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Micropollutants removal during high rate thermophilic and hyper-thermophilic anaerobic digestion of concentrated black water

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ABSTRACT

Source separated toilet water (black water; BW) is an important alternative nutrient source for agriculture. However, reuse and recovery of nutrients from BW is limited by the presence of pollutants, such as pathogens and micropollutants. In this study, the fate of micropollutants during thermophilic and hyper-thermophilic anaerobic digestion (AD) of concentrated vacuum collected BW is assessed. A total of eight pharmaceuticals were selected and spiked with two distinct loading rates to concentrated BW treated in an Upflow Anaerobic Sludge Blanket Reactors (UASB). The removal of these micropollutants was followed by measuring concentrations in the liquid phase. It was shown that the micropollutant loading rate did not affect the removal efficiency. Irbesartan, propanol, sulfamethoxazole and trimethoprim were almost completely removed under both conditions (>95% removal). Metoprolol had 74% removal under thermophilic conditions. Caffeine showed high desorption from BW solids, whereas carbamazepine is thought to be removed by sorption to the sludge in the UASB reactor. Diclofenac removal was < 30% during both temperature conditions, which may have been caused by the lack of sludge adaptation which limits the biodegradation. There were no differences in micropollutant removal efficiencies between thermophilic and hyper-thermophilic AD of concentrated BW. Therefore, it is concluded that thermophilic AD is sufficient for safe nutrient recovery in terms of micropollutants presence.

1. Introduction

Nutrients from domestic wastewater, which are currently mainly wasted due to technical and legal constrains, can contribute to a more sustainable agro-food system when they are recovered as fertilizers [1]. The framework of the Horizon 2020 project Run4Life proposes new concepts for nutrient and energy recovery from source separated domestic waste streams [1]. Such a source separated system provides a concentrated toilet water (black water; BW) stream that can be treated separately from the more diluted voluminous kitchen, bathroom and rain water streams [2]. BW contains 60–70% of the organic matter and 70–90% of the nutrients that are normally present in domestic waste water [3]. When collected with ultra-low flush volume vacuum toilets, this concentrated BW is suitable for energy and nutrient recovery using high-rate anaerobic processes, like thermophilic (55 °C) and hyper-thermophilic (70 °C) anaerobic digestion (TAD/HTAD) in Upflow Anaerobic Sludge Blanket (UASB) reactors [1,2]. Recovered nutrients can be reused in agriculture and thereby reduce the dependence on depleting rock reserves or energy intensive processes for fertilizer production [1]. However, the main fraction of pathogens and pharmaceuticals, end up in the (concentrated) BW stream [4,5]. TAD and HTAD have been proposed as novel treatment strategies for simultaneous energy and nutrient recovery and pathogen removal [1,6]. Prior to reuse of recovered nutrients in agriculture, pathogens and micropollutants (MPs) need to be sufficiently eliminated to guarantee food safety. Previously, it was shown that both TAD and HTAD result in high pathogen removal, however TAD outperformed HTAD in terms of biogas production and thus energy recovery [6,7]. Based on these results TAD was found to be a more suitable technology [7], but the fate of MPs has, to our knowledge, not yet been determined during TAD and HTAD of concentrated BW.

As a consequence of source separated collection, pharmaceuticals and hormones form the majority of the found MPs in BW. Therefore, in

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this study the focus is on MPs belonging to the pharmaceuticals class. MPs are of increasing concern, because they are potentially harmful [5, 8]. MPs can have an adverse effect on environmental and human health as these compounds can bioaccumulate in soils, organisms and crops [5]. Reuse of BW-derived products in agriculture could result in contamination of the agro-food chain, since MPs can bioaccumulate in the crops which could eventually lead to health issues after human or animal consumption [9,10]. Adverse effects of MPs need to be prevented through the application of effective treatment. Several studies have described removal of MPs during psychrophilic, mesophilic and thermophilic AD of sewage sludge [11–15]. The main focus in this study is on BW, since it potentially is an important source of nutrients. Few studies have been performed on mesophilic AD of BW (collected with conventional vacuum toilets) [4,5], BW sludge [16] and mesophilic and thermophilic AD with faecal sludge [17]. Gros et al. (2020) found that thermophilic AD of faecal sludge in batch systems increased the removal of the majority of the MPs compared to mesophilic AD [17]. A study by de Graaff et al. (2011) showed that mesophilic AD of BW in an UASB was not able to remove all pharmaceuticals and hormones [4]. Samaras et al. (2014) found no clear influence of temperature on MP removal during anaerobic sewage sludge treatment at mesophilic and thermophilic conditions [15].

