Simultaneous calcium phosphate precipitation in anaerobic treatment of black water: a new approach to phosphorus recovery

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Abstract
Phosphorus recovery from wastewater by precipitation as calcium phosphate could reduce the depletion of scarce phosphate rock resources and the need for mining. This study will introduce simultaneous phosphorus recovery by precipitation of calcium phosphate granules in the anaerobic treatment of black water. The reduction of humic acids in tap water had a minor effect on the free calcium concentration, yet appeared to be the key for the occurrence of calcite seed crystals and subsequent precipitation of amorphous calcium phosphate granules. The granules formed in the Upflow Anaerobic Sludge Blanket (UASB) reactor were inspected with Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), and direct spectral analysis using Raman spectroscopy. The granules had a diameter of 1-2mm and a thin organic layer on the outside of the granule. The phosphorus content of the amorphous calcium phosphate granules was 15-17 wt%. Phosphorus recovery from the black water UASB reactor with these granules has to be further quantified.

INTRODUCTION

The production of artificial fertilizers from phosphate rock is energy intensive and involves significant emissions of carbon, radioactive by-products and heavy metals (Cordell *et al*., 2009). As an alternative for mining of phosphate rock, phosphorus can be recovered from wastewater by precipitation as calcium phosphate (Driver *et al*., 1999). Calcium phosphate is often recovered in its crystalline form hydroxyapatite, and further processed into water-soluble fertilizer.

Recovery of calcium phosphate from municipal wastewater has been established in a fluidized bed with DHV Crystalactor®, requiring chemical additions to increase the super saturation and pH (Eggers *et al*., 1991). Mañas *et al*. (2011) introduced a new way to recover calcium phosphate within activated sludge process by accumulation of hydroxyapatite in Enhanced Biological Phosphorus Removal (EBPR) process. In the study of de Graaff *et al*. (2010), 40% of the incoming phosphorus was retained in the Upflow Anaerobic Sludge Blanket (UASB) reactor operated on black water, but no precipitation of calcium phosphate granules was observed.

This study will present precipitation of amorphous calcium phosphate granules in the anaerobic treatment of black water, initiated by reduction of humic acids in tap water and subsequent changes in tap water composition. Amorphous calcium phosphate has higher solubility than hydroxyapatite, and could be therefore used as a complete fertilizer. The chemical composition of the produced granules is investigated by direct optical and spectral analyses, and quantitative elemental analysis. To investigate the initiation of calcium phosphate precipitation in black water, the saturation index of mineral species in tap water and black water is evaluated. Finally, the recovery of phosphorus as amorphous calcium phosphate granules from the black water UASB reactor is discussed.

MATERIALS AND METHODS

UASB reactor operation and sampling

A 50 L lab-scale UASB reactor was operated for 750 days on vacuum collected black water at an HRT of 8.7 days and at 25°C. The reactor was started in 2010 using the same reactor configuration and operational conditions as in the study of de Graaff *et al*. (2010), and 20 L of anaerobic sludge as an inoculum from the same study. A demonstration-scale UASB reactor (2.4 m^3) was operated on the same black water at an HRT of 3.6 days at 35°C from 2009 on at the Decentralized Sanitation and Reuse (DESAR) demonstration site in Sneek, the Netherlands (Kujawa-Roeleveld *et al*., 2012). The granules used for the analyses were taken from the bottom of the UASB reactor sludge bed, 2 and 4 months after the granule formation started in the beginning of 2012. The granules were sieved from the sludge sample with a 500µm sieve and rinsed with milliQ water.

SEM and elemental analysis (EDX and ICP)

Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) were used to analyse the structure and elemental composition of four granules from the lab-scale UASB reactor. Prior to the analysis the granules were dried at 105°C overnight. Quantitative elemental analysis was done on two samples of inorganic granule cores (0.5g per sample, burned at 550°C for 2 hours) from both lab- and demo-scale UASB reactors using acid destruction and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

Raman analyses

Raman spectroscopy was used to analyse the precipitated species in four granule cores from both lab- and demo-scale UASB reactors. The granules were dried at room temperature overnight prior to the analysis. Reference spectra used in the analysis were taken from RRUFF library.

Saturation index calculations

Saturation index calculations for calcite in tap water and hydroxyapatite (as an indicator for calcium phosphate precipitation) in black water were performed with the OLI Stream Analyzer (version 3.1, OLI Systems, 2012). Saturation index was defined as the logarithm of the ratio of the ion activity product to the solubility product.

RESULTS AND DISCUSSION

Granule formation in black water UASB reactor

Formation of granules was observed in the flocculent sludge bed of the lab-scale UASB reactor after 1.5 years of operation. The dried granules had a diameter of 1-2mm. The granule formation was also observed in the demo-scale UASB reactor.

Elemental composition of granules: SEM, EDX and ICP analyses

Figure 1 presents a SEM picture of a dried granule showing the outer layer (a) and the inner part (b) that were analysed with EDX. Table 1 presents the main elemental composition of the outer layer and inner part of the granules from the lab-scale UASB reactor, and the quantitatively analysed inorganic core of the granules from both lab- and demo-scale UASB reactor. The outer layer was mostly composed of carbon (C), oxygen (O) and nitrogen (N) with traces of calcium (Ca), phosphorus (P) and magnesium (Mg), indicating an organic layer. The inner part had increased levels of Ca and P with lower levels of C, O and N, indicating an inorganic core with some organics. The molar Ca/P ratios of the quantitatively analysed inorganic cores (ICP) were slightly higher (1.68 lab-scale and 1.63 demo-scale) than the theoretical ratio of amorphous calcium phosphate (1.5), due to presence of carbonate ions in black water (Combes and Rey, 2010).

