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Effect of temperature during the hydrothermal carbonization of sewage sludge on the aerobic treatment of the produced process waters

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ABSTRACT

The treatment of the highly contaminated process water produced during the hydrothermal carbonization (HTC) of waste activated sludge is of major concern for the full-scale implementation of the HTC process. So far, no satisfying treatment strategies have been elaborated and the biodegradability under aerobic conditions has hardly been studied. To fill these gaps, aerobic tests were first carried out in batches with HTC process waters produced at 190 °C, 218 °C and 249 °C, and two parallel sequencing batch reactors (SBR) were operated to treat process waters produced at 190 °C and 217 °C. Both experiments show that the HTC temperature has only a little effect on the elimination of dissolved organic carbon (DOC). In the aerobic batch tests, DOC removal were 80.5–81.9 %. In the SBR, 28 % of the initial DOC was found to be recalcitrant, and 25–28 % of the initial nitrogen. In the SBR experiments, the nitrification was also monitored, and nitrification inhibition test were conducted on both process waters obtained at 190 °C and 217 °C. Nitrification the initial SBR reactors was only possible after dilution of the process waters, which indicates the presence of inhibiting substances. The inhibition tests validated those observations, and showed that process waters derived at 217 °C had a higher inhibition potential. This study demonstrates that aerobically treated HTC process waters are still too polluted to be discharged in a wastewater treatment plant: model calculations showed an increase in effluent DOC of 8.3 mg C/L.

1. Introduction

Hydrothermal carbonization (HTC) is an alternative technology for recovering resources from waste materials such as sewage sludge. It has gained increasing attention in recent years to produce hydrochars, a coal-like solid with high carbon density and high dewatering properties. During HTC, temperatures up to 300 °C break down the sewage sludge structure by mechanisms like dehydration and decarboxylation [1,2]. The higher the reaction temperatures, the higher the coalification of the generated hydrochars. One formation pathway of hydrochars is the polymerization of dissolved reaction by-products [3]. However, a substantial amount of slowly or non-polymerizing organic matter remains dissolved and form a high strength wastewater with high amounts of refractory compounds: Aragón-Briceño et al. [4] reported total organic carbon (TOC) concentrations up to 29,778 mg C/L and total Kjeldahl nitrogen (TKN) concentrations of 8064 mg N/L. Also others studies showed the high loading of HTC process waters [5,6]. Such high concentrations result from various components like volatile fatty acids (VFA), humic-like substances, N-heterocycle compounds, phenols, ketones, or aldehydes [7–9].

Readily biodegradable substances, such as acetic acid, suggest the use of anaerobic digestion for process water treatment and has been studied intensively [8,10–12]. Weide et al. [13] investigated two-stage anaerobic digestion to treat process waters from the hydrothermal treatment of sewage sludge, using a continuous stirred tank reactor and an expanded granular sludge bed reactor with aerobic downstream treatment. This removed 55–58 % of the chemical oxygen demand (COD) and the subsequent aerobic digestion led to an overall COD removal of 71–78 %. In general, increasing hydrothermal reaction temperature lead to a drop in biogas yield during anaerobic digestion [14,15], indicating the formation of slow biodegradable or inhibiting substances [16].

Unlike anaerobic digestion, the use of aerobic processes for HTC process water treatment has not gained much attention yet. Nevertheless, aerobic treatment could be advantageous regarding the removal of refractory compounds, such as polycyclic aromatic hydrocarbons (PAH), phenols, N-heterocyclic compounds, or melanoidins [17]. Melanoidins, which are the brownish reaction products from the Maillard reaction,

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are of particular concern, as they are formed during thermal sewage sludge treatment and have antimicrobial properties and limited biodegradability [18]. As a result, lag phases were prolonged and growth rates were lower [19]. However, the role of melanoidins and recalcitrant dissolved organic nitrogen (rDON) and their evaluation needs further research [20]. The few studies focusing on aerobic treatment used different HTC feedstock, and reported COD removal rates of 58–89 %, and the inhibition of nitrification. Inhibition could be reduced by anaerobic pretreatment and dilution [21–23]. At high dilution, no toxicity of HTC process water to heterotrophic biomass of a municipal wastewater treatment plant (WWTP) was observed and the readily biodegradable compounds could serve as an external carbon supplement [24,25].

To the best of our knowledge, the aerobic biodegradation and the inhibition of nitrification associated with HTC process water from sewage sludge has not been given much attention in international literature and systematic studies on biodegradation and quantification of refractory compounds are lacking. However, the process water is of major concern for the full scale implementation of the HTC process, but no satisfying treatment strategies have been elaborated so far. Discharge into municipal WWTP must be well evaluated considering the loading and the amount of refractory compounds in the process water. In order to find solutions for the treatment of HTC process water, established strategies for the treatment of high strength wastewaters (e.g. for industrial wastewater or landfill leachate) must also be considered. Against this background, this study aims to assess the effect of the HTC temperature on the aerobic biodegradability of process waters. The total biodegradability of DOC was determined in batch tests. Continuous sequencing batch reactors (SBR) were used to evaluate the recalcitrant DOC (rDOC) and rDON, and the nitrification performance. Subsequent nitrification tests revealed the inhibition potential of process water and aerobically pre-treated process water.

2. Materials and methods

2.1. Preparation of HTC process water

Waste activated sludge (WAS) was obtained from a nitrifying municipal WWTP in Germany which serves 50,000 people. After sampling, the sludge was frozen in portions at −20 °C to obtain similar feedstock. Before use, the samples were thawed overnight at ambient temperature. Total solids were 9.1 ± 0.1 % and volatile solids 6.8 ± 0.1 % (n = 7). To produce process water, hydrothermal runs were performed using an electrically heated and water-cooled 0.5 L batch reactor (midiclave Typ 3E/0,5lt, Büchi AG, Switzerland). The stirrer was set to 2000 rpm. Hydrothermal temperatures were set to 189 ± 0.6 °C, 218 ± 0.1 °C, and 249 ± 0.3 °C for 30 min (ZW190, ZW218 and ZW249) and average pressures were 16.0, 31.6 and 54.5 bar. Setting cover low, medium and upper temperature range of HTC processes. After hydrothermal treatment, a folded filter (Whatman 520 B 1/2240 mm, GE Healthcare, UK) was used to separate the process water from the coal slurry. As suggested in literature, for continuous tests technical more relevant HTC conditions of 190 ± 1 °C and 217 ± 3 °C for 60 min (Feed SBR190, Feed SBR217) at average pressures of 16.3 bar and 32.2 bar were chosen [9,26]. At each temperature, 12 hydrothermal runs were carried out and the process waters were mixed after filtration with folded filters. The process waters were stored refrigerated at 4 °C. These process waters were also used for nitrification inhibition tests. Table 1 gives an overview of the characteristics of the process waters.