The aim of this study is, in the light of nutrient recovery and reuse in agriculture, to assess and compare TAD and HTAD in terms of MP removal and thus safe nutrient production. To this end the removal of MPs during TAD and HTAD of concentrated BW is determined at different MP loading rates while spiking a mix of MPs to continuous reactor systems.

2. Materials and methods

2.1. Micropollutants

A total of eight widely used pharmaceuticals were selected based on their occurrence in black water, covering a wide range of physical-chemical properties, biodegradability, and absorbability (Supporting Information; Tables S1 and S2). Selected pharmaceuticals include two antibiotics (trimethoprim and sulfamethoxazole), two beta blockers (metoprolol and propranolol), one anti-inflammatory (diclofenac), one cardiovascular agent (irbesartan), one anti-epileptic (carbamazepine), and one stimulant (caffeine). Spike solutions were administered through a concentrated stock solution containing each MP in methanol. The used BW was obtained from an office area where pharmaceutical usage is low, therefore MP spiking was applied to meet concentrations in the low μg/L range which are representative for BW [3]. The stock solution was kept in the freezer (−20 ℃) until use.

2.2. Reactor operation and sampling

Treatment and collection of BW was performed as described by Moerland et al. (2021) [6]. Briefly, BW was collected through ultra-low flush volume vacuum toilets (Qua-vac B.V., Almere, The Netherlands, type: EVAC VT910) and treated in UASB reactors (working volume 4.9 L). During two different phases, concentrated MP solutions (nominal concentrations of 0.05 and 0.1 mg/L) were spiked into the BW. MPs were spiked close to the inlet of the reactors, through syringe pumps which were placed in cooled boxes (Fig. 1). The spiking solution in the syringes was refreshed twice a week. Before and after changing the spiking solution a sample was taken to check the stability of the MPs in the spiking solution. Two operational phases can be distinguished in this experiment. During Phase I (P1: Day 1 - Day 37), the reactors were operated at a hydraulic retention time (HRT) of roughly 6 days and an organic loading rate (OLR) of 2.5 ± 0.85 and 2.7 ± 0.87 kgCOD/m^3/day for the TAD and HTAD respectively. In the second Phase (P2: Day 38 - Day 52), the HRT was reduced to around 5 days, the OLR was 3.7 ± 1.5 and 3.9 ± 1.5 kgCOD/m^3/day for TAD and HTAD respectively. The MP load was doubled in the second phase.

For the MP analysis, influent samples were taken twice a week in triplicate. Effluent samples were taken daily. Three or four effluent samples were mixed in a 1:1 vol ratio (stability of effluent values over the course of three to four days was confirmed, data not shown) to end up with two mixed samples per week for analysis. 1.9 mL sample was mixed with 0.1 mL acetonitrile (to prevent sorption of MPs to the container) and stored at −20 °C. Prior to analysis, influent and effluent samples were centrifuged twice at 15000 rpm for 10 min, to separate the solid and liquid fractions. The solid fraction was collected and stored in the freezer (−20 ℃), and the liquid fraction (the supernatant for second-time centrifugation) was mixed with internal standard solution

