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Recovery of calcium phosphate granules from black water using a hybrid upflow anaerobic sludge bed and gas-lift reactor



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ABSTRACT

Adding calcium during anaerobic digestion of vacuum collected black water (BW) in an up-flow anaerobic sludge bed (UASB) reactor increased the retention of total phosphorus (P) in the reactor from 51% to 87%. However, the insufficient mixing in the reactor caused cementation and relatively high content of organics in the recovered calcium phosphate (CaP) granules, limiting the P recovery. In this study, the UASB reactor was mixed with an internal gas-lift (UASB-GL) to prevent cementation and to enhance the P content in CaP granules. The novel UASB-GL reactor operated for 300 days, treating concentrated BW. At steady state, the removal of total COD and P was 92% and 90%, respectively. The gas injection created a sludge bed with an average total suspended solids concentration of 73 \pm 16 g/L at the bottom and 31 \pm 5 g/L at the top of the reactor. The concentration was obtained (0.75 \pm 0.32 gP/L). 89% of the CaP granules was found at the bottom of the reactor. The harvested CaP granules (> 0.4 mm diameter) contained on average 7.8 \pm 0.6 wt% of P. A potential recovery of 57% of P in BW as CaP granules was calculated, considering actual application of the UASB-GL reactor in source separated sanitation.

1. Introduction

The natural source of phosphorus (P), phosphate rock, is dwindling and geopolitically imbalanced. Moreover, the costs for P extraction from phosphate rock are increasing due to the rising contamination with heavy metals and radioactive by-products (Cordell et al., 2009; Koppelaar and Weikard, 2013). Additionally, P runoff from agriculture and P discharge from wastewater treatment plants to surface water are causing a loss of biodiversity in aquatic environments due to eutrophication (Jarvie et al., 2006). Therefore, the recovery of P from waste streams is essential for protecting the environment and for providing future generations with P, which is a vital nutrient for food production (Elser, 2012; Mehta et al., 2015; Yuan et al., 2012). For instance, the recovery and use of P from human excreta could decrease the input of mined P rock in Europe by 21% (Cordell et al., 2011). Source separated sanitation is a promising concept that enables the separation and concentration of black water (feces and urine, BW) containing 1.3 gP/person/day at the source (Tervahauta et al., 2013). The separation of BW at the source avoids contamination with household chemicals from grey water or contaminants (i.e. organic disinfectants and heavy-metals) from industrial wastewater often mixed with household wastewater for centralized treatment.

In Sneek (The Netherlands), 32 households are equipped with vacuum toilets, using 1 L of water per flush. Thus, due to the separation from grey water and vacuum collection, BW is highly concentrated in organic matter and nutrients, containing on average 10 g/L of COD, 0.2 g/L of P, and relatively low levels of organic micropollutants and heavy-metals (Butkovskyi et al., 2017; Graaff et al., 2010; Tervahauta et al., 2014b). Therefore, BW is an interesting stream for resource recovery. Simultaneous recovery of calcium phosphate granules (CaP granules) and methane could be achieved using an up-flow anaerobic sludge bed (UASB) reactor for BW treatment (Tervahauta et al., 2014c). The formation of CaP granules occurs by agglomeration of precipitated calcium phosphate species (Ca_x(PO₄)_y) and organic material, containing

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Fig. 1. Technical illustration of the UASB-GL reactor set up (a), and detailed representation of the riser and bottom of the reactor (b).

microorganisms and extracellular polymeric substances (EPS) (Cunha et al., 2019; A. Mañas et al., 2012b; Mañas et al., 2012a). In time, the agglomerates grow in size along with the maturation of the $Ca_x(PO_4)_y$ rich core, forming CaP granules (Cunha et al., 2018b; A. Mañas et al., 2012). The addition of calcium (Ca²⁺) increases both the retention of P in the UASB reactor from 51% to 89% and the CaP granulation rate (Cunha et al., 2018a). Moreover, the formation of CaP granules in the sludge bed does not hinder the anaerobic digestion, but from the 89% accumulated P, only 31% was so far recovered as CaP granules (Cunha et al., 2018a).

The high concentration of solids in BW requires a relatively long hydraulic retention time (HRT), and therefore, low upflow velocity (< 1 m/h), resulting in low mixing (Graaff et al., 2010). Dosing of Ca^{2+} further limits the mixing due to the increased concentration of solids in the sludge bed by bridging of Ca²⁺ with negatively charged compounds (EPS and microbial cell surfaces) and precipitation of Ca_x(PO₄)_v and calcium carbonate (CaCO₃) (Dang et al., 2014; Ding et al., 2015). Although the P removal reported in Cunha et al. (2018a) is already at high levels (89%), the recovery was inhibited due to limited mixing at the bottom of the UASB reactor. The lack of mixing triggered cementation by precipitation of bare CaCO₃ and Ca_x(PO₄)_v particles, which were not recoverable. Additionally, the low upflow velocity led to a stagnant sludge bed, which hindered the settling of mature CaP granules. Therefore, mature CaP granules were undesirably spread throughout the sludge bed. Thus, for feasible full-scale application of CaP granulation within the current concept for source separated sanitation the aforementioned issues with the reactor design need to be mitigated.