2.2. Zahn-Wellens tests

Zahn-Wellens tests were performed according to EN ISO 9888 (1999) [27]. One day before the experiments, aerobic inoculum from a nitrifying municipal WWTP in Germany was rinsed three times with tap water and sieved (400 μm) to remove coarse particulate substances. In addition, one test (ZW218*) was inoculated with pre-exposed biomass from a previous Zahn-Wellens test, following the same procedure. The inoculum activity was checked using ethylene glycol, and also inoculum blanks were set up. The test vessels (2 L) were filled with inoculum to a total mixed liquid suspended solids concentration (MLSS) of 0.88 g/L. The process waters were diluted to achieve an initial DOC of 350 mg C/L. The vessels were mixed with magnetic stirrers and aerated with a diaphragm pump via a wash bottle containing deionized water at 22.2 ± 0.4 °C. To ensure sufficient dissolved oxygen (DO) in the reactors (>2 mg O_2/L), DO was measured using a Multi 3620 IDS and an FDO 925 (Xylem Analytics Germany Sales GmbH & Co. KG), and aeration was regulated if necessary. The pH was adjusted several times a day to 6.7–7.8 using H_2SO_4 (0.5 M) or NaOH (0.5 M). Before each sampling, water losses due to evaporation were measured gravimetrically and replaced with deionized water. All tests with process waters were carried out in triplicates, with blanks in duplicates, and with references in singles. The DOC removal of the reference compound was almost 100 % after 15 days of incubation, which proves a sufficient activity of the

Table 1
Overview and loading of the HTC process waters tested. Feed SBR190 and Feed SBR217 were analyzed every two weeks, but no changes became apparent.

Parameter	ZW190	ZW218	ZW249	Feed SBR190		Feed SBR217	
	Mean	Mean	Mean	Mean	STD[5]	Mean	STD
DOC [mg C/L]	16,621	18,200	14,351	16,881	320	16,468	457
COD [mg O_2/L]	47,275	n.d.[4]	44,050	49,163	866	48,556	1183
COD/DOC[1] [mg O_2/mg C]	2.8	–	3.1	2.9	–	2.9	–
UV_{254} [1/m]	22,553	26,001	18,413	25,165	651	23,640	512
SUVA[2] [L/(mg·m)]	1.36	1.43	1.28	1.49	0.04	1.44	0.05
UV_{475}[1/m]	688	533	532	918	57	578	20
TKN [mg N/L]	n.d.	n.d.	n.d.	4674	141	5009	101
TN [mg N/L]	4170	n.d.	4508	4481	130	4843	73
DON[3] [mg N/L]	n.d.	n.d.	n.d.	3327	117	3126	96
NH_4-N [mg N/L]	1084	1530	1867	1153	37	1701	41
NO_3-N [mg N/L]	n.d.	n.d.	n.d.	<1	–	<1	–
NO_2-N [mg N/L]	n.d.	n.d.	n.d.	<1	–	<1	–
PO_4-P [mg P/L]	n.d.	n.d.	n.d.	573	11	419	8
Cl^- [mg Cl/L]	n.d.	n.d.	n.d.	132	4	124	1
SO_4^{2-}[mg SO_4/L]	n.d.	n.d.	n.d.	575	39	572	6

[1] COD/DOC was constant during SBR tests and therefore used to calculate effluent COD.
[2] Specific UV absorbance: SUVA = UV_{254} / DOC.
[3] Dissolved organic nitrogen: DON = TN − NH_4-N − NO_3-N − NO_2-N.
[4] Not determined.
[5] Standard deviation.

inoculum.

To calculate the DOC removal rate, the initial DOC in the suspensions was used. This differs from EN ISO 9888 (1999), which recommends using the DOC 2.5 to 3.5 h after starting the experiments to account for adsorption processes at the beginning. During the first 3 h, the DOC removal was already 15–26 % indicating, as expected, a high concentration of readily biodegradable substances. Such high organics removal was considered unlikely for adsorption only and was therefore attributed to biological degradation.

2.3. SBR setup

Two continuous activated sludge reactors (SBR190 and SBR217) were operated in parallel. Each vessel had a reaction volume of 300 mL and was aerated and mixed in the same way as the Zahn-Wellens tests. The SBRs were inoculated with nitrifying biomass from a lab-scale reactor, which was fed with HTC-process water. Temperature, conductivity, redox potential, and pH were measured continuously using Condumax CLS21D and Memosens CPS16D sensors (Endress+Hauser Conducta GmbH+Co. KG, Germany). A pH-controlled peristaltic pump (Ismatec ISMB833C, Cole-Parmer GmbH, Germany) dispensed H_2SO_4 (0.5 M) or NaOH (0.5 M) to ensure a pH between 6.8 and 7.5. The temperature was 19.7–20.5 °C. The DO was controlled manually several times a day to assure sufficient DO in the reactors (>2 mg O_2/L). The SBRs had one cycle per day: (i) the reactor was filled manually with a volumetric pipette with 30 mL or 60 mL, which depended on the operation phase (see Table 2), (ii) aeration and mixing started for 23 h, (iii) settling for 30 min and (iv) effluent was removed manually with a volumetric pipette. Again, losses due to evaporation were recorded gravimetrically and replaced with deionized water before step iv. The effluent was analyzed 2–3 times a week, and the influent once every two weeks. Samples for MLSS and mixed liquor volatile suspended solids (MLVSS) were taken from the fully mixed suspension once a week. Beyond that, no additional sludge was removed from the systems and the sludge retention time (SRT) should be sufficiently high for nitrification. Due to strong foaming, 10 μL silicon-free defoaming agent based on fatty alcohols was added daily (ECSO 8361, EnviroChemie GmbH, Germany).

