



Contents lists available at ScienceDirect

## Journal of Environmental Management

journal homepage: [www.elsevier.com/locate/jenvman](http://www.elsevier.com/locate/jenvman)

## Research article

## Simultaneous recovery of calcium phosphate granules and methane in anaerobic treatment of black water: Effect of bicarbonate and calcium fluctuations

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## ARTICLE INFO

## Article history:

Received 4 January 2017

Received in revised form

20 July 2017

Accepted 4 September 2017

Available online xxx

## Keywords:

Source separated black water

Calcium phosphate recovery

Granules

Methane

UASB reactor

## ABSTRACT

Calcium phosphate (CaP) granules were discovered in the anaerobic treatment of vacuum collected black water (BW), using upflow anaerobic sludge blanket (UASB) technology. This allows simultaneous recovery of CaP granules and methane in the UASB reactor. However, the role of BW composition on CaP granulation is not yet understood. Moreover, CaP granulation was not observed in previous research on anaerobic treatment of BW, although similar treatment conditions were applied. Therefore, this study shows specifically the influence of bicarbonate and calcium fluctuations in BW on the phosphorus accumulation in the UASB reactor, which directly affects CaP granulation. Without calcium addition, 5% of the total phosphorus (P) fed was found as CaP granules in the reactor (61 mgP g<sup>-1</sup> dried matter), after 260 days of operation. Simultaneously, 65% of the COD in BW was efficiently converted into methane at 25 °C. Variations of bicarbonate and calcium concentrations in raw BW showed a significant influence on phosphorus accumulation in the UASB reactor. Geochemical modelling showed that the increase of soluble calcium from 39 to 54 mg L<sup>-1</sup> in BW triggers supersaturation for calcium phosphate precursors (Ca<sub>x</sub>(PO<sub>4</sub>)<sub>y</sub>). Concurrently, bicarbonate decreased from 2.7 to 1.2 g L<sup>-1</sup>, increasing further the ionic activity of calcium. Formation and accumulation of seed particles possibly enhanced CaP granulation. Preliminary results showed that addition of calcium (Ca<sup>2+</sup>/PO<sub>4</sub><sup>3-</sup> molar ratio of 3) increased the accumulation of total P in the UASB reactor to more than 85%. This further increases the granulation rate and consequently, the process feasibility.

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## 1. Introduction

Phosphate (PO<sub>4</sub><sup>3-</sup>) is finite and essential for humankind, and 88% of the rock phosphate reserves are predicted to be controlled by Morocco in the early 22nd century (Cooper et al., 2011). Introduction of recycling measures and sustainable use can extend the global resource longevity beyond the 22nd century (Koppelaar and Weikard, 2013). Source separated black water (BW) contains 75% of the domestically wasted phosphorus (P) (Tervahauta et al., 2013).

Thus, P recovery from BW could significantly extend PO<sub>4</sub><sup>3-</sup> availability. The relatively high concentration of P and organics is achieved by vacuum collection of BW (0.19 ± 0.08 gP L<sup>-1</sup> and 8 ± 2 gCOD L<sup>-1</sup>), which consumes much less water when compared with the conventional toilet flushing system (6 and 34 L person<sup>-1</sup> d<sup>-1</sup> of water use, respectively) (Tervahauta et al., 2013). The separate treatment of BW creates attractive conditions for implementation of recovery techniques as demonstrated at full scale by Graaf and Hell (2014).

The existing treatment concept of BW consists of an upflow anaerobic sludge blanket (UASB) reactor for COD removal and methane (CH<sub>4</sub>) production, followed by an oxygen-limited autotrophic nitrification-denitrification (OLAND) reactor for nitrogen removal, and finally a P removal stage where magnesium oxide (MgO) is added to induce struvite precipitation (Graaf and Hell, 2014; Tervahauta et al., 2013). This concept has been applied at

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full scale since 2008 for a community with 232 houses in Sneek, The Netherlands (Graaf and Hell, 2014).