In this study, we propose a novel bioreactor design with improved mixing behavior. The mixing is expected to increase the contact between added Ca^{2+} , PO_4^{3-} , EPS, and microbial cells, stimulating the formation of CaP granules, and to concentrate mature CaP granules at the harvesting location. As a result, the weight percentage of P in the recovered CaP granules and the P recovery efficiency increase. The conventional UASB reactor is modified by placing a concentric draft tube (riser) with gas injection at the bottom of the reactor, which is typical for gas-lift (GL) reactors (Chisti and Moo-Young, 1987;

Coughtrie et al., 2013; Van Benthum et al., 1999). The injection of gas at the lower end of the riser lifts the liquid in the riser by decreasing the density of the gas-liquid mixture. Accordingly, the density outside the riser (downcomer) is kept higher than inside and the liquid flows downward, creating a loop flow, which lifts particles from the bottom of the reactor (Lestinsky et al., 2012). The novelty behind the proposed design is the combination of a riser with a sludge bed reactor. The riser is placed at the bottom of the reactor with only 25% (0.35 m) of the reactor height (1.5 m). This contrasts with conventional gas-lift reactors where the relative riser height is higher and the lifting force commonly induces mixing in the entire reactor and effectively transfers the solid/liquid mixture to the top of the reactor.

The novel UASB-GL reactor was operated and monitored in this study. The particle size and P distributions of the sludge bed were analyzed to determine the effect of the mixing. CaP granules from the bottom of the UASB-GL reactor were harvested and characterized. Finally, the internal loop flow in the UASB-GL reactor was modeled to evaluate the liquid motion.

2. Materials and methods

2.1. Experimental setup

The parameters selected for the reactor operation, such as organic loading rate (OLR), HRT, temperature, and Ca^{2+} dosage, were based on previous work on calcium phosphate granulation (Cunha et al., 2018a; Graaff et al., 2010; Tervahauta et al., 2014c) to enable comparison. The UASB-GL reactor has an effective working volume of 45 L, while in Cunha et al. (2018a) the working volume was 5 L. Also, the construction material changed from doubled walled glass to doubled walled acrylic. Fig. 1 illustrates the experimental setup. The reactor was double walled and continuously heated at 25 °C with a water bath (Thermo Fischer 003–2859). The inoculum (20 L) was taken from a UASB reactor treating BW (Tervahauta et al., 2014c). BW was vacuum collected in Sneek (The Netherlands) and stored at 7 °C in a stirred storage tank of 200 L. Influent BW and CaCl₂:2H₂O solution were pumped into the reactor by Masterflex (7523-70) pumps as shown in Fig. 1. CaCl₂·2H₂O was added at 250–300 gCa²⁺/L_{BW} (adapted from Cunha et al. (2018a)), representing 8% of the volumetric loading rate (VLR, L/d) of BW. Nitrogen (N₂) gas was injected in between the two cylinders of the riser, escaping from the outlet at the bottom (Fig. 1b). The electrically steered gas valve controlled the injection of N₂ from a 2×10^5 Pa pressured gas line. All inlets (BW, CaCl₂·2H₂O, and N₂) were steered via an external master timer. BW and CaCl₂·2H₂O solution were pumped for 1 min every 119 min with flows of 0.25 L/min and 0.02 L/min, respectively. N₂ gas was injected 1 min every 29 min with an approximate flow of 0.3 L/min, which was monitored with a gas flow meter. The pH, temperature, and redox were measured by three vertically distributed sensors (Memosens CPS16D-1014/0 Orbisint) and monitored on a transmitter from Endress + Hauser (F1035805G00). The total volume of produced biogas and N₂ was measured daily using a Ritter TG/05/5. The reactor is equipped with five vertically distributed valves shown as sampling points in Fig. 1.

2.2. Sampling and analysis program

Daily, the CaCl₂·2H₂O solution and effluent containers were weighed. Furthermore, the amount of gas leaving the GLS, the flow of N₂ gas entering the reactor, and the three measuring points of pH, redox potential, and temperature were also noted daily. Influent, effluent, and gas composition were measured once a week. The overflow effluent was continuously collected in a jerrycan, but for weekly analysis, a new collection was performed for 24 h. BW was sampled from a T-connection immediately before entering the reactor. The measurements and methods were adapted from Cunha et al. (2018a) and included: total and volatile suspended solids (TSS and VSS, respectively); total, colloidal, and soluble COD (COD_{Total}, COD_{Colloidal}, and COD_{Soluble}, respectively); total, organic, and inorganic carbon (TC, TOC, and IC, respectively); volatile fatty acids (VFA); ammonium (NH_4^+) ; anions (Cl^-) , NO_3^- , NO_2^- , SO_4^{2-} , and PO_4^{3-}); and total and soluble elements (P, Ca, Mg, K, and Na). The gas passing the GLS was weekly collected in a gas bag after the flow meter during approximately 4 h to obtain a representative mixture of biogas and N2 gas. The gas mixture was analyzed as described by Cunha et al. (2018a). Sampling of the sludge bed was performed on operation days 167, 204, 258, and 300. Sludge was taken from sampling points 4 to 1 and at the bottom in the same order. From point 4 to 1 about 0.2 L of sludge were taken, while at the bottom the amount was increased to 0.5 L. For sampling, the valves were shortly and widely opened. The sampled sludge was separated with mesh sieves in size fractions of < 0.4 mm, 0.4-0.9 mm, 0.9-1.4 mm, 1.4–2 mm, 2–2.5 mm, and > 2.5 mm. After the particle size separation, the solids were analyzed for total elements, TSS, and VSS as described in Cunha et al. (2018a). Only particles > 0.4 mm diameter were considered as CaP granules. Inductively coupled plasma with optical emission spectroscopy (ICP-OES, PerkinElmer Optima 5300 DV) was used to detect the elements in solution and in solids. Membrane filtered samples were used for the soluble elements. Samples with solids had to undergo an acid digestion for 45 min assisted by microwave heating at 148 °C to be liquified before analysis. The treatment and analyses were similar for influent, effluent, and sludge bed samples.