The test reactors were operated in 3 phases with different process water share and hydraulic retention times (HRT), according to Table 2. In phases 2 and 3, process water was diluted 1:10 with deionized water. Data evaluation was done 2.5 HRTs after changing the influent regime.

The activity of ammonium oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB) measured during SBR treatment were used to calculate the AOB rate (R_{AOB}) in mg N/(g MLSS·h) and the nitrification rate (R_N) in mg N/(g MLSS·h) with Eq. (1) and (2).

$$R_{AOB} = \frac{c_{NO_2-N} + c_{NO_3-N}}{c_{MLSS} \bullet t} \tag{1}$$

$$R_N = \frac{c_{NO_3-N}}{c_{MLSS} \bullet t} \tag{2}$$

$c_{NO2\text{-}N}$: nitrite concentration, mg/(L·d)$c_{NO3\text{-}N}$: nitrate concentration, mg/(L·d)c_{MLSS}: MLSS concentration, g/Lt: reaction time, t = 23 h/d.

Table 2
Operation conditions in phases 1–3 during SBR treatment.

Reactor	Parameter	Phase 1	Phase 2	Phase 3
	Operation days [d]	44	43	21
	Dilution of process water	–	10	10
	HRT [d]	10	10	5
	Exchange ratio [%]	10	10	20
SBR190	MLSS [g/L]	8.9	4.9	5.7
	F/M$_C$ [mg C/(g MLSS·d)]	190	34	60
SBR217	MLSS [g/L]	8.0	4.5	5.0
	F/M$_C$ [mg C/(g MLSS·d)]	212	38	67

2.4. Nitrification inhibition

To assess the nitrogen inhibition of the process waters, tests were performed according to DIN EN ISO 9509 in 150 mL glass vessels [27,28]. The inoculum was taken from the same WWTP and prepared the same way as described in Section 2.2. Mixing, aeration and temperature were also similar. The DO was checked regularly and ensured to be above 3 mg/L, and the pH was checked at the beginning and the end of the tests. All tests ran for 3.5 h starting with the addition of inoculum. MLSS was adjusted to 2.3–3.3 g/L and the initial NH_4-N concentration was 50 mg N/L to avoid ammonia inhibition. $(NH_4)_2SO_4$ was added to set the different shares of process water to 50 mg N/L in each batch. However, the high NH_4-N concentrations in the process waters only allowed a process water share of 4 %. Therefore, a second series was conducted with an initial NH_4-N concentration of 250 mg N/L, allowing a share of up to 22 %. In addition to Feed SBR190 and Feed SBR217, the treated effluents of the SBRs during phase 1 were tested on nitrification inhibition again. The tests needed to be performed with a defoaming agent as described in Section 2.3. After each test, the samples were filtered (0.45 μm) and stored at 4 °C before being analyzed for oxidized nitrogen (nitrite and nitrate). The inhibition rates (I_N) in % and maximum nitrification rate R_N in mg N/(g MLSS·h) were calculated according to Eqs. (3) and (4). The concentrations of NO_2-N and NO_3-N at the beginning of a test were subtracted from $c_{ON,c}$, $c_{ON,t}$ and $c_{ON,b}$.

$$I_N = \left(\frac{c_{ON,c} - c_{ON,t}}{c_{ON,c} - c_{ON,b}}\right) \bullet 100 \tag{3}$$

$c_{ON,c}$: oxidized nitrogen in blank suspension without inhibitor at t = 3.5 h, mg N/L$c_{ON,t}$: oxidized nitrogen in test suspension without inhibitor at t = 3.5 h, mg N/L$c_{ON,b}$: oxidized nitrogen in reference suspension with inhibitor at t = 3.5 h, mg N/L.

$$R_N = \left(\frac{c_{ON,t} - c_{ON,b}}{c_{MLSS} \bullet t}\right) \bullet 100 \tag{4}$$

c_{MLSS}: concentration of MLSS, g/Lt: reaction time, t = 3.5 h.

2.5. Chemical analysis

Solids were analyzed either in terms of total solids and volatile solids according to DIN EN 12880:2001 and DIN EN 15936:2012, or in terms of MLSS and MLVSS according to DIN 38409:1987 at 105 °C and 550 °C. The process water samples were filtered via 0.45 μm PES syringe filters before analysis. Dissolved organic carbon (DOC) was analyzed using a vario TOC cube (Elementar Analysensysteme GmbH, Germany). Nitrite (NO_2-N), nitrate (NO_3-N) were analyzed with a Compact IC Flex and a Metrosep A Supp 7 column (Metrohm AG, Suisse). For COD, total nitrogen (TN) and ammonium (NH_4-N) HACH tests LCK 514, LCK 338 and LCK 303 as well as a HACH Photometer DR 3900 were used (Hach Lange GmbH, Germany). UV_{254} and UV_{475} were determined with a HACH Photometer DR 5000 with a cell length of 10 mm (100-QS, Hellma GmbH, Germany). The ratio of UV_{254}/DOC (SUVA) was used to quantify the aromaticity. The brownish color of samples, which is mostly caused by melanoidins, was evaluated by measuring specific UV absorbance at 475 nm as proposed by Arimi et al. [29].