At 25 °C, 54% of the organic load is converted into biogas in the UASB reactor with a hydraulic retention time (HRT) of 8.7 days and an organic loading rate (OLR) of 1 kgCOD m<sup>-3</sup> d<sup>-1</sup> (Graaff et al., 2010), 85% of the nitrogen is removed in the OLAND reactor (Graaff et al., 2011b) and 56% of the total P is precipitated as struvite in a subsequent reactor (Graaff et al., 2011a). However, a large fraction of P (39%) accumulated in the UASB reactor (Graaff et al., 2011a). Moreover, the accumulation of P increased from 39 to 51% after a decrease in bicarbonate (HCO<sub>3</sub><sup>-</sup>) and an increase in soluble calcium (Ca<sup>2+</sup>) in BW (Graaff et al., 2011a; Tervahauta et al., 2014b). This change was most likely due to changes in drinking water composition and dilution of BW (Graaff et al., 2011a; Mulder et al., 2014). The increase in P accumulation coincided in time with formation of calcium phosphate granules (CaP granules) in the UASB reactor, most likely due to the intensified accumulation of calcium phosphate (Ca<sub>x</sub>(PO<sub>4</sub>)<sub>y</sub>) particles which seeded CaP granulation (Tervahauta et al., 2014b). Because P recovery as struvite has a limited yield due to P accumulation in the UASB reactor, the recovery of CaP granules is a process with higher potential. Moreover, it allows the simultaneous recovery of P and methane from BW in a single reactor. To increase the recovery of CaP granules and to make the struvite step obsolete, more insight into the influence of HCO<sub>3</sub><sup>-</sup> and Ca<sup>2+</sup> in BW on P accumulation is crucial.

Therefore, this study evaluates the effect of fluctuations of HCO<sub>3</sub><sup>-</sup> and Ca<sup>2+</sup> in BW on accumulation of P, during the anaerobic treatment of BW using a UASB reactor. The effect of these fluctuations on the supersaturation state of Ca<sub>x</sub>(PO<sub>4</sub>)<sub>y</sub> phases in BW is assessed with correlations between chemical measurements and geochemical modelling. Simultaneously, the physical and chemical development of the sludge bed and treatment performance is monitored. Additionally, CaP granules are quantified and characterized. Finally, Ca<sup>2+</sup> is added in treated BW (effluent from the UASB reactor) to predict its potential effect on the P accumulation.

## 2. Materials and methods

### 2.1. Experimental set up

A UASB reactor (5 L) fed with vacuum collected BW was started and monitored for 260 days at 25 °C, with a HRT of 8 days and a total OLR of 1 kgCOD m<sup>-3</sup> d<sup>-1</sup>. The HRT of 8 days was chosen at a temperature of 25 °C in order to have a similar upflow velocity and solids retention time (SRT) as achieved by Tervahauta et al. (2014b). The reactor was inoculated with 2 L of sludge from the aforementioned full scale UASB reactor (Graaf and Hell, 2014). Respectively, one and two times per week, influent and effluent were sampled and analysed for total and volatile suspended solids (TSS and VSS, respectively), chemical oxygen demand (COD), elements (P, Ca, Mg, Na and K), PO<sub>4</sub><sup>3-</sup>, volatile fatty acids (VFA) and ammonium (NH<sub>4</sub><sup>+</sup>). Sludge bed analysis at 5 cm from the bottom of the UASB reactor was performed approximately every 30 days. 100 ml of sludge were taken for each sampling point and analysed for TSS, VSS, P, Ca, Mg, Na and K. Duplicates were performed for influent, effluent and sludge analyses.