In this study, we used the same analytical methods and instruments as in Cunha et al. (2018a) to enable direct comparison of influent, effluent, and biogas compositions and sludge bed size distribution and composition over the reactor height.

2.3. Calculations

The HRT was calculated based on the weight of the collected effluent, the $CaCl_2:2H_2O$ solution, and the effective reactor volume. The difference between the produced effluent and the consumed $CaCl_2:2H_2O$ solution for a defined time was assumed as the volume of BW fed. The amount of biogas was calculated by taking the cumulative

amount of N2 entering the reactor and subtracting it from the total amount of gas leaving the GLS based on daily averages. The COD of suspended solids (COD_{SS}), COD_{Colloidal}, and OLR were calculated as described by Graaff et al. (2010) and Halalsheh et al. (2005). The concentration of HCO_3^{-} is a function of measured inorganic carbon, temperature, and pH (Cunha et al., 2018a). The concentration of TSS, VSS, and particulate P in the reactor (Solids, g/L_{reactor}) was calculated according to eq. (1) for each sampling day (167, 204, 258, and 300). The solids retention time (SRT, d) was calculated according to eq. (2). For SRT_{Bottom} was considered the mass of VSS at the bottom of the reactor (12 L) and the VSS sampled from taps 0 and 1. For SRT_{Top} was considered the mass of VSS at the top of the reactor (34 L), the VSS sampled and wasted from Taps 2. 3, and 4, and the VSS washout in the effluent. The retention times for total P and P as CaP granules were calculated with eq. (2), but using the mass of total P and P as CaP granules instead of VSS. The sludge (gVSS/d) and solid P (gP/d) productions were calculated according to eqs. (3) and (4), respectively. The solid P production was further divided into CaP granules (> 0.4 mm diameter) and fine particles (< 0.4 mm diameter).

$$Solids = \frac{\sum_{i=0}^{4} (x_i V_i)}{V_{reactor}}$$
(1)

where V_i (L_{Sludge}) is the sludge volume of each sampled height (3.46, 8.27, 8.49, and 8.47 L for sampling point 0, 1, 2, and 3, respectively, and for the sampling point 4, V_4 was adapted according to the sludge bed height), x_i (g/L_{Sludge}) is the concentration of TSS, VSS, or particulate P, and $V_{reactor}$ is the total effective reactor volume (45.38 L). Note that all volumes were gravimetrically measured before the start of the reactor operation.

$$SRT = \frac{[VSS]_{reactor}}{[VSS]_{Wash out} + [VSS]_{wasted and sampled}}$$
(2)

where $[VSS]_{reactor}$ (g) is the overall concentration of VSS in the reactor, $[VSS]_{Wash out}$ (g/d) is the VSS loading in washout with the effluent, and $[VSS]_{wasted and sampled}$ (g/d) is the amount of sampled VSS and VSS in purged excess sludge divided by the operation time.

$$Sludge \ production = \frac{VSS_{wasted \ and \ sampled} + VSS_{washout}}{t}$$
(3)

where $VSS_{wasted and sampled}$ (g) is the mass of VSS wasted and sampled, $VSS_{washout}$ (g) is the mass of VSS in the effluent, and t (d) is the associated operation time.

$$Total P production = \frac{P_{wasted and sampled}}{t}$$
(4)

where $P_{wasted and sampled}$ (g) is the mass of total P sampled and waste. For P production as CaP granules $P_{wasted and sampled}$ corresponded to the mass of P sampled as particles > 0.4 mm diameter.

2.4. Multiphysics modulation (COMSOL)

The reactor was true to scale built in COMSOL in a two-dimensional axis symmetric study. The software incorporated physics "turbulent bubbly flow" solvers for liquid velocity, gas volume fraction, pressure, and viscosity of a gas-liquid mixture. The solvers were used to model the gas lift induced loop flow. It is based on the two-fluid Euler-Euler model. This macroscopic model treats the gas and liquid phase as interpenetrating media and is tracking the averaged concentration of each phase. Based on a momentum balance and a continuity equation the individual velocity fields of each phase interact with each other. The assumptions made in this model are that the gas density is negligible compared to the density of the liquid, both phases share one pressure field, and the balance between viscous drag and pressure forces determines the motion of the gas bubbles relative to the liquid (COMSOL, 2014; Sokolichin et al., 2004). The model simulated the flow

regimes during gas injection. Tested variables were the volumetric gas inflow (Q_{eas}) , the distance from the bottom of the reactor to the riser (h_r) , and the diameter of the riser (d_r) . The selected operating values for Q_{gas} , h_r , and d_r were 0.3 L/min, 40 mm, and 26 mm, respectively. The selection was based on preliminary laboratory tests, using the UASB reactor with integrated gas-lift system. Then, COMSOL modelling was performed to study the cause of the deviation from the obtained mixing based on the preliminary tests. The Q_{gas} was varied from 0.3 to 2 L/min, the h_r from 10 to 40 mm, and the d_r from 13 to 26 mm. In the model, the time of injection was 1 min, but was shortened if a stationary flow field developed in less than a minute, in order to minimize computation time. The different flow behavior of the sludge bed compared to water was approached by increasing the dynamic viscosity of the liquid phase to 1 Pas, based on rheology measurements and studies investigating dynamic viscosities of sludge mixtures (Dai et al., 2014; Pevere et al., 2006). The model was tested on different mesh sizes and is mesh independent. The mesh layout used is shown in Appendix A.

