation within activated sludge systems. SMX metabolites were not investigated in this study, although the same effect is suspected. In all three phases, similar initial concentrations were present resulting in end concentrations of 1.4 ± 0.36, 0.55 ± 0.49, and 0.19 ± 0.10 μg/L for phases 1–3, respectively. The fluctuation was the highest in phase 2 with the shorter HRT of 7 days. In phase 3, a positive elimination was observed, see discussion in Section 3.4. An SMX reduction by PAC or GAC adsorption is also fluctuating with 3–89% (Evers et al., 2022; Gidstedt et al., 2022; Sturm et al., 2022), whereas ozone led to > 86 to 93% (Abegglen et al., 2012; Altmann et al., 2014; Margot, 2015). For SMX, an additional ozonation unit could be feasible (see Section 1.2) depending on biotransformation potential of SMX by-products.

Further investigated micropollutants

BEZ was only detected once during phase 1 and near LOQ for each experiment in phase 3. The average elimination ratio resulted in > 47 ± 17% with BEZ being fully reduced to below LOQ within nitrification, showing the elimination ratio is highly dependent on the initial concentration. Varying results of 41–78% were shown in literature with k_{biol} expecting moderate removal of 20–90% (Abegglen et al., 2012; Joss et al., 2006; Luo et al., 2014). While in this study no influence of nitrification can be concluded, a positive effect by nitrification can be drawn from literature with an elimination of 9% without nitrification and 67% with nitrification as shown by Margot (2015). Elimination by ozone and PAC is also incomplete and only slightly higher with > 68% to 81% and 69% to > 92%, respectively (Abegglen et al., 2012; Margot, 2015). Further, CYC was not detected during phase 1. For phases 2 and 3, it was partly detected within the reactor fluid close to LOQ but not in the Conc-2 fed. Because of unreliable data fluctuations around LOQ, no further evaluation on CYC is performed.

Elimination under nitrification and denitrification

As the biological degradation of micropollutants can vary with aerobic and anoxic conditions (Suarez et al., 2010), the elimination ratios under nitrification and denitrification are investigated. Within phases 2 and 3, a full nitrification and denitrification were achieved after 1 and 2 days, respectively, leading to aerobic and anoxic conditions with peak nitrification/denitrification within the reactors. GBP and IOM were fully reduced to below LOQ under nitrifying conditions. Because the aerobic reactor was passed first, no evaluation on anoxic conditions on the elimination of GBP and IOM can be performed. MET was only detected in the effluent for the first half of phase 2 without conclusive results, while being fully removed under aerobic conditions for all other experiments. Therefore, it is not taken into consideration here.

Elimination rates of CMP, CMP-10,11, DIC, and SMX under individual nitrification, denitrification, and overall biological treatment step (nitri + denitri) are shown in Figures 3-1 and 3-2, for HRT of 7 and 14 days overall,

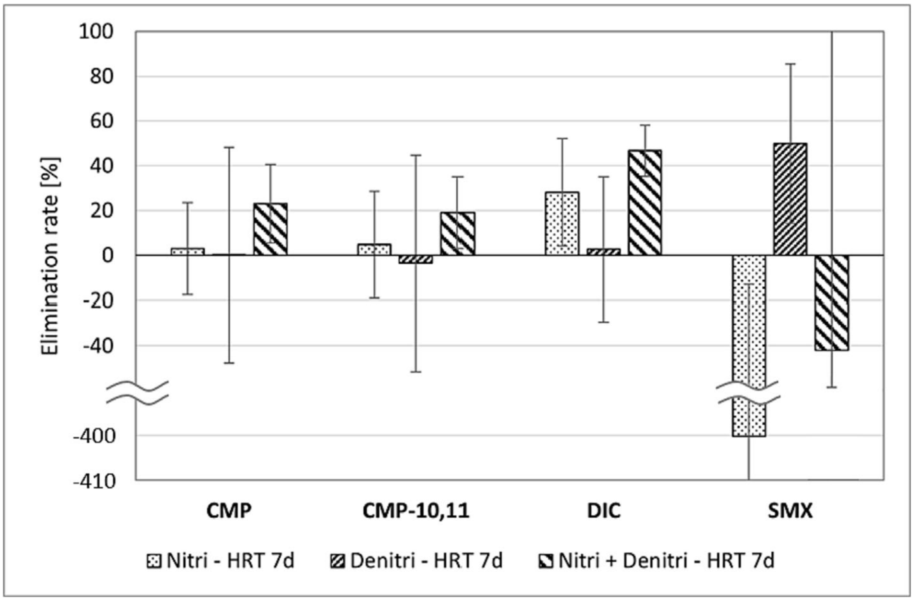

FIGURE 3-1 Average elimination rates for CMP, CMP-10,11, DIC, and SMX under nitrification, denitrification, and overall biological treatment step (nitri + denitri) with 95% confidence range ($n = 5$) for an HRT of 7 days. HRT, hydraulic retention time.