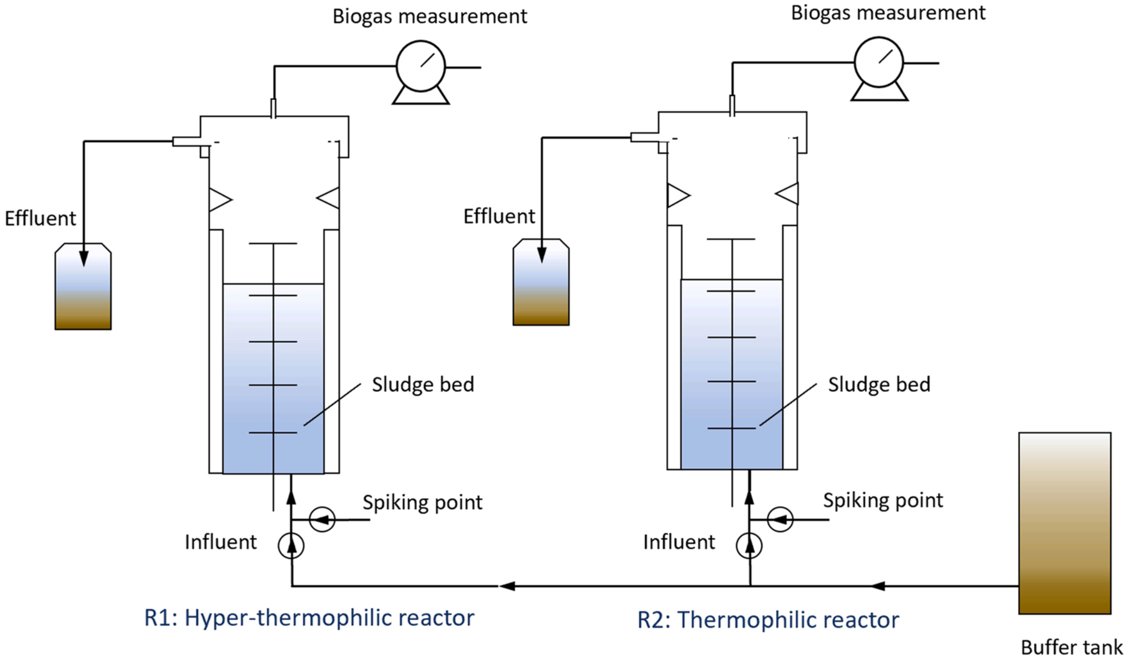

Fig. 1. Schematic overview of two UASB reactors.

(Supporting Information; Table S4).

MP analysis was performed with an ultra-high performance liquid chromatograph (ExionLC AD-30 System) equipped with a tandem mass spectrometer (Triple QuadTM 5500 + System), both from SCIEX. The chromatographic separation of MPs was performed using a phenyl-hexyl based analytical column as stationary phase and a combination of water and acetonitrile based eluents, both acidified with 0.1% (v/v) formic acid, as mobile phase. Components were quantified against a calibration curve in the range of 50–1000 ng/l and corrected for matrix effects with internal standards using SCIEX OS 1.7 software. Detailed LC and MS settings and the calculations for the removal efficiency are presented in the Supporting Information (Section S2 and S3).

3. Results and discussion

The TAD and HTAD were fed with MP spiked BW in semi batch mode to compare the MP removal performance of the two reactors. MP spiking was done at two periods with distinct MP loading rates to investigate the effect of MP loading on the reactor performance. Reactor performance in terms of COD removal, methanisation and VFA accumulation can be found in the Supporting Information (Table S6).

3.1. *The effect of micropollutant loading rates on the removal efficiency*

Four of the tested MPs were almost completely removed (>94%), and also metoprolol had a high removal efficiency (>70% in the TAD) (Fig. 2). Removal rates were not related to the K_{OW} or other characteristics of the MPs and largely independent of the MP loading rate, since in both the TAD and the HTAD the removal efficiencies were similar in the high and low MP loading rate periods. Average loadings of the MPs for caffeine, carbamazepine, irbesartan, propranolol, sulfamethoxazole and trimethoprim for the low and high MP loading periods where 154 and 380 ng/L_R/day respectively (Supporting information; Figs. S1 and S2). Metoprolol loadings where 20–40 times higher than the loadings of other MPs and showed high variation (>50%) due to high and unstable concentrations in the un-spiked influent, which can be attributed to the fact that real BW was used in this study. Diclofenac was only analysed during the period with high MP loading rate.

Caffeine (not shown in Fig. 2) showed strong removal variety ranging from negative 4000% to positive 70%. Humans excrete caffeine mainly through urine [18]. The negative caffeine removals, which were mainly observed in the HTAD, are explained by desorption of caffeine at high temperatures. Similar levels of caffeine desorption from the initial BW were confirmed in the batch experiment, in which after three days of incubation the caffeine concentration in the liquid phase increased by a factor of 57 and 215 for incubation of BW at thermophilic and hyper-thermophilic conditions respectively (Table 1/Supporting information Section S7).