2.6. Assessing the effect of HTC on the effluent of a WWTP

For this estimation, SBR treatment of the HTC process water was considered as a pretreatment step before discharge into an exemplary full-scale WWTP. From this WWTP we obtained the WAS for HTC experiments. The inflow (Q_{WWTP}) was 5400 m^3/d and the WAS flow (Q_{WAS}) was 11.1 m^3/d with 9.2 % total solids on average in 2020 and 2021. DOC and DON after SBR treatment were expected to be refractory for biodegradation in the WWTP and therefore increase the effluent concentrations of the WWTP. Assuming constant mass during HTC and

65 % total solids after dewatering the HTC coal slurry [30], the mass balance in Eq. (5) was used to determine the volume of the dewatered hydrochar. The effluent concentrations of refractory compounds were calculated according to Eq. (6).

$$Q_{Hydrochar} = Q_{WAS} \bullet \frac{9.2\%}{65\%} \tag{5}$$

$$DOC = \left(\frac{\left(Q_{WAS} - Q_{Hydrochar}\right) \bullet rDOC}{Q_{WWTP}}\right) \tag{6}$$

DOC: DOC (or DON) in the WWTP effluent, mg/LrDOC: recalcitrant DOC (or DON) after SBR treatment, mg/L.

3. Results and discussion

3.1. Total biodegradability

The evolution of DOC removal and SUVA for ZW218 and ZW218* (with pre-exposed inoculum) are depicted in Fig. 1a. Both batches show that the HTC process waters contain a large fraction of readily biodegradable organics, which resulted in a DOC removal of 67.1 ± 1.5 % and 74.9 ± 0.7 % within 3 days of incubation. Between days 3 and 10 the DOC removal was lower, which indicates the presence of a slowly biodegradable fraction. From day 10 on, DOC was only marginally reduced, implying that biodegradable DOC had been almost completely removed. Pre-exposed inoculum in ZW218* showed a slightly faster and further reduction of DOC. This indicates that adaption of aerobic microorganisms enables a faster removal of readily biodegradable compounds and additional removal of some of the slowly biodegradable compounds. On day 28, the regular test duration to identify non-biodegradable compounds according to EN ISO 9888 (1999), DOC was removed by 78.5 ± 0.3 % and 81.9 ± 0.2 % for ZW218 and ZW218*, respectively. Extending the test period to 50 days had no significant effect on DOC removal.

The SUVA increased from 1.4 L/(mg·m) to 3.2 and 3.3 L/(mg·m) for ZW218 and ZW218* on day 28. It followed the overall trend of DOC removal by already reaching values above 3 L/(mg·m) after 8 days and by showing only a minor raise in the further course of tests. Increasing SUVAs indicate the removal of compounds that do not absorb UV light, and the enrichment of hydrophobic, humic-like compounds [31], which are not available for biological treatment. This could be caused by heterocyclic and aromatic structure of melanoidins, which show a high UV quenching and therefore a high SUVA [32]. Accordingly, the SUVA curve shows that a majority of readily biodegradable substances were degraded in the first days. Gupta et al. [33] obtained similar results by investigating the removal of organic matter from return liquors from dewatering thermal hydrolysis digestate. After 28 days of aerated incubation, they observed a humic substances (UV_{254}) removal of 15–20 % and a DOC removal of 35–40 %. With this, an increase in SUVA from 1.5 to 2.1 L/(mg·m) can be calculated.

All batches using non-pre-exposed biomass (ZW190, ZW218, ZW249) lead to very similar maximum DOC removal (Fig. 1c). So, the

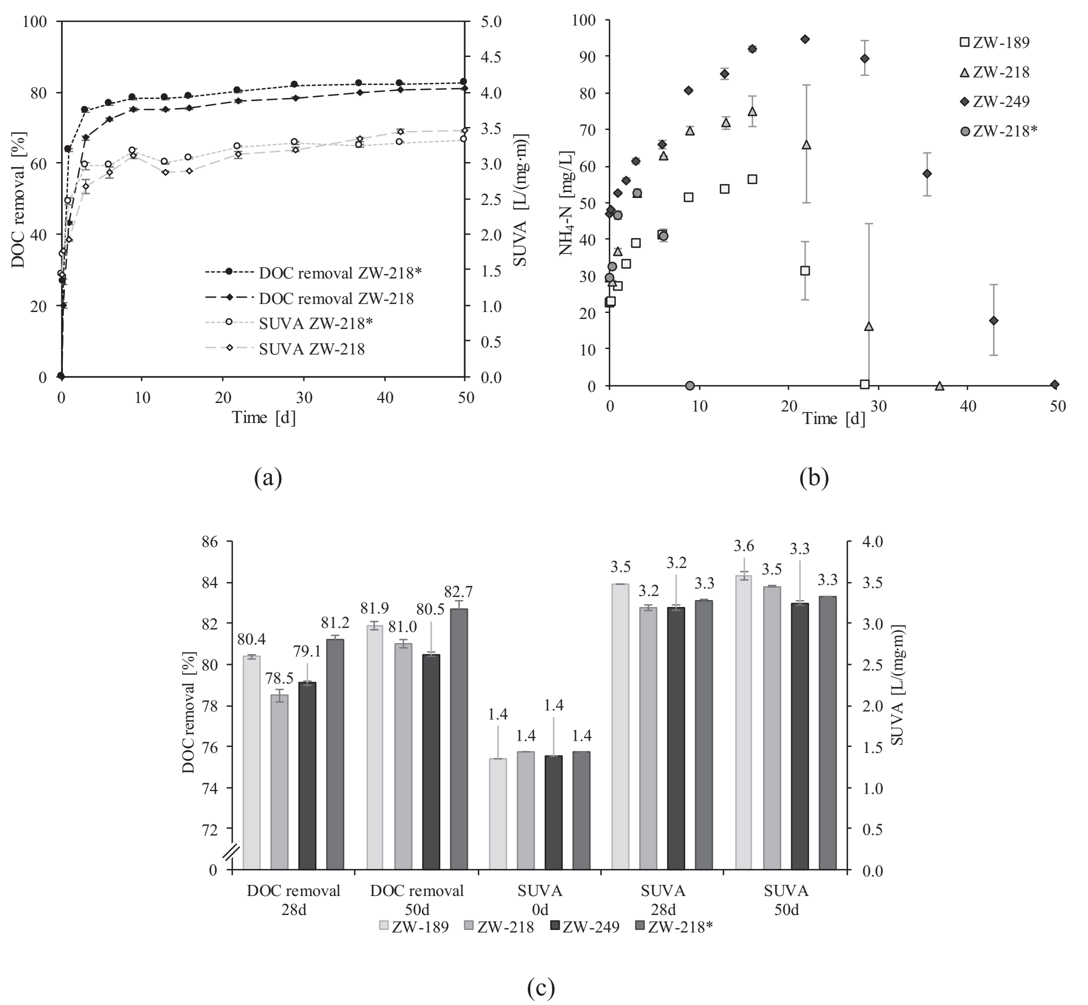


Fig. 1. Evolution of (a) DOC removal and SUVA during Zahn-Wellens tests for ZW218 and ZW218*, (b) NH_4-N and (c) DOC removal and SUVA for the process waters after 28 d and 50 d incubation time.