3. Results

3.1. Treatment performance

The operational period was divided into three phases (Table 1 and Fig. 2). Phase 1, from 0 to 84 days, was considered the start-up period. In phase 2, from day 84–189, the BW was significantly less concentrated at the collection point in Sneek (the Netherlands). Phase 3 lasted from day 189–300 and was a period with highly concentrated BW, due to the accumulation of solids in the vacuum collection tank at the community site in Sneek. The feeding of BW was lowered during phase 3 to keep an OLR close to 1 gCOD/Ld comparable with the previous studies (Cunha et al., 2018a; Tervahauta et al., 2014c).

The key performance parameters are presented in Table 1. The removal of COD_{Total} was consistently above 80% during phase 1 and 3 except for operations days 210, 280, and 287, where sludge washout was observed due to high solids input from BW (10–20 gTSS/L as shown in Fig. 2). The removal of COD_{Total} dropped during phase 2, due to the higher ratio of dissolved inert COD to COD_{Total} in the influent BW (Fig. 2). The concentration of COD_{Total} in the effluent was similar for phase 1 and 2. The cumulative COD mass balance is presented in Fig. 3, including the sludge washout and wasted (sampled and excess sludge). From the total 9.3 kgCOD_{Total} fed, 36% was measured as CH_4 , 14% left the reactor with the effluent, 18% was accumulated in the reactor, and 8% was wasted and sampled (Fig. 3). The unquantified fraction of COD_{Total} represented 24%. The missing COD fraction in the mass balance can be explained by two factors: (1) inaccurate sludge bed sampling, underestimating the COD accumulated in the reactor, and (2) undetected variations in N₂ flow (13 \pm 4 L/d), resulting in inaccurate CH₄ quantification. Undetected COD in the effluent is improbable because effluent was weekly measured and during the periods with washout a higher monitoring frequency was performed to estimate the COD washout accurately. The measured ratio gCOD/gVSS was 2.

The calculated sludge production during phase 3 (phase with high COD_{SS} loading) was 4.29 gVSS/d, representing 0.126 gVSS/gCOD_{BW}. The loading rate during phase 2 was only 0.3 gCOD/L.d. Consequently, the SRT in phase 2 became extremely long (719 d) and decreased to 290 d in phase 3. The TSS and VSS concentrations in the sludge bed over time are presented in Fig. 3 c and d, respectively. During phase 3, the sludge bed contained 73 ± 16 gTSS/L and 40 ± 7 gVSS/L at the bottom (harvesting location) and 31 ± 5 gTSS/L and 23 ± 4 gVSS/L at the top of the reactor (tap 4). Although sludge was sampled from all taps, the SRT for the top part of the reactor was higher than for the bottom part, because of VSS washout from the top with the effluent and higher volume of VSS sampled (tap 2, 3, and 4).

The average pH in the UASB-GL reactor went from 6.87 \pm 0.04 on operation day 10 up to 7.75 \pm 0.06 on operation day 181. Accordingly, the concentration of HCO₃⁻ changed from 0.92 \pm 0.003 up to 3.95 \pm 0.01 gHCO₃⁻/L (Fig. 2). The concentration of VFA in the effluent was < 1 mg/L during the entire operation, and the average of NH₄⁺-N concentration in the effluent was 0.79 \pm 0.19 g/L (results not shown).

The average P_{Total} removal in phase 3 was 90%, excluding the days with washout. Most of the P_{Total} entered the reactor in the solid form (~75%). The removal efficiency of soluble P (PO₄³⁻) was the highest in phase 3 (88%) and the lowest during startup in phase 1 (73%) as shown in Table 1. According to the P mass balance (Fig. 3), during the 300 days of operation, 127 g of P_{Total} were fed to the UASB-GL reactor. Then, from the P_{Total} fed, 15% was measured in the effluent and 56% was measured in the sludge bed, sampled, and wasted, resulting in 29% of P that remained unquantified but most likely due to inaccurate quantification of P in the sludge bed, since the effluent composition was thoroughly measured. The P measured as CaP granules (> 0.4 mm diameter) represented 29% of the total P fed (Fig. 3). Throughout all phases, the accumulation of Ca_{Total} from BW plus added Ca²⁺ was 80 \pm 11%.

3.2. Sludge bed particle size distribution

The TSS concentration and particle size distribution in the sludge

Table 1

Key operational and performance parameters of the UASB-GL reactor for the three operation phases. Average values for removal efficiencies during phase 3 do not include operation days 210, 280, and 287, because excess of sludge was not taken on time to avoid washout of solids, which resulted from the high solids inflow (Appendix B).

Parameter	Unit	Phase 1	sd	Phase 2	sd	Phase 3	sd
Operation days		0–84		84–189		189–300	
$\begin{array}{c} {\rm HRT} \\ {\rm OLR} \\ {\rm Influent\ COD}_{{\rm Total}} \\ {\rm Influent\ COD}_{{\rm SS}} \\ {\rm Effluent\ COD}_{{\rm Total}} \\ {\rm COD}_{{\rm Total}} \\ {\rm Removal} \\ {\rm COD}_{{\rm Soluble}} \\ {\rm Removal} \\ {\rm Influent\ P}_{{\rm Total}} \\ {\rm Influent\ P}_{{\rm Total}} \\ {\rm Effluent\ P}_{{\rm Total}} \end{array}$	d gCOD/L.d gCOD/L gCOD/L gCOD/L % % mgP/L mgPO ₄ ³⁻ - P/L mgP/L	17.22 0.82 14.39 8.67 0.9 93.05 83.79 203.44 49.80 25.12	1.95 0.02 3.90 3.66 0.3 2.59 5.32 54.23 14.03 15.98	18.51 0.30 5.25 2.77 0.9 78.07 67.08 144.06 32.73 14.64	1.41 0.14 2.19 1.94 0.1 7.15 8.70 56.51 8.34 1.00	31.57 0.96 26.66 20.80 2.9 92.21 79.87 257.69 68.26 42.89	15.13 0.30 8.65 7.51 2.4 4.24 5.45 54.88 22.08 50.50
P _{Total} Removal PO ₄ ³⁻ Removal SRT SRT _{Bottom} SRT _{Top}	% % d d	87.08 72.51 Startup	9.97 22.65	89.69 76.98 719	4.39 7.08	90.43 88.22 290 436 261	3.61 6.40