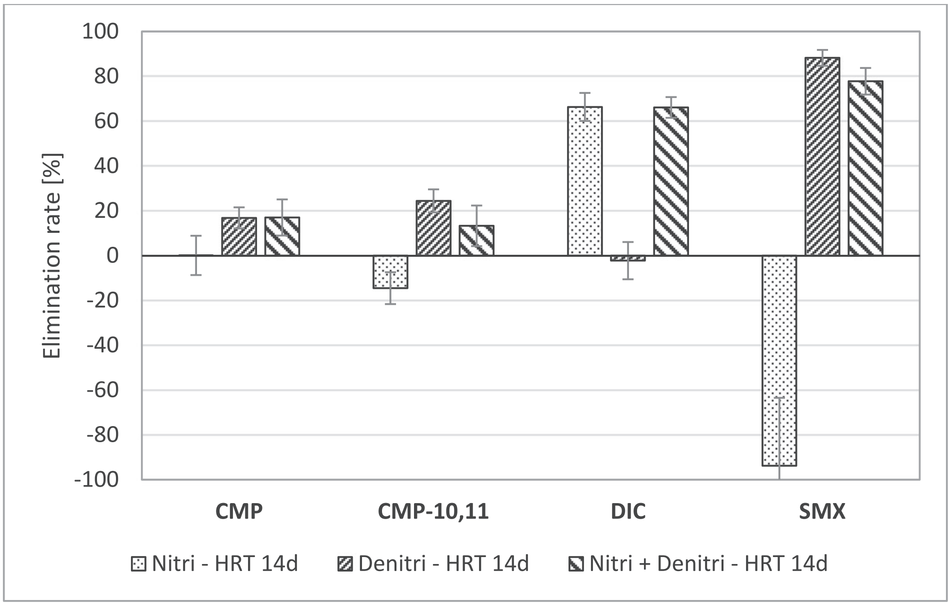

FIGURE 3-2 Average elimination rates for CMP, CMP-10,11, DIC, and SMX under nitrification, denitrification, and overall biological treatment step (nitri + denitri) with 95% confidence range (*n* = 6) for an HRT of 14 days. HRT, hydraulic retention time.

respectively. For CMP and CMP-10,11 under HRT of 7 days, no clear trend can be seen because of data fluctuation as discussed in Section 3.3.2. With an increase of HRT to 14 days, a reduction trend under anoxic conditions can be seen. While in this study a positive influence by anoxic conditions was observed, no clear trend was seen in other studies because of generally low elimination ratios (Falås et al., 2013; Suarez et al., 2010). Accumulation stated in literature was observed under aerobic conditions (Blair et al., 2015; Burzio et al., 2022), supporting this study's results.

With DIC, it can clearly be stated that the major elimination took place under aerobic conditions (both with and without nitrification). Under anoxic conditions, a minor degradation or increase was observed. This is consistent with Suarez et al. (2010), where in a CSTR under nitrification elimination ratios of 22 ± 28% were achieved, while results under denitrification were 10 times lower with 2 ± 5%.

For SMX, the individual results under aerobic and anoxic conditions fluctuated strongly, leading to the higher fluctuation in phase 2 than in phase 3 as stated in Section 3.3.2 and shown in Table 5. The highest reduction observed in comparison literature was by Fernandez-Fontaina et al. (2016) with 93% under heterotrophic conditions with the addition of ethanol and acetate. A reduction of SMX by AMO under nitrification is hindered by nitrogen heterocyclic aromatic groups, aromatic amines, and amides in chemical structure of SMX (Fernandez-Fontaina et al., 2016), rather leading to retransformation as described by Göbel et al. (2005). Göbel et al. (2007) observed no influence of HRT on SMX removal and the importance of the nutrient-to-substrate ratio. Therefore, it is more likely that the increased CH_3COOH addition within denitrification under extended HRT (14 days) led to an increased elimination rather than the HRT increase itself. This effect is further to be investigated.