increasing HTC reaction temperatures had only little impact on aerobic biodegradation. This is quite surprising, as lower biodegradability with increasing HTC temperature was shown for anaerobic digestion of HTC process waters [34]. Aerobic microorganisms are able to degrade the compounds that can form at elevated HTC temperature to the same extent. For example, Yeom et al. [35] and Pradeep et al. [36] showed the adaption of biomass and biodegradation of phenols, which are present in HTC process water [9]. Also PAHs were shown to be aerobically degraded [37].

The degradation of N-containing compounds was also shown in the evolution of ammonium (Fig. 1b), which was similar for all tests with non-pre-exposed biomass. The increase in ammonium concentration with increasing HTC temperature results from deamination, which is the breakdown of dissolved nitrogen into lower molecular products releasing NH_4-N [38]. The evolution of NH_4-N resulted from two simultaneous processes which cannot clearly be distinguished from each other: the ammonification, which releases ammonium due to the degradation of nitrogenous compounds, and the nitrification, which consumes ammonium. The increase of NH_4-N in the beginning of the tests shows that the rate of ammonification was higher than the rate of nitrification. After 16 to 22 days, ammonification slowed down and nitrification led to the decrease of NH_4-N. Ammonia stripping could not be quantified in the tests, but the pH and temperature (see Section 2.2) suggest that it is of minor importance. Comparing ZW190, ZW218 and ZW249, higher HTC temperatures seem to produce either nitrogenous compounds harder to degrade or more nitrification inhibition substances, or both. The evolution of NH_4-N in ZW218* shows the positive effect of biomass pre-exposition. NH_4-N in ZW218* increased until day 3 and was not detectable any longer after day 9. For ZW218 with non-pre-exposed biomass, the removal of NH_4-N lasted beyond day 30. Overall, the tests show that nitrification can be achieved once microorganisms are adapted to HTC process water.

3.2. Biodegradability in SBRs

Similar to the Zahn-Wellens test, the HTC temperature had only a small effect on the DOC removal and the SUVA in SBR190 and SBR217, but a slight dependence on the F/M_C ratio was observed (Fig. 2). For F/M_C ratios from 31 to 76 mg C/(g MLSS·d), the DOC removal varied between 70 and 74 % and the SUVA between 2.9 and 3.1 L/(mg·m). These F/M_C ratios were set during phases 2 and 3 with a 1:10 dilution of feed. For higher F/M_C ratios of 185–263 mg C/(g MLSS·d), which resulted from the undiluted process water in phase 1, DOC removal was 68–74 %, and SUVA was 2.5–2.7 L/(mg·m). The lower SUVAs for higher F/M_C ratios imply that despite comparable DOC removal, fewer non-aromatic compounds were removed in phase 1 [32].

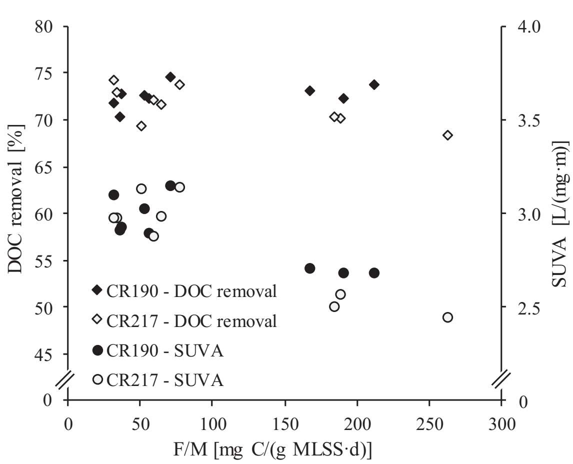


Fig. 2. DOC removal and SUVA in SBRs.

Since the COD/DOC ratio of the feed and the SBR effluent was 2.9 mg O_2/mg C during every phase, the COD removal can also be calculated from the DOC. Fettig et al. [23] reported a COD removal of about 80 % at a sludge loading of 0.08–0.2 g O_2/(g MLSS·d) during the aerobic treatment of HTC process water. At a similar sludge loading of 0.09 to 0.23 g O_2/(g MLSS·d) in SBR190 and SBR217, the DOC removal was roughly 72 %. This lower DOC removal may be attributed to the use of different feedstock for HTC and consequently, differences in the process water composition. The average DOC removal of 72 % equals rDOC of 28 %.