Fig. 2. Influent and effluent concentrations of total COD and TSS during the entire operational period (310 days) (a). Average pH of the sludge bed and bicarbonate (HCO₃⁻) concentration in the influent BW (b).

bed of a non-mixed UASB reactor with Ca^{2+} addition (Fig. 4b) studied by Cunha et al. (2018a) and of a non-mixed UASB reactor without Ca²⁺ addition (Fig. 4c) studied by Tervahauta et al. (2014c) were more evenly distributed over the sludge bed height when compared to the UASB-GL reactor (Fig. 4a). The UASB-GL reactor operated at the same temperature and similar OLR, but with longer HRT (17-31 d) due to the higher inflow of particulate organic matter (Fig. 2), when compared with the mentioned UASB reactors (HRT of 7-8 days and approximately 6 gCOD_{SS}/L). With the Ca²⁺ addition, particles are generally larger, and particles > 0.4 mm diameter contained more P than without Ca²⁺ addition (Fig. 4d). The concentration of P at the bottom of the reactor (harvesting location) is the highest for the UASB-GL reactor (4.6 \pm 1.3 gP/L) when compared with the other non-mixed UASB reactors. The concentration of P as CaP granules is only slightly higher for the UASB-GL reactor (3.2 \pm 1.1 gP/L) when compared with a non-mixed UASB reactor with Ca²⁺ addition (2.9 \pm 0.8 gP/L), but much higher than the non-mixed UASB reactor without Ca^{2+} addition, indicating that both Ca^{2+} addition and mixing are needed.

3.3. Elemental composition of particles

In the UASB-GL reactor, CaP granules (particles > 0.4 mm diameter) from the bottom were on average richer in P when compared with CaP granules from the bottom of a non-mixed UASB reactor, which was also dosed with extra Ca²⁺ (77.91 ± 5.66 and 67.27 ± 9.12 mgP/gTSS, respectively) (Fig. 5). Average values for the UASB-GL reactor are based on samples taken on operation days 167, 204, 258, and 300. Particles > 0.4 mm diameter contained substantially more P than smaller particles (< 0.4 mm diameter) in both reactors (Fig. 5). The magnesium concentration was < 0.5 wt% for all size fractions of both reactors (results not shown).

The Ca to P molar ratio in CaP granules (> 0.4 mm diameter) from



Fig. 3. COD (a) and P (b) mass balances for 300 days of operation. The COD_{Total} fed was 9.3 kg and the start inoculum was 0.9 kg, which was subtracted from the reactor COD. The P_{Total} fed was 127 g and the start inoculum was 34 g, which was subtracted from the P in the reactor. TSS (c) and VSS (d) concentrations in the inoculum and the sludge bed over time.



Fig. 4. Averaged vertical distribution of TSS concentration categorized in six size fractions (< 0.4 mm, 0.4–0.9 mm, 0.9–1.4 mm, 1.4–2 mm, 2–2.5 mm, and > 2.5 mm) from sludge taken from the UASB-GL reactor (45 L) on operation days 167, 204, 258, and 300 (a), the non-mixed UASB reactor with Ca²⁺ addition from Cunha et al. (2018a) (b), and the non-mixed UASB reactor without Ca²⁺ addition from Tervahauta et al. (2014c) (c). For the latter a different size categorization was used (< 0.315 mm). Results for sludge bed size distribution of each sampling time for the UASB-GL reactor are in Appendix C, which shows the variation over time. The average distribution of P as CaP granules (> 0.4 mm diameter) and as fines (< 0.4 mm diameter) at the bottom and at the top of the three reactors aforementioned (d). The deviation for d) did not exceed 21%.

the bottom of the mixed and non-mixed reactors was similar $(2.0 \pm 0.2 \text{ and } 1.9 \pm 0.1$, respectively). The samples of CaP granules (> 0.4 mm diameter) from the bottom of the UASB-GL reactor contained considerably less VSS than from the bottom of a non-mixed UASB reactor (17.25 ± 4.73 gVSS/L, representing a VSS/TSS ratio of 0.42 ± 0.24, for the mixed reactor and 32.15 ± 2.74 gVSS/L,

representing a VSS/TSS ratio of 0.76 \pm 0.14, for the non-mixed reactor).

In both reactor, CaP granules with a diameter between 0.4 and 2.5 mm contained most inorganics. Visually, the SEM image in Figure E1a in Appendix E shows that a representative CaP granule from the UASB-GL reactor has a thinner outer biofilm ($20 \mu m$) when compared to



Fig. 5. Average P content and VSS concentration for different sized particles from the bottom of the UASB-GL reactor (a) and the bottom of the non-mixed UASB reactor with Ca^{2+} addition from Cunha et al. (2018a) (b). Average values for the UASB-GL reactor are from samples taken on operation days 167, 204, 258, and 300. Results for each sampling day are in Appendix D.