CONCLUSION

This study shows biotransformation potential for DIC, GBP, IOM, and MET under increased initial concentrations within fixed-bed bioreactors. The following findings were achieved within this study:

- Under aerobic conditions (without nitrification) and 14 days HRT (phase 1), GBP, IOM, and MET were reduced to below LOQ with 96%, 69%, and 72%, respectively. For DIC, a reduction of 67% was achieved.
- With the implementation of nitrification/denitrification and HRT of 7 days (phase 2), no influence on the reduction of below LOQ for GBP and MET was seen. The reduction of IOM was increased to > 92% because of an increase of initial concentration rather than change of aerobic conditions. The reduction of HRT under aerobic condition showed a negative effect on DIC, only being reduced at 47%.
- Increasing HRT to 14 days with nitrification/denitrification (phase 3) led to similar results for GBP and MET as in previous phases. The elimination of DIC increased to 66%. For CMP and CMP-10,11, though showing persistent behavior, a positive influence of anoxic conditions on elimination ratios was

seen whereas an increase of substances took place under aerobic conditions. SMX was eliminated by overall 78% with an accumulation under aerobic conditions and an elimination under anoxic conditions taking place, which was most likely positively influenced by increased CH_3COOH concentration within this experimental phase.

As next steps from this feasibility study, a continuous process under nitrification and denitrification conditions in pilot plant scale should be implemented. This process in combination with a nanofiltration step can further investigate the potential of biological treatment of highly concentrated retentate as well as the influences on the membrane system. Additionally, the number of nanofiltration steps needed to achieve a high initial micropollutant concentration should be investigated.

AUTHOR CONTRIBUTIONS

Birthe K. Stricker: Conceptualization; methodology; data curation; investigation; validation; formal analysis; funding acquisition; writing—original draft; writing—review and editing; visualization. **Dana A. Tamim:** Conceptualization; methodology; investigation; data curation. **Dorothea Rechtenbach:** Conceptualization; methodology; validation; funding acquisition; project administration; resources; supervision. **Joachim Behrendt:** Funding acquisition; project administration; resources; supervision; validation; conceptualization; methodology. **Ralf Otterpohl:** Conceptualization; funding acquisition; project administration; resources.

ACKNOWLEDGMENTS

We would like to thank our cooperation Partner *Hamburg Wasser* for exchange of information and financial support.

We would like to express our special thanks to the following people, whose support was essential for this work: Susanne Eggers (internal lab affairs), Dipl.-Ing. Alina Stahl/Dipl. Chem. Anna-Lena Schulze (Central Laboratory, TUHH), Lena Schultheiss/Lina Jacubczick (student assistants), Leonardo Leyva Amezcua (proofreading), and all students, who carried out their student works on this project. Open Access funding enabled and organized by Projekt DEAL.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

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REFERENCES

Abegglen, C., & Siegrist, H. (2012). *Mikroverunreinigungen aus kommunalem Abwasser: Verfahren zur weitergehenden Elimination auf Kläranlagen. Umwelt-Wissen* (Vol. 1214). Bundesamt für Umwelt (BAFU).

Acero, J. L., Benitez, F. J., Real, F. J., & Teva, F. (2016). Micropollutants removal from retentates generated in ultrafiltration and nanofiltration treatments of municipal secondary effluents by means of coagulation, oxidation, and adsorption processes. *Chemical Engineering Journal*, *289*, 48–58. https://doi.org/10.1016/j.cej.2015.12.082

Ahmadi, N., Abbasi, M., Torabian, A., van Loosdrecht, M. C., & Ducoste, J. (2023). Biotransformation of micropollutants in moving bed biofilm reactors under heterotrophic and autotrophic conditions. *Journal of Hazardous Materials*, *460*, 132232. https://doi.org/10.1016/j.jhazmat.2023.132232

Altmann, J., Ruhl, A. S., Zietzschmann, F., & Jekel, M. (2014). Direct comparison of ozonation and adsorption onto powdered activated carbon for micropollutant removal in advanced wastewater treatment. *Water Research*, *55*, 185–193. https://doi.org/10.1016/j.watres.2014.02.025

Athing, M., Brauer, F., Duffek, A., Ebert, I., Eckhardt, A., Hassold, E., Helmecke, M., Kirst, I., Krause, B., Lepom, P., Leuthold, S., Mathan, C., Mohaupt, V., Moltmann, J. F., Müller, A., Nöh, I., Pickl, C., Pirntke, U., Pohl, K., … Winde, C. (2018). *Recommendations for reducing micropollutants in waters*. Umweltbundesamt (UBA).