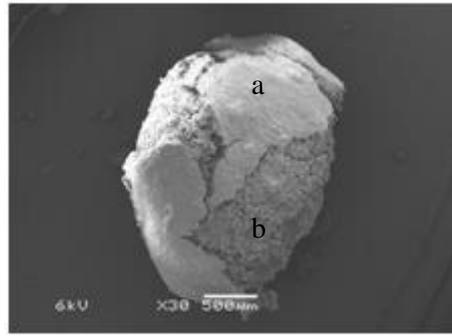Precipitation of struvite in the granules was not expected due to the low measured Mg concentration (Table 1).

Figure 1 SEM picture showing the outer layer (a) and inner part (b) of dried granule (lab-scale UASB)

Table 1 Elemental composition of outer layer and inner part of granule (lab-scale UASB) (EDX) and inorganic core (lab-and demo-scale UASB) (ICP)

Element	Unit	Outer layer	Inner part	Unit	Inorganic core (lab-scale UASB)	Inorganic core (demo-scale UASB)
C		64	22		-	-
O		15	23		-	-
N	mol%	11	9	wt%	-	-
Ca		2	30		33	35
P		1	12		15	17
Mg		0.8	0.2		1	1

- not determined

Raman analyses

Figure 2 presents the Raman spectra of the granule cores from both the lab- and demo-scale UASB reactors and reference spectra of hydroxyapatite. The spectra of the granule cores had a peak at around 950 cm^{-1} (945-948 cm^{-1} lab-scale, 947-958 cm^{-1} demo-scale), 10 cm^{-1} lower than that of hydroxyapatite, corresponding to the spectra of amorphous calcium phosphate (Combes and Rey, 2010).
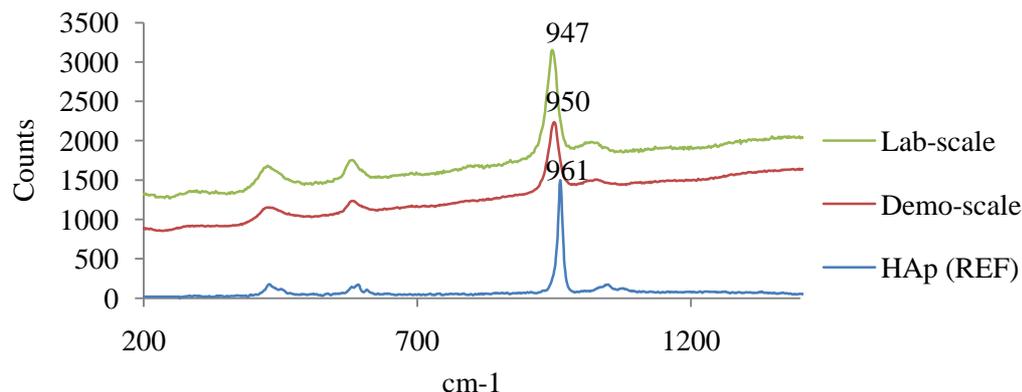

Figure 2 Raman spectra of granule cores indicating precipitation of amorphous calcium phosphate and reference spectra of hydroxyapatite

Initiation of calcium phosphate granule precipitation in black water

Calcium phosphate granules observed in this study were not formed in the study of de Graaff *et al.* (2010) with the same reactor. An explanation can be the reduction of humic acids in tap water after the installation of an ion exchanger in the drinking water treatment facilities supplying water to the

demonstration site in Sneek in 2010. Humic acids inhibit the precipitation of mineral species in two ways: decreasing the super saturation by binding free ions, and decreasing the precipitation kinetics by adsorbing onto the crystal growth sites (Alvarez *et al.*, 2004; Lin *et al.*, 2005). The reduction of humic acids led to slight increase in the free Ca concentration in tap water (data not shown) (Vitens, 2012), increasing the saturation index of calcite in tap water from 0.54 to 0.63. The increased super saturation could have resulted in formation of calcite seed crystals in tap water, and subsequent increased precipitation of calcium phosphate on these seed crystals in black water (Song *et al.*, 2006). Raman spectra corresponding to those of calcite were identified from a small distinct white area in the granule cores, confirming the presence of calcite seed crystals (data not shown). Furthermore, the higher free Ca concentration in black water (data not shown) resulted in the increase of saturation index of hydroxyapatite from 8.1 to 9.3 compared to the study of de Graaff *et al.* (2010). The predominance of calcium phosphate precipitation in the granules can be expected due to the lower SI of calcite in black water (1.3) compared to the one of hydroxyapatite (9.3). According to the Raman analysis, amorphous calcium phosphate was the dominant calcium phosphate species in the granules. Humic acids and Mg present in black water could have inhibited the transformation of amorphous calcium phosphate into more stable hydroxyapatite (Alvarez *et al.*, 2004; Kibalczyc *et al.*, 1990).

Phosphorus recovery from black water UASB reactor

The produced amorphous calcium phosphate granules had comparable phosphorus content (15-17 wt%, Table 1) to phosphate rock (9-13 wt%), struvite (13-14 wt%) and common phosphorus fertilizer triple superphosphate (20 wt%) (Global Phosphorus Network, 2012), and can be therefore considered as a new phosphorus product. Phosphorus recovery from the black water UASB reactor with these granules has to be further quantified. Further research should also investigate the particle size distribution, water solubility and heavy metal content of the granules, and a practical application to separate the granules from the UASB reactor biomass.

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