Fig. 6. COMSOL surface graphs of the liquid velocity and direction in the UASB-GL reactor presented by color and arrows, respectively. Image a) gives an overview of the true to scale reactor in a 3D partial cut view. Image b) is a 2D zoom-in of the entrance of the riser at the flow and geometry tested. Image c) is a similar representation but with different gas volumetric flow and distance from the bottom of the riser to the bottom of the reactor. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

CaP granules from a non-mixed UASB reactor (Cunha et al., 2018a). Furthermore, EDX of a fine (Figure E1d) showed Mg containing precipitates while in the EDX of a larger particle (Figure E1b) only CaP precipitates (green) could be observed.

3.4. Flow characteristics in UASB-GL reactor

The liquid flow in the UASB-GL reactor was influenced by the gas (N_2) injection around the riser at the bottom of the reactor (Fig. 6a). The modeled velocities presented in Fig. 6 are reached after 20 s of gas injection and remained stable. The liquid flow was directed upwards inside the riser with a velocity up to 18 m/h (Fig. 6b). Outside the riser (downcomer) the liquid velocity was 10 times lower than inside the riser. However, the bottom of the cone was unmixed, due to the high TSS concentration and consequent high fluid viscosity (~1 Pa s for a mixed liquor suspended solids (MLSS) containing 60 gTSS/L) which was not considered in the design. Increasing the Q_{gas} from 0.3 to 2 L/min and decreasing the h_r from 40 to 20 mm the velocity in the riser increased to about 85 m/h and the upward drag force had a higher influence at the bottom of the cone (Fig. 6c).

4. Discussion

4.1. Influence of gas-lift mixing on the treatment of BW

The implementation of the gas-lift principle in a UASB reactor did

not affect the anaerobic treatment efficiency (Table 1), considering the difference in COD and P removals between the UASB-GL reactor and non-mixed UASB reactors treating BW. Unfortunately, the solid content in BW during operation of the UASB-GL reactor (16 \pm 6 gCOD_{SS}/L) was much higher than during the operation of the non-mixed UASB reactors from Cunha et al. (2018a) and Graaff et al. (2010) (6 \pm 2 and 5 ± 3 gCOD_{ss}/L, respectively). To compensate for the higher solids content, the HRT for the UASB-GL reactor was extended to assure sufficient SRT and hydrolysis. The OLR in the UASB-GL reactor (0.96 gCOD/Ld in phase 3) was similar to UASB reactors tested in previous studies without Ca²⁺ addition (0.9–1 gCOD/Ld) (Graaff et al., 2010; Tervahauta et al., 2014a). The lower CH₄ production, when compared to previous studies for anaerobic BW treatment, is most likely due to the lower biodegradability of the BW fed to the UASB-GL reactor. This is supported by the higher sludge production obtained in the UASB-GL reactor (0.126 gVSS/gCOD_{BW}) when compared to the non-mixed UASB reactor (0.09 gVSS/gCOD_{BW}) reported in Cunha et al. (2018a). Thus, the effect of the mixing on the CH₄ production was inconclusive. Yet, earlier studies showed that Ca²⁺ addition and increased mixing stimulated anaerobic digestion, by enhancing retention of solids in a UASB reactor and increasing the mass transfer of substances within the sludge bed, respectively (Das et al., 2018; Ghangrekar et al., 2005; Saner et al., 2016).

By adding Ca^{2+} to the UASB-GL reactor, the increased retention of solids and the production of CaP granules in the sludge bed could have decreased the diffusive mass transport, resulting in lower treatment

functionality by cementation of the bottom of the reactor (Ahmadi-Pirlou et al., 2017; Batstone et al., 2002; Li et al., 2012; Liu and Tay, 2004). The Ca²⁺ injection in the upper end of the riser and the mixing enhanced the spread of Ca²⁺ throughout the reactor, assuring improved removal of PO_4^{3-} by stimulation of $Ca_x(PO_4)_y$ precipitation, avoiding cementation of the sludge bed, and stimulating biomass aggregation and retention in the reactor. Thus, the combination of principles from bubble column bioreactors, industrial crystallisers, and the high retention of solids in UASB reactors enabled the efficient PO_4^{3-} precipitation (73–88%) and retention of particulate P in the reactor (90%). Compared to mechanical mixing alternatives, gas-induced mixing exerts low shear stress on the mixed media, and therefore, it lowers the risk of microbial activity inhibition, breakage of precipitates, and disruption of CaP granulation (Laspidou and Rittmann, 2004; Rochex et al., 2008; Sindall et al., 2013; Soare et al., 2012).

4.2. Effect of gas-lift on the particle size distribution of the sludge bed

The gas-lift mixing created a significantly different sludge bed when compared to non-mixed UASB reactors treating BW (Fig. 4). Fluidization at the bottom resulted in a more pronounced gradient of solids, with a TSS concentration of $73 \pm 16 \text{ g/L}_{\text{Sludge}}$ at the bottom to $31 \pm 5 \text{ g/L}_{\text{Sludge}}$ on the top during phase 3. Wang et al. (2018) showed a similar distribution of solids in a UASB reactor treating BW and kitchen waste with a frequent injection of recycled biogas. The exerted shear stress on the solid agglomerates induced a higher selectivity for denser and faster settling particles, especially at the bottom of the UASB-GL reactor, where most of the mixing occurred when compared to non-mixed UASB reactors (Batstone et al., 2005; Daintree and Biggs, 2010; Gjaltema et al., 1995; Kwok et al., 1998). Additionally, the movement in the sludge bed allowed particles to rearrange and let biogas escape, forming an overall denser sludge bed by enhancing compactness of solids (Mahmoud et al., 2003; Shin and Paik, 1990). The settling of larger P containing particles enables purging of excess sludge in the upper part of the sludge bed (tap 4) with low P content, maximizing the P harvesting at the bottom of the reactor (Fig. 4d). In nonmixed UASB reactors, the percolation of small particles through the spacing between larger particles enhanced the packing effect and hindered sedimentation of the densest and largest particles to the bottom as shown in Fig. 4 (Cunha et al., 2018a; Landman and White, 1994; Langerak et al., 1998).