Behera, S. K., Kim, H. W., Oh, J.-E., & Park, H.-S. (2011). Occurrence and removal of antibiotics, hormones and several other pharmaceuticals in wastewater treatment plants of the largest industrial city of Korea. *Science of the Total Environment*, *409*, 4351–4360. https://doi.org/10.1016/j.scitotenv.2011.07.015

Bever, J. G., Stein, A., & Teichmann, H. (Eds.). (2002). *Weitergehende Abwasserreinigung (4. Auflage)*. Oldenbourg Industrieverlag.

Blair, B., Nikolaus, A., Hedman, C., Klaper, R., & Grundl, T. (2015). Evaluating the degradation, sorption, and negative mass balances of pharmaceuticals and personal care products during wastewater treatment. *Chemosphere*, *134*, 395–401. https://doi.org/10.1016/j.chemosphere.2015.04.078

Büning, B., Rechtenbach, D., Behrendt, J., & Otterpohl, R. (2020). Removal of emerging micropollutants from wastewater by nanofiltration and biofilm reactor (MicroStop). *Environmental Progress & Sustainable Energy*, *40*(3), e13587. https://doi.org/10.1002/ep.13587

Burzio, C., Ekholm, J., Modin, O., Falås, P., Svahn, O., Persson, F., van Erp, T., Gustavsson, D. J. I., & Wilén, B. M. (2022). Removal of organic micropollutants from municipal wastewater by aerobic granular sludge and conventional activated sludge. *Journal of Hazardous Materials*, *438*, 129528. https://doi.org/10.1016/j.jhazmat.2022.129528

Clara, M., Kreuzinger, N., Strenn, B., Gans, O., & Kroiss, H. (2005). The solids retention time-a suitable design parameter to evaluate the capacity of wastewater treatment plants to remove micropollutants. *Water Research*, *39*(1), 97–106. https://doi.org/10.1016/j.watres.2004.08.036

Evers, M., Lange, R.-L., Heinz, E., & Wichern, M. (2022). Simultaneous powdered activated carbon dosage for micropollutant removal on a municipal wastewater treatment plant compared to the efficiency of a post treatment stage. *Journal of Water Process Engineering*, *47*, 102755. https://doi.org/10.1016/j.jwpe.2022.102755

Falås, P., Baillon-Dhumez, A., Andersen, H. R., Ledin, A., & la Cour Jansen, J. (2012). Suspended biofilm carrier and activated sludge removal of acidic pharmaceuticals. *Water Research*, *46*, 1167–1175. https://doi.org/10.1016/j.watres.2011.12.003

Falås, P., Longrée, P., la Cour Jansen, J., Siegrist, H., Hollender, J., & Joss, A. (2013). Micropollutant removal by attached and suspended growth in a hybrid biofilm-activated sludge process. *Water Research*, *47*(13), 4498–4506. https://doi.org/10.1016/j.watres.2013.05.010

Fernandez-Fontaina, E., Gomes, I. B., Aga, D. S., Omil, F., Lema, J. M., & Carballa, M. (2016). Biotransformation of pharmaceuticals under nitrification, nitratation and heterotrophic conditions. *The Science of the Total Environment*, *541*, 1439–1447. https://doi.org/10.1016/j.scitotenv.2015.10.010

Fernandez-Fontaina, E., Omil, F., Lema, J. M., & Carballa, M. (2012). Influence of nitrifying conditions on the biodegradation and sorption of emerging micropollutants. *Water Research*, *46*(16), 5434–5444. https://doi.org/10.1016/j.watres.2012.07.037

Ge, S., Feng, L., Zhang, L., Xu, Q., Yang, Y., Wang, Z., & Kim, K. H. (2017). Rejection rate and mechanisms of drugs in drinking water by nanofiltration technology. *Environmental Engineering Research*, *22*(3), 329–338. https://doi.org/10.4491/eer.2016.157

Gidstedt, S., Betsholtz, A., Falås, P., Cimbritz, M., Davidsson, Å., Micolucci, F., & Svahn, O. (2022). A comparison of adsorption of organic micropollutants onto activated carbon following chemically enhanced primary treatment with microsieving, direct membrane filtration and tertiary treatment of municipal wastewater. *The Science of the Total Environment*, *811*, 152225. https://doi.org/10.1016/j.scitotenv.2021.152225

Göbel, A., McArdell, C., Joss, A., Siegrist, H., & Giger, W. (2007). Fate of sulfonamides, macrolides, and trimethoprim in different wastewater treatment technologies. *The Science of the Total Environment*, *372*(2–3), 361–371. https://doi.org/10.1016/j.scitotenv.2006.07.039