3.3. Nitrification performance and rDON in SBRs

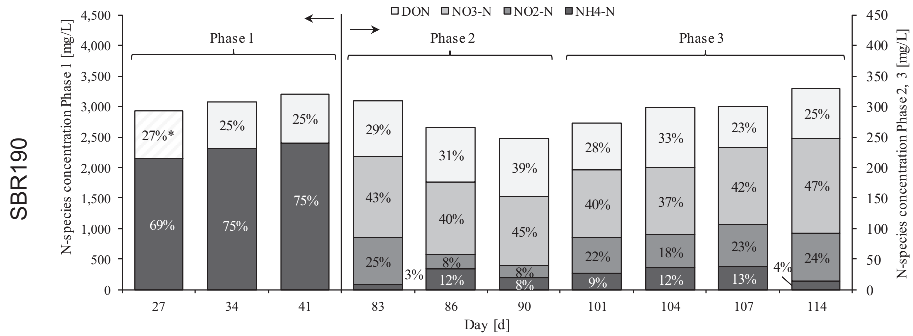
The type and concentration of nitrogen species during the different phases are summarized in Fig. 3a and b. During phase 1 and for both SBRs, nitrogen was present as ammonium and DON. No nitrification was observed in phase 1, probably due to inhibiting compounds, but also due to NH_3 which inhibits Nitrosomonas in the range of 10–150 mg N/L [39]. The DON concentration was 770–830 mg/L and 470–830 mg/L for SBR190 and SBR217. NH_4-N was higher than in Feed SBR190 and Feed SBR217 suggesting that ammonification took place, but was not complete. With 69–75 % NH_4-N and 25–27 % DON for SBR190 and 75–85 % NH_4-N and 15–26 % for SBR217, the degree of mineralization was almost similar. Similar mineralization rates have been observed in anaerobic batch tests [26]. The observation of limited mineralization was also reported in literature, as some melanoidins like pyridines and pyrazines were shown to mineralize to ammonium [40–42], whereas no complete biological removal of coloring melanoidins was reported [43].

The DON was removed to an almost similar extent, despite the proportion of NH_4-N in Feed SBR217 (35 %) compared to Feed SBR190 (26 %) (see Table 2) being higher. This differences are due to the increased decomposition of organic nitrogen compounds into ammonium at higher hydrothermal temperatures [44]. Still, DON in Feed SBR190 could be degraded to the same extent as Feed SBR217 at higher hydrothermal reaction temperatures. In addition, HTC temperature didn't affect the overall biodegradability of DON. However, higher reaction temperatures than in our study (270 °C to 345 °C) were reported to cause a lower biodegradability of DON and higher rDON [44]. Compared to the TN in Feed SBR190 (4400 mg N/L) and Feed SBR217 (4800 mg N/L), concentrations in both SBRs were noticeable lower (around 3000 mg N/L and 3350 mg N/L, respectively). This gap in TN of approx. 1500 mg/L can partly be attributed to biomass growth: With the given feed COD and TN and at 20 °C, the estimated nitrogen for cell growth would be somewhere between 950 and 1.700 mg N/L depending on the assumed biomass growth rates [45]. In addition, stripping of NH_3 could explain some of the differences in TN. Although NH_4 dominates at a pH of 7.5 according to the ammonium-ammonia equilibrium, NH_3 was also present. For both SBRs, NH_3 was calculated to be 41–45 mg/L [39]. Ammonia stripping could not be quantified, but probably contributed to the nitrogen loss.

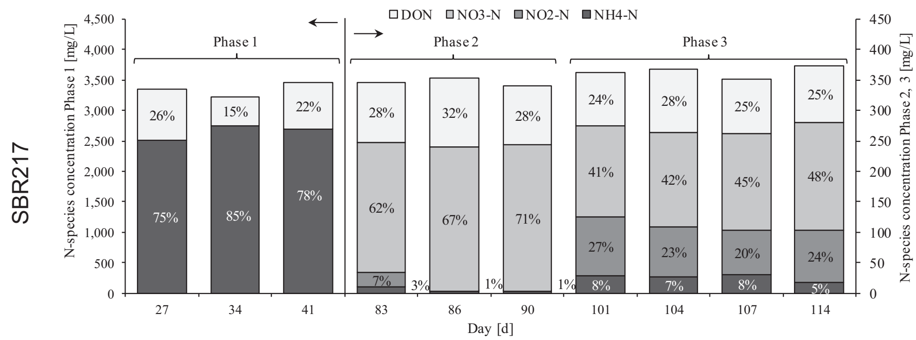
In the Zahn-Wellens tests it could not be clarified whether nitrification or ammonification is the limiting step. However, the comparison with the SBR test suggests that nitrification was the limiting step and not ammonification.

In phases 2 and 3, ratio DON/TN of SBR190 ranged between 23 and 39 % (69–103 mg N/L). For SBR217, DON was 24–32 % (87–113 mg N/L). As the DON was very similar for SBR190 and SBR217 at different operation settings, the remaining DON seems to be non-biodegradable. Coloring substances such as Maillard products were not or only slightly removed, as the UV_{475} (see Table 3) remained constant during biodegradation. A decolorization due to the biological removal of melanoidins as summarized by Chandra et al. [43] could not be observed. On average, the recalcitrant DON/TN was 28 % for SBR190 and 25 % for SBR217.

The TN sludge loading significantly decreased due to the dilution of process water to 1:10 in phase 2, and nitrification set in. No notable concentrations of ammonium and nitrite were measured in SBR217,



(a)



(b)

Fig. 3. Different nitrogen species in phases 1–3 for (a) SBR190 and (b) SBR217. *TN was not measured on this day; therefore, DON was calculated by the average DON.

Table 3
Mean R_{AOB}, R_N and UV_{475} ± standard deviation.

Reactor	Parameter	Phase 1	Phase 2	Phase 3
SBR190	F/M_N [mg TN/(g MLSS·d)]	50.6 ± 5.9	9.1 ± 0.8	16.0 ± 2.6
	R_{AOB} [mg N/(g MLSS·h)]	n.d.[1]	1.4 ± 0.4	1.5 ± 0.2
	R_N [mg N/(g MLSS·h)]	n.d.	1.1 ± 0.1	1.0 ± 0.2
	UV_{475} [1/m]	895 ± 52	87 ± 10	84 ± 5
SBR217	F/M_N [mg TN/(g MLSS·d)]	62.4 ± 13.0	11.3 ± 3.0	19.6 ± 2.7
	R_{AOB} [mg N/(g MLSS·h)]	n.d.	2.0 ± 0.0	2.1 ± 0.1
	R_N [mg N/(g MLSS·h)]	n.d.	2.0 ± 0.1	1.4 ± 0.1
	UV_{475} [1/m]	683 ± 21	72 ± 12	71 ± 8

[1] Not determinable.

indicating a high level of nitrification. R_{AOB} and R_N were almost identical with 2.05 mg N/(g MLSS·h) and 1.98 mg N/(g MLSS·h), respectively. Although the TN loading rate was lower than in SBR217, a lower level of nitrification could be achieved in SBR190. Both ammonium and nitrite were not completely oxidized, and R_{AOB} and R_N were lower at 1.4 and 1.5 mg N/(g MLSS·h), respectively.