4.3. Influence of the fluid properties on the mixing efficiency

The upward drag force (Fig. 6b) formed by the loop was not sufficient to efficiently lift fine particles (< 0.4 mm diameter) from the very bottom of the reactor, because of the high solids concentration (Fig. 4) and increased viscosity. Bollon et al. (2013) showed that the diffusive mass transfer is decreasing substantially in the range of 0-15% with increasing solid content, due to the elevated viscosity. The higher viscosity reduced the liquid velocity in the riser from 70 m/h, which was the designed velocity, to 18 m/h, according to modelling. Thus, the riser geometry and gas flow for the recirculation can be changed to improve the upward velocity and drag force at the bottom of the reactor as showed in Fig. 6c by increasing Q_{gas} and the h_r . Besides Q_{gas} and h_r , another critical parameter is the diameter of the riser (d_r) . A smaller d_r would increase the upflow velocity of the liquid in the riser, but decrease the force and area of the upward dragging field at the bottom of the reactor which is not wanted (Figure A2e in Appendix A). Additionally, the N₂ gas used for internal recirculation in this study could be replaced by produced biogas, which is readily available during anaerobic digestion of BW. Then, by controlling the pressure build-up, the excess of biogas is purged from the system.

4.4. Effect of mixing on the growth mechanism of CaP granules

Particles < 0.4 mm diameter represented 67% of the whole sludge bed in the UASB-GL reactor and contained 3.9 wt% of P, while only 10% and 2.8 wt% of P in a non-mixed UASB reactor at comparable Ca^{2+} inflow (Cunha et al., 2018a), indicating that the shear stress decreased the growth of larger organic CaP granules and increased the number of P fines in the reactor and P content in CaP granules (Figs. 4 and 5). The lower density and strength of the outer biofilm in CaP granules (> 0.4 mm diameter), when compared to the inorganic core, resulted in reduced organic content in CaP granules produced in the UASB-GL reactor (Fig. 5b).

The main reason for biofilm detachment from carriers in air-lift reactors was the interaction between particles, leading to abrasion or breakage (Gjaltema et al., 1997; Wan et al., 2011). Thus, particle interactions in the UASB-GL reactor are mainly expected in the loop around the riser, where both detachment mechanisms are expected. Furthermore, the density and thickness of the biofilm in carrier particles in an air-lift reactor depend on the detachment force and the surface substrate loading (Kwok et al., 1998; Pronk et al., 2015; Wu et al., 2012). High substrate loading and low shear force lead to thick and less dense biofilms, whereas high shear force and low substrate loading lead to thin and dense biofilms (Pronk et al., 2015; Wu et al., 2012). The biofilm thickness of a representative CaP granule (> 0.4 mm diameter) from the mixed UASB reactor is significantly lower (~20 μm) compared to the CaP granules from non-mixed UASB reactors, due to the increased detachment force exerted on the biofilm; the substrate loading was comparable in both reactors. CaP granules from the UASB-GL reactor generally had a single inorganic core, while CaP granules from a non-mixed UASB reactors frequently contained several inorganic clusters in the core (Cunha et al., 2018a). This can be explained by the higher shear force applied, promoting precipitation of $Ca_x(PO_4)_v$ on the surface of the core over nucleation in the outer biofilm. Thus, by controlling the gas flow to obtain the desired liquid upflow velocity in the riser, the size and purity of harvested CaP granules can be controlled during their formation and maturation.

4.5. Effect of mixing on harvested CaP granules

Harvested CaP granules (> 0.4 mm diameter) from the mixed UASB contained 7.8 \pm 0.6 wt% of P, which is a higher average than for CaP granules taken from a non-mixed UASB reactor (6.7 \pm 1.1 wt% of P), indicating that the mixing enhanced the $Ca_x(PO_4)_v$ content in the granules (Cunha et al., 2018a). Since the Mg content was < 0.5 wt%(results not shown), struvite is not expected to be present in the granules. The Ca to P molar ratio in CaP granules (> 0.4 mm diameter) increased on average from 1.80 ± 0.03 on operation day 167 to 2.20 ± 0.11 on day 258 (Appendix D). The higher Ca to P molar ratio in CaP granules on day 258 is explained by the higher HCO_3^- concentration in BW during the preceding period, resulting in higher bulk pH (> 7.5) and precipitation of CaCO₃. The role of the bulk pH on CaP granulation was previously explained by Cunha et al. (2018b). For bulk pH higher than 7.5, CaCO₃ precipitation is kinetically favored, although HAP is still the thermodynamically most stable phase (Lei et al., 2018; Rokidi et al., 2011; Schiller and Epple, 2003). Over time, the formed $CaCO_3$ will most likely dissolve again, providing Ca^{2+} for $Ca_x(PO_4)_y$ precipitation (Rokidi et al., 2011; Song et al., 2006). The increase in HCO3⁻ and bulk pH during phase 2 was considerable (Fig. 2), increasing the co-precipitation of CaCO₃ from 8% on day 167 to 26% on day 258. Therefore, bulk pH and HCO₃⁻ concentration in BW, which might be related to organic composition and BW storage time, are critical parameters for the purity of the harvested CaP granules. During phase 2, the concentration of COD_{SS} represented only 53% of the $\mbox{COD}_{\mbox{Total}}\xspace$, which might have decreased the formation of \mbox{H}_2 and \mbox{H}^+ and consequently the transformation of HCO_3^{-} during hydrogenotrophic methanogenesis. During phase 1 and 3, the COD_{SS} and COD_{Total} ratio was 60% and 78%, respectively.