Göbel, A., Thomsen, A., McArdell, C. S., Joss, A., & Giger, W. (2005). Occurrence and sorption behavior of sulfonamides, macrolides, and trimethoprim in activated sludge treatment. *Environmental Science & Technology*, *39*(11), 3981–3989. https://doi.org/10.1021/es048550a

Guo, W., Ngo, H.-H., & Vigneswaran, S. (2012). Enhancement of membrane processes with attached growth. In T. C. Zhang, R. Y. Surampalli, S. Vigneswaran, R. D. Tyagi, S. Leong Ong, & C. M. Kao (Eds.), *Membrane technology and environmental applications* (pp. 603–634). American Society of Civil Engineers. https://doi.org/10.1061/9780784412275.ch20

Herrmann, M., Menz, J., Olsson, O., & Kümmerer, K. (2015). Identification of phototransformation products of the antiepileptic drug gabapentin: Biodegradability and initial assessment of toxicity. *Water Research*, *85*, 11–21. https://doi.org/10.1016/j.watres.2015.08.004

Hillenbrand, T., Tettenborn, F., Menger-Krug, E., Marscheider-Weidemann, F., Fuchs, S., Toshovski, S., Kittlaus, S., Metzger, S., Tjoeng, I., Wermter, P., Kersting, M., & Abegglen, C. (2015). *Maßnahmen zur Verminderung des Eintrages von Mikroschadstoffen in die Gewässer: Kurzbericht*. Umweltbundesamt (UBA).

Jelic, A., Gros, M., Ginebreda, A., Cespedes-Sánchez, R., Ventura, F., Petrovic, M., & Barcelo, D. (2011). Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment. *Water Research*, *45*(3), 1165–1176. https://doi.org/10.1016/j.watres.2010.11.010

Joss, A., Zabczynski, S., Göbel, A., Hoffmann, B., Löffler, D., McArdell, C. S., Ternes, T. A., Thomsen, A., & Siegrist, H. (2006). Biological degradation of pharmaceuticals in municipal wastewater treatment: Proposing a classification scheme. *Water Research*, *40*(8), 1686–1696. https://doi.org/10.1016/j.watres.2006.02.014

Keen, O. S., Baik, S., Linden, K. G., Aga, D. S., & Love, N. G. (2012). Enhanced biodegradation of carbamazepine after UV/H2O2 advanced oxidation. *Environmental Science & Technology*, *46*(11), 6222–6227. https://doi.org/10.1021/es300897u

Kruglova, A., Ahlgren, P., Korhonen, N., Rantanen, P., Mikola, A., & Vahala, R. (2014). Biodegradation of ibuprofen, diclofenac and carbamazepine in nitrifying activated sludge under 12°C temperature conditions. *The Science of the Total Environment*, *499*, 394–401. https://doi.org/10.1016/j.scitotenv.2014.08.069

Luo, Y., Guo, W., Ngo, H. H., Nghiem, L. D., Hai, F. I., Zhang, J., Liang, S., & Wang, X. C. (2014). A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Science of the Total Environment*, *473-474*, 619–641. https://doi.org/10.1016/j.scitotenv.2013.12.065

Margot, J. (2015). Micropollutant removal from municipal wastewater: From conventional treatments to advanced biological processes [Dissertation]. Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland.

Metcalf & Eddy Inc., Tchobanoglous, G., Stensel, D. H., Tsuchihashi, R., & Burton, F. (2014). *Wastewater engineering: Treatment and resource recovery* ((Fifth edition). ed.). McGraw-Hill Education.

Nakada, N., Tanishima, T., Shinohara, H., Kiri, K., & Takada, H. (2006). Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment. *Water Research*, *40*(17), 3297–3303. https://doi.org/10.1016/j.watres.2006.06.039

Parrott, J. L., & Blunt, B. R. (2005). Life-cycle exposure of fathead minnows (Pimephales promelas) to an ethinylestradiol concentration below 1 ng/L reduces egg fertilization success and demasculinizes males. *Environmental Toxicology*, *20*(2), 131–141. https://doi.org/10.1002/tox.20087

Powerstep. (2019). Homepage Powerstep. http://www.powerstep.eu/

Ramaswami, S., Behrendt, J., Kalyanasundaram, S., Eggers, S., & Otterpohl, R. (2018). Experiences from an investigation on the potential of packed bed reactors for high rate nitrification of mature landfill leachates. *Journal of Water Process Engineering*, *22*, 59–65. https://doi.org/10.1016/j.jwpe.2018.01.006

Rogers, H. R. (1996). Sources, behaviour and fate of organic contaminants during sewage treatment and in sewage sludges. *The Science of the Total Environment*, *185*(1–3), 3–26. https://doi.org/10.1016/0048-9697(96)05039-5

Stahl, A., & Frerichs, H. (2019). Quantitative Analyse verschiedener Pharmaka und Pestizide in Wasser mittels LC-MSMS.