In phase 3, TN loading was increased to 16–19 mg TN/(g MLSS·d), which led to partial nitrification in both SBRs. Shares of nitrogen species were present on a similar scale in SBR190 and SBR217 of 4–13 %, 18–27 %, and 37–48 % for ammonium, nitrite and nitrate, respectively. R_{AOB} of both SBRs in phase 3 was only slightly higher than in phase 2. Consequently, nitrification was unlikely to be limited by ammonium shortage, but the maximum AOB activity seems to have been reached. Lower R_N in phase 3 suggest a greater inhibition of NOBs with increasing sludge loading.

Calculated according to Anthonisen et al. [39] free ammonia (FA) and free nitrous acid (FNA) reached 0.15 mg/L and 0.18 mg/L during phase 2, as well as 0.02 mg/L and 0.05 mg/L during phase 3 (SBR190). For SBR217, FA reached 0.03 mg/L and 0.13 mg/L, and FNA 0.01 mg/L and 0.06 mg/L during phases 2 and 3, respectively. Accordingly, FA and FNA should have no significant effect on nitrification. Even though SBR217 showed a slightly better nitrification performance, the inhibition of nitrification could not be further differentiated in SBR tests. Therefore, subsequent inhibition tests were initiated to clarify whether lower nitrogen conversion in SBR190 was due to increased inhibition of nitrification.

3.4. *Nitrification inhibition*

The inhibition of nitrification by Feed SBR190 starts at low DON sludge loadings and rapidly increases with raising DON sludge loading (Fig. 4a). 50 % inhibition (IC_{50}) was reached at around 28 mg DON/g MLSS. For Effluent SBR190, the IC_{50} dropped 10 mg DON/g MLSS. This is equivalent to volumetric shares of 2–3 % for Feed SBR190 and about 5 % for Effluent SBR190. For Feed SBR217 and Effluent SBR217 (Fig. 4b), inhibition followed a similar trend but was more pronounced. The IC_{50} was at 16 mg DON/g MLSS and at 7 mg DON/g MLSS, respectively. The volumetric shares were 1–2 % for Feed SBR217 and 4 % for Effluent SBR217, indicating that higher HTC temperatures lead to the increased formation of nitrification inhibiting substances. Accordingly, low HTC temperatures are favorable for lower inhibition of nitrification. However, even at lower temperatures, the process water has a strong inhibitory effect. Looking at the volumetric shares, the inhibitory effect has been halved by the biological treatment, but was still strong. The specific inhibition in mg DON/g MLSS, on the other hand, shows a different result: the SBR effluents inhibited nitrification more than the HTC process waters themselves. This indicates that the inhibiting substances were still present after biodegradation and that these refractory compounds were primarily responsible for nitrification inhibition.

Pagga et al. [46] reported similar findings, as nitrification inhibition caused by poorly degradable compounds was more severe compared to biodegradable ones. Nitrification inhibition of HTC process waters could