For carbamazepine the removal efficiency changed over time, especially during the high loading period for the HTAD reactor (Fig. 3). This indicates that, carbamazepine removal could be a result of sorption and not biodegradation, which is in line with other studies showing carbamazepine to be recalcitrant towards biodegradation [12,19]. The sorption capacity was saturated at day 20, resulting in the drop in carbamazepine removal. Because the MP and organic loading was increased at day 39, the removal by sorption increased again around that time as a result of the establishment of a new equilibrium. However, extraction experiments from (H)TAD sludge showed that only 10% of the total removed carbamazepine could be recovered from the sludge (Supporting information; Section S6). This means that besides sorption, other removal mechanisms also play a role for carbamazepine. However, sorption cannot be ruled out since sludge extraction measurements in (thermophilic) anaerobic digesters are challenging and should be interpreted with caution. Especially since this is the first attempt to quantify MPs in the sludge samples from (hyper-)thermophilic BW treatment systems.

Table 1
Results from the sorption batch experiments for caffeine. Final and initial concentrations are given, as well as the fraction of the final concentration over the initial concentration. The batch experiment lasted three days. The coefficient of variation of the used analysis method for caffeine in the raw black water was 6.5% (based on triplicates taken throughout the experiment).

Batch condition	Initial caffeine concentration (ng/L)	Final caffeine concentration (ng/L)	Desorption factor (final/initial concentration)
Mesophilic (30 °C)	138	54	0.4
Thermophilic (55 °C)	101	5826	57
Hyper-thermophilic (70 °C)	133	28548	215

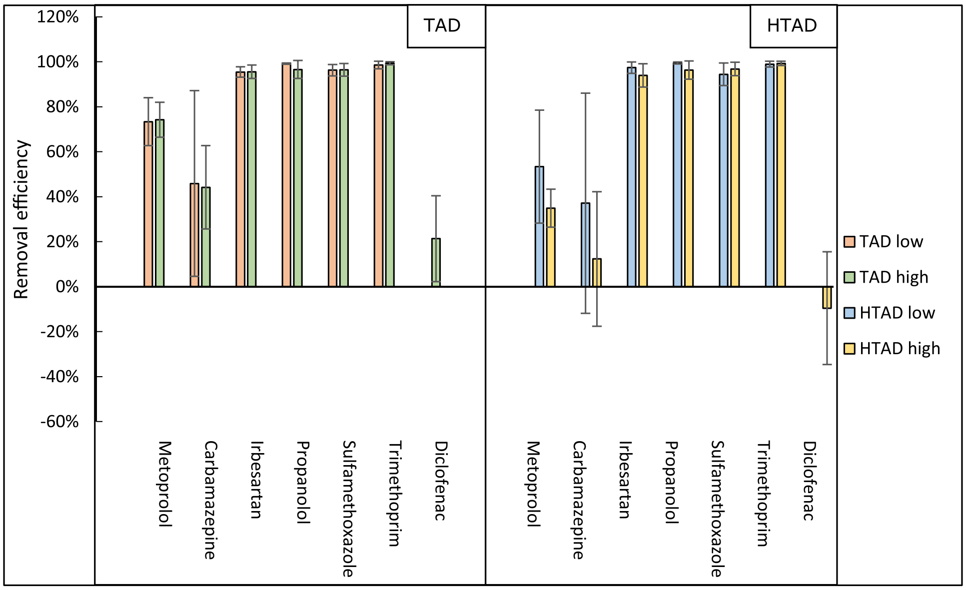

Fig. 2. Average removal efficiencies during low and high MP loading rates for the TAD (left) and HTAD (right) reactors.