M3.026.02. Technische Universität Hamburg, Zentrallabor Chemische Ananlytik.

Sterkele, B., & Gujer, W. (2009). *Einsatz von Pulveraktivkohle zur Elimination von Mikroverunreinigungen aus dem Abwasser: 2.* Zwischenbericht Eawag.

Sturm, M. T., Myers, E., Schober, D., Thege, C., Korzin, A., & Schuhen, K. (2022). Adaptable process design as a key for sustainability upgrades in wastewater treatment: Comparative study on the removal of micropollutants by advanced oxidation and granular activated carbon processing at a German municipal wastewater treatment plant. *Sustainability*, *14*(18), 11605. https://doi.org/10.3390/su141811605

Suarez, S., Lema, J. M., & Omil, F. (2009). Pre-treatment of hospital wastewater by coagulation-flocculation and flotation. *Bioresource Technology*, *100*(7), 2138–2146. https://doi.org/10.1016/j.biortech.2008.11.015

Suarez, S., Lema, J. M., & Omil, F. (2010). Removal of pharmaceutical and personal care products (PPCPs) under nitrifying and denitrifying conditions//removal of pharmaceutical and personal care products (PPCPs) under nitrifying and denitrifying conditions. *Water Research*, *44*(10), 3214–3224. https://doi.org/10.1016/j.watres.2010.02.040

Ternes, T., Siegrist, H., & Joss, A. (2006). Vorkommen und Herkunft von Arzneistoffen in Fließgewässern. In F. H. Frimmel & M. B. Müller (Eds.), *Heil-Lasten: Arzneimittelrückstände in Gewässern* (pp. 89–103). Springer-Verlag. https://doi.org/10.1007/3-540-33638-9_6

The Royal Society of Chemistry. (n.d.) ChemSpider. The Royal Society of Chemistry. http://www.chemspider.com/

Tran, N. H., Reinhard, M., & Gin, K. Y.-H. (2018). Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions—A review. *Water Research*, *133*, 182–207. https://doi.org/10.1016/j.watres.2017.12.029

Verlicchi, P., Al Aukidy, M., & Zambello, E. (2012). Occurrence of pharmaceutical compounds in urban wastewater: Removal, mass load and environmental risk after a secondary treatment—A review. *Science of the Total Environment*, *429*, 123–155. https://doi.org/10.1016/j.scitotenv.2012.04.028

Wellbrock, K., Knobloch, J. K.-M., Heim, M., & Grottker, M. (2019). Spurenstoffe und Multiresistente Bakterien in den Entwässerungssystemen Schleswig-Holsteins: Ableitung von Kennwerten zur Quantifizierung der Herkunft, der Ausbreitung und des Rückhaltes.

Xu, Y., Yuan, Z., & Ni, B.-J. (2016). Biotransformation of pharmaceuticals by ammonia oxidizing bacteria in wastewater treatment processes. *The Science of the Total Environment*, *566-567*, 796–805. https://doi.org/10.1016/j.scitotenv.2016.05.118

Yu, J. T., Bouwer, E. J., & Coelhan, M. (2006). Occurrence and biodegradability studies of selected pharmaceuticals and personal care products in sewage effluent. *Agricultural Water Management*, *86*(1–2), 72–80. https://doi.org/10.1016/j.agwat.2006.06.015

Zhang, L., Sun, F., Wu, D., Yan, W., & Zhou, Y. (2020). Biological conversion of sulfamethoxazole in an autotrophic denitrification system. *Water Research*, *185*, 116156. https://doi.org/10.1016/j.watres.2020.116156

SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

How to cite this article: Stricker, B. K., Tamim, D. A., Rechtenbach, D., Behrendt, J., & Otterpohl, R. (2023). Removal of emerging micropollutants from nanofiltration retentate of municipal wastewater within biological fixed-bed reactors under nitrifying and denitrifying conditions. *Water Environment Research*, *95*(12), e10953. https://doi.org/10.1002/wer.10953