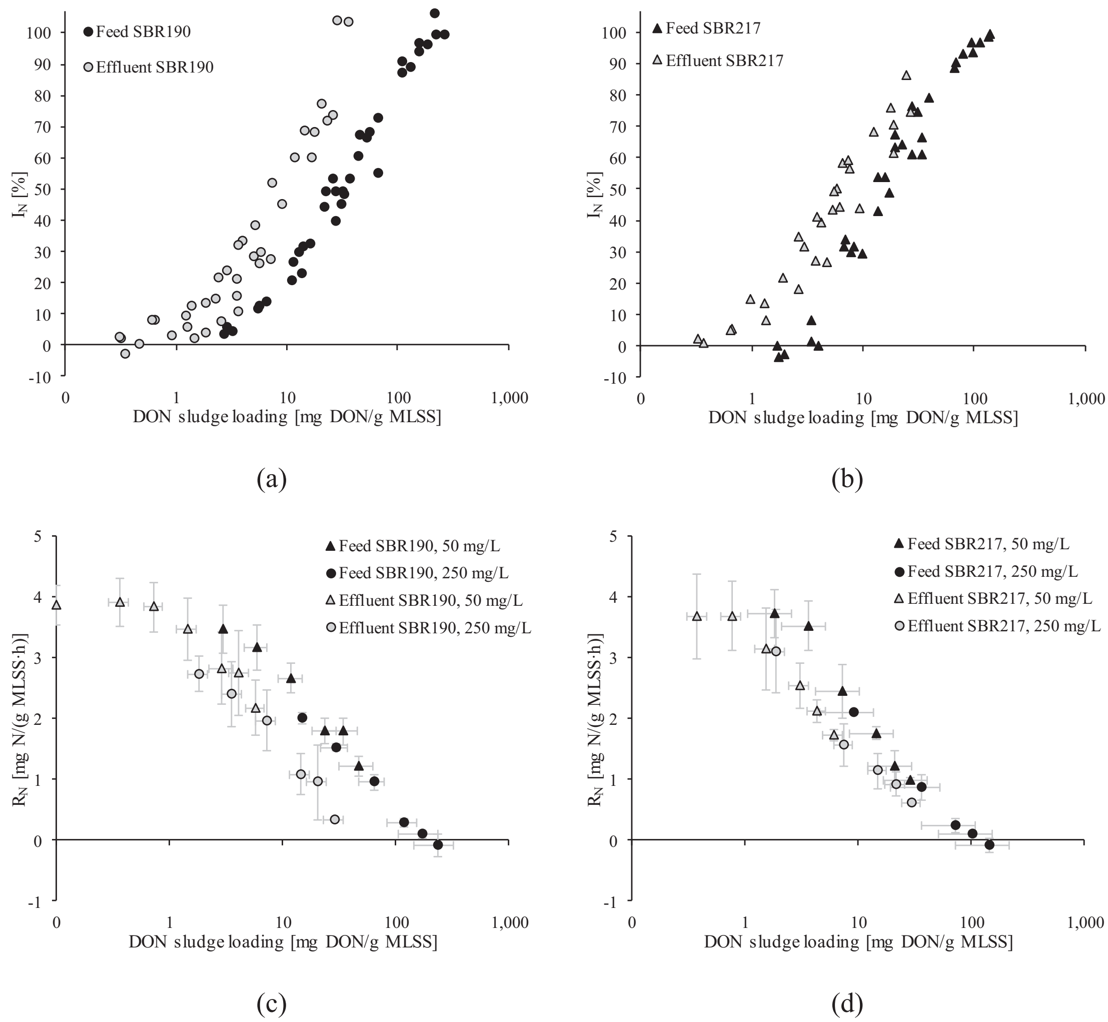


Fig. 4. Nitrification inhibition of feed and phase 1 effluent process waters for SBR190 (a) and SBR217 (b) and corresponding average nitrification rates and STD at different NH_4-N concentrations of 50 mg/L and 250 mg/L (c), (d).

also not be reduced by ultrafiltration pretreatment as shown by Kühni et al. [21]. In addition, the authors recommend a 100-fold dilution of process water before discharging into nitrifying wastewater treatment plans to avoid inhibition. In contrast to the aerobic pretreatment in this study, the anaerobic pretreatment of brewer's grain HTC process water could reduce the inhibition from 90 to 35 % at a dilution of 1:50 [23]. Beyond that, no further studies dealing with nitrification inhibition of HTC process waters are available. The obtained results indicate that even biologically pre-treated process water is of major concern for WWTPs, as HTC process water not only contains recalcitrant DOC and DON but also disturbs nitrification.

As illustrated in Fig. 4(c) and (d), R_N reached 3.8 mg N/(g MLSS·h) at low DON sludge loadings. With increasing DON sludge loadings, nitrification rates declined and dropped to zero at 240 mg DON/g MLSS (Feed SBR190) and 145 mg DON/g MLSS (Feed SBR217). Standard deviations were quite high for the tests, which is due to the use of new inoculum with different nitrification rates for each series of tests. However, each inoculum was within the required range between 2 and 6.5 mg N/(g MLSS·h).

Batch inhibition tests do not directly relate to continuous tests, since no long-term effects can be deducted. Still, they give an idea of the extent of inhibition. Even though Feed SBR190 was less inhibiting than Feed SBR217, the nitrification rate in SBR190 was lower than in SBR217 (Table 3). A possible explanation for those differences may be amount of nitrifying biomass present in the tests or the degree of adaption.

3.5. Effect of HTC on WWTP effluent

rDOC and rDON were used to calculate the effect of HTC on the effluent of a full-scale WWTP. Since there were no major differences, the refractory concentrations across all phases 1–3 were used. Concentrations were lower in phases 2 and 3 due to the dilution. The results of these calculations indicate that the effluent concentrations of the WWTP could be increased to a considerable extent, especially for phase 1 effluent (Table 4). In particular, the increase in effluent DOC by up to 8.3 mg/L and effluent COD by up to 24.1 mg O_2/L may cause serious problems with regard to legal discharge limits. For example, the discharge limit of the model wastewater treatment plant is 40 mg O_2/L,

Table 4
Predicted effluent concentrations for DOC, COD and DON after SBR treatment.

Parameter	SBR190	SBR217
rDOC[1] [mg C/L]	4727	4611
rCOD[2] [mg O_2/L]	13,766	13,596
rDON[3] [mg N/L]	1255	1211
Increase in effluent DOC [mg C/L]	8.3	8.1
Increase in effluent COD[2] [mg O_2/L]	24.1	23.5
Increase in effluent DON [mg N/L]	2.2	2.1

[1] 28 % of DOC was refractory in SBR190 and SBR217
[2] Average COD/DOC was 2.9 mg O_2/mg C during the tests.
[3] 28 % and 25 % DON was refractory in SBR190 and SBR217.

which would be difficult to meet if the HTC process water was recirculated. Higher effluent DON is of minor importance as the concentrations were lower and dilution would be high enough to avoid inhibition of nitrification. In general, this approximation is not transferable to other WWTPs, as boundary conditions such as inflow conditions, treatment steps or effluent regulations vary. Yet, the results suggest that an aerobic biological treatment step alone is not sufficient for the treatment of HTC process water. Additional treatment steps such as advanced oxidation processes are necessary.

Similar results were found by Toutian et al. [47], who calculated an increase in effluent COD for thermal hydrolysis and anaerobic digestion. Reactions resemble those of HTC, but the lower temperatures lead to less refractory compounds. They found a sharp increase in effluent COD at 170 °C of 12–21 mg O_2/L compared to lower temperatures, which is within the range of our predicted increase in effluent COD. Elevating the temperature from 170 °C to 190 °C does not seem to increase refractory compounds significantly.

4. Conclusions

To make HTC a proper alternative for the treatment of sewage sludge, solutions to deal with the produced HTC process water must be developed. In summary, this study showed that aerobic treatment cannot achieve satisfactory purification of the process water and further post-treatment steps are required. The following findings were obtained:

- Increasing HTC temperature had basically no effect on the DOC removal, but increased the potential inhibition of nitrification.
- DOC removal in continuously operated SBRs was around 72 %, resulting in an effluent rDOC of 28 %.
- The effluent rDON/TN ratio was 25–28 %.
- Nitrification was inhibited to a large extent by substances that could not be effectively biodegraded.
- Discharging the undiluted, pretreated HTC process water in a WWTP plant could increase the effluent DOC by 8.3 mg/L, and the effluent COD by 24.1 mg/L.

CRediT authorship contribution statement

Conceptualization: TB; Data curation: TB, PL; Formal analysis: TB; Investigations: TB, PL; Methodology: TB, Writing – original draft preparation: TB; Writing – review and editing: PL, ME; Visualization: TB; Funding acquisition: ME; Project administration TB; Supervision: ME.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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