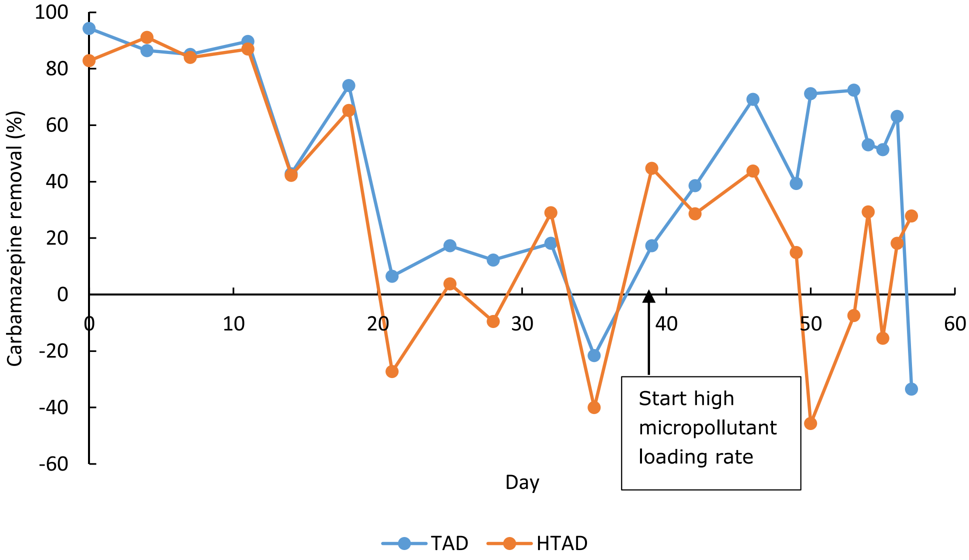

Fig. 3. Carbamazepine removal during the experimental period in the TAD and HTAD. The coefficient of variation of the used analysis method for carbamazepine was 14.8% (based on triplicates taken throughout the experiment).

3.2. Micropollutant removal during thermophilic and hyper-thermophilic anaerobic digestion

The removal efficiencies of TAD are equal to (or in some cases higher than) those of HTAD for the tested MPs. Fig. 1 shows that irbesartan, propanol, sulfamethoxazole and trimethoprim are almost completely removed under both conditions. The metoprolol removal was lower during HTAD, possibly due to high influent concentrations resulting in a higher total MP loading rate of metoprolol compared to the other components (3000–16000 ng/L_r/day versus 150–380 ng/L_r/day). For TAD this resulted in a stable removal of 74%, whereas the HTAD reactor had a lower metoprolol removal (43%) with a high deviation. This confirms for the TAD that even high fluctuations in MP load (factor 5) do not influence the stability of the removal process. High removal of irbesartan, propranolol, sulfamethoxazole and trimethoprim is in good accordance with previous studies on MP removal during thermophilic AD [11,13,17]. Diclofenac showed low removal during TAD and no removal during HTAD. Diclofenac was only monitored during the second phase with high MP loading rate since the analytical method was not adequate during phase I with low MP loading rates. Studies with sewage sludge or wastewater treatment effluent showed low (<50%) diclofenac removal during TAD [13,20]. However, there are also studies that show higher removal (>60%) for diclofenac during TAD of sewage sludge [12,15]. Mesophilic treatment of source separated BW also resulted in a low removal (<20%) of diclofenac [15,21]. Possibly the ambiguity in removal rates between different studies is explained by sludge adaptation, as was suggested in several studies [12,20]. Also during mesophilic BW treatment, Butkovskyi et al. (2016) found an increased removal of diclofenac during the second sampling period. For TAD, the metoprolol removal efficiency in this study is comparable to mesophilic combined treatment of black and grey water which resulted in 72% removal [21].

4. Conclusion

This study showed that, independent of the applied MP loading rates, high removal (>94%) of irbesartan, propranolol, sulfamethoxazole and trimethoprim were achieved under thermophilic and hyper-thermophilic treatment of concentrated BW. Metoprolol had lower removal efficiencies of roughly 70%. The three other tested MPs, carbamazepine, diclofenac and caffeine, were removed to a lower extent possibly which appears to be influenced by various processes, i.e. either by a limited sorption capacity (carbamazepine, especially at high MP loading rates) and/or insufficient sludge adaptation (diclofenac). Negative removal of caffeine was observed as a result of desorption from solids. MP removal was assessed for the first time during HTAD of concentrated BW, however this did not result in elevated removal efficiencies compared to TAD. Therefore, TAD appears to be the most suitable treatment technology for concentrated BW in terms of mitigating MP contamination of recovered nutrients.

CRediT authorship contribution statement

Marinus J. Moerland: Writing – original draft, Conceptualization, Formal analysis, Methodology, Visualization. **Koen van Gijn:** Writing – original draft, Conceptualization, Formal analysis, Methodology, Visualization. **Xiangyu Ji:** Formal analysis, Methodology. **Cees J.N. Buisman:** Supervision, Writing – Review & Editing, Funding acquisition. **Huub H.M. Rijnaarts:** Supervision, Writing – review & editing, Funding acquisition. **Alette A. M. Langenhoff:** Supervision, Writing – review & editing, Conceptualization, Project administration, Funding acquisition. **Miriam H.A. van Eekert:** Supervision, Writing – review & editing, Conceptualization, Project administration, Funding acquisition.

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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2022.107340.

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