4.6. Phosphorus recovery potential in the UASB-GL reactor

 Ca^{2+} addition is a key factor in the recovery of P as CaP granules, as in BW there is not enough Ca to trap all the P. Mixing and reactor design can enhance this potential by improving the quality and concentration of CaP granules at the harvesting location. The concentration of P at the harvesting location in the UASB-GL reactor was 4.58 ± 1.34 gP/ L_{Sludge} , from which 70% was as CaP granules (> 0.4 mm diameter) and only 30% was as fine particles (< 0.4 mm diameter). According to the P mass balance (Figs. 3), 29% of the P fed was found as CaP granules after 300 days.

Samples were taken every 2 months at five locations in the reactor to evaluate the effect of mixing on particle size distribution of the sludge bed over time. The frequent sampling from all the sampling points and low mixing efficiency reduced the P recovery efficiency as CaP granules due to the harvesting of P from the middle of the reactor and harvesting of P as particles < 0.4 mm diameter. The P recovery efficiency can be enhanced by increasing the retention time of P at the bottom of the reactor while wasting excess of sludge (VSS) in the upper part of the sludge bed. During phase 3, the calculated SRT of VSS for the bottom of the reactor was 1.7 times higher than the top part (Table 1), because more solids were purged and washed out from the top. Furthermore, the retention time of CaP granules in the reactor (578 d) was 1.6 times higher than the retention time of total P (353 d), using eq. (2) with the mass of P instead of VSS during phase 3. Thus, the decoupling of VSS SRT from top and bottom of the reactor and the efficient lifting of smaller particles from the bottom are essential to enable concentration and maturation of CaP granules at the harvesting location.

Considering the measured daily sludge production during phase 3 (4.3 gVSS/d), the estimated amount of P wasted with the purged sludge from the top part of the reactor is 0.14 gP/d, representing 33% of the total P incoming from BW. The measured P content in wasted sludge is 0.03 gP/g of VSS. Then, the remaining P (0.23 gP/d, representing 57% of the total P incoming from BW) can be recovered as CaP granules at the harvesting location. Note that on average 10% of P in BW leaves the reactor with the effluent. However, for a lower sludge production (lower concentration of COD_{SS} in the influent and higher biodegradability of organic solids) the recovery potential as CaP granules increases, due to the higher P retention time. Therefore, the recovery efficiency of CaP granules in the UASB-GL reactor can be much higher when sludge production is minimized. The mass of P as CaP granules in the UASB-GL reactor decreased from 71% on day 167 (phase 2) to 46% on day 300 (phase 3), most likely due to oversampling during phase 3.

CaP granules recovered from the UASB-GL reactor are a promising P product to replace mined phosphate rock in the fertilizer industry or to be applied as P rich direct fertilizer (European Commission, 2016). The UASB-GL reactor enhanced the average P content in CaP granules from 15 wt% of P₂O₅ in a non-mixed UASB reactor to 18 wt% of P₂O₅, which is close to the minimum of 25 wt% of P_2O_5 required by the phosphate industry. The minimum of 25 wt% of P2O5 can be achieved by enhancing the lifting force (i.e. increasing the gas flow) at the bottom of the reactor (Fig. 6c). A higher lifting force can further decrease the organic content in CaP granules by exerting higher shear stress and detaching light organic particles from the granule core. Consequently, the P content in the CaP granules increases. Additionally, recovered products from BW will have a low heavy metal content when compared with P products recovered from sewage or even certain mined phosphate rocks (Aydin et al., 2010; Cooper et al., 2011; Tervahauta et al., 2014b). Therefore, the application of CaP granulation using a UASB-GL reactor in the source separated sanitation can simultaneously reduce P discharge to natural water bodies and enable the local P recycling, stimulating the circular and sustainable use of P from human excreta.

5. Conclusions

The integration of gas-lift mixing and Ca²⁺ addition in a UASB reactor (UASB-GL reactor) resulted in a harvesting location at the bottom, vielding potentially 57% of the P in BW as CaP granules (> 0.4 mm diameter) based on full-scale operation (i.e. sludge discharge is based on sludge production and not sampling program as in this study). The excessive sampling from the upper part of the sludge bed reduced the recovery of P as CaP granules from the bottom to 29%. At the top of the reactor the total P concentration was reduced by 84% when compared to the bottom part, enabling the purge of excess VSS (sludge) at low expense of P. The P total removal was already 87% during phase 1, due to the Ca^{2+} addition, and remained above 90% during stable and continuous operation at a loading rate of 0.96 \pm 0.30 gCOD/L d at 25 °C. The UASB-GL reactor exhibited high stability in treatment performance even with substantial fluctuations in the influent suspended material (COD_{SS}). The average P content in recovered CaP granules (> 0.4 mm diameter) from the bottom of the reactor increased 16%, from 67 \pm 9 to 77 \pm 6 mgP/gTSS, due to the shear of the gas-lift mixing. The P as CaP granules represented 71% of the total P in the UASB-GL reactor on operation day 167, but due to the high sludge production during phase 3 (0.126 gVSS/gCOD_{BW}) and oversampling it decreased to 46% after 300 days of operation. As a result, the recovery efficiency as CaP granules is hindered because of the lower SRT (increase in sludge production). The critical geometric parameters for the lifting force field at the bottom of the reactor are the injected gas volumetric flow (Q) and the height of the riser with respect to the bottom of the reactor (h_r) .

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Appendix A. Supplementary data

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