### 2.2. Physical and chemical analyses

TSS and VSS were quantified according to the standard methods (Clesceri et al., 1998). Total and soluble COD were measured with cuvette tests Hach Lange (LCK114). Biogas composition was analysed through gas chromatography (Varian CP4900 Micro GC with two separate column models Mol Sieve 5 Å PLOT (MS5) and PorapLOT U (PPU)). Liquid and solid elemental analyses (P, Ca, Mg, Na

and K) of influent, effluent and sludge samples were performed through inductively coupled plasma – optical emission spectrometry (ICP-OES Perkin Elmer Optima 5300 DV). An acid digestion at 148 °C for 45 min was performed beforehand to dissolve solids. PO<sub>4</sub><sup>3-</sup> and volatile fatty acids (VFA) were quantified through ion chromatography (Metrohm 761 Compact IC, for VFA determination Silica Gel with C18 alkyl groups as carrying material was used). Ammonium (NH<sub>4</sub><sup>+</sup>) was analysed using cuvette tests Hach Lange (LCK302). Soluble compounds were measured after membrane filtration (0.45 µm Cronus filter PTFE). HCO<sub>3</sub><sup>-</sup> was calculated according to standard methods (Tchobanoglous et al., 2004), using the inorganic carbon (IC) concentration, which was measured with a Shimadzu TOC analyser, and pH at 25 °C. SRT, level of hydrolysis of solids and methanization were calculated according to Graaff et al. (2010), for the steady state period between days 55 and 260. A vertical characterization of the sludge bed at 5, 10, 20 and 30 cm high was performed at the end of the monitoring period (day 260). In this characterization, TSS, VSS and COD concentrations and P, Ca and Mg contents in TSS were measured.

### 2.3. Separation and characterization of calcium phosphate granules

CaP granules were quantified through a separation by specific density of particles from sludge bed samples (100 ml). These were taken on days 218 and 300 at two different heights of the UASB reactor (5 and 20 cm). The separation of CaP granules in these samples was carried out in an upflow column (100 × 2 cm), using paper (black ribbon ashless Schleicher & Schuell) filtered effluent from the UASB reactor to fluidize the sample. An upflow velocity of 57 m h<sup>-1</sup> was applied and solids were divided in 5 fractions by density. Solids from the densest fraction were considered as CaP granules, due to the higher specific density (inorganic content) and size compared to organic sludge and smaller inorganic particles. Elements (P, Ca and Mg), TSS and VSS were determined for each fraction in the separation column. The procedure was performed twice for each height sampled. The morphology and elemental distribution of 10 CaP granules were analysed with a scanning electron microscope in backscattering mode coupled with energy dispersive X-ray (SEM-EDX). The crystal phases in the granules were identified through X-ray diffraction (XRD) analysis.

### 2.4. Phosphorus mass balance

The P mass balance was calculated by adding up the entire measured incoming total P (influent and inoculum) and measured outgoing (accumulated, effluent and sampled). The fraction sampled consists of excess sludge, sludge bed sampling and inorganic solids attached at the reactor walls. A detailed description of the calculation used for the P mass balance is in [supplementary material](#). The fraction non-quantifiable consists of P accumulation at the bottom of the reactor and P precipitation directly in the inlet tube, perhaps due to the low feeding flow (Rohde, 2016).

### 2.5. Ionic activity and saturation state calculations

Precipitation of Ca<sub>x</sub>(PO<sub>4</sub>)<sub>y</sub> and CaCO<sub>3</sub> species in BW and treated BW was evaluated according to the saturation index (SI), using the software Visual MINTEQ version 3.1 (KTH, Sweden). The software considers the Davies model to calculate the activity coefficients (Mullin, 2001). SI of a certain specie (y) was calculated through the ratio IAP<sub>y</sub>/K<sub>sp</sub>, where IAP is the ion activity product of the elements in y and K<sub>sp</sub> is the solubility product constant of y. For SI > 1 y is supersaturated, for SI < 1 y is under saturation and for SI = 1 y is in apparent equilibrium. The chemical matrix (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, PO<sub>4</sub><sup>3-</sup>, HCO<sub>3</sub><sup>-</sup> (alkalinity), Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, soluble humic acids and pH) of

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