Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Calcium phosphate granulation in anaerobic treatment of black water: A new approach to phosphorus recovery

Taina Tervahauta [a,b,*], Renata D. van der Weijden [a,b], Roberta L. Flemming [c], Lucía Hernández Leal [a], Grietje Zeeman [b], Cees J.N. Buisman [a,b]

[a] Wetsus, Centre of Excellence for Sustainable Water Technology, P.O. Box 1113, 8900CC Leeuwarden, The Netherlands

[b] Sub-department Environmental Technology, Wageningen University, P.O. Box 17, 6700AA Wageningen, The Netherlands

[c] Department of Earth Sciences, University of Western Ontario, 1151 Richmond Street, London, ON N6A 5B7, Canada

ARTICLE INFO

Article history:
Received 11 May 2013
Received in revised form
3 September 2013
Accepted 6 October 2013
Available online 19 October 2013

Keywords:
Phosphorus recovery
Calcium phosphate
Black water
UASB reactor

ABSTRACT

Recovery of phosphorus from wastewater as calcium phosphate could diminish the need for mining of scarce phosphate rock resources. This study introduces a novel approach to phosphorus recovery by precipitation of calcium phosphate granules in anaerobic treatment of black water. The granules formed in the Upflow Anaerobic Sludge Blanket (UASB) reactor at lab- and demonstration-scale were analyzed for chemical composition and mineralogy by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), Electron microprobe (EMP), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and micro X-ray Diffraction (XRD). The granules had a diameter of 1–2 mm, organic content of 33 wt%, and phosphorus content of 11–13 wt%. Three calcium phosphate phases were identified in the granules: hydroxyapatite, calcium phosphate hydrate and carbonated hydroxyapatite. Without any addition of chemicals, 7 gP/person/year can be recovered with the calcium phosphate granules, representing 2% of the incoming phosphorus in the UASB reactor. As the heavy metal content was lower compared to other phosphorus recovery products, phosphate rock and phosphorus fertilizer, the calcium phosphate granules could be considered as a new phosphorus product.

1. Introduction

The production of artificial phosphorus 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 magnesium ammonium phosphate (struvite) $MgNH_4PO_4$ and calcium phosphate $Ca_x(PO_4)_y$ (Driver et al., 1999). Several studies have investigated the recovery of

* *Corresponding author*. Wetsus, Centre of Excellence for Sustainable Water Technology, P.O. Box 1113, 8900CC Leeuwarden, The Netherlands. Tel.: +31 (0)58 284 30 00; fax: +31 (0)58 284 30 01.
E-mail address: taina.tervahauta@wetsus.nl (T. Tervahauta).

0043-1354/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.watres.2013.10.012

Nomenclature

FBR	fluidized bed reactor
HAp	hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$
PAO	polyphosphate accumulating organisms
EBPR	enhanced biological phosphorus removal
ACP	amorphous calcium phosphate $Ca_x(PO_4)_y{}^*nH_2O$
UASB	upflow anaerobic sludge blanket
SI	saturation index
HRT	hydraulic retention time
SRT	solids retention time
DESAR	decentralized sanitation and reuse
TP	total phosphorus mg/L
TSS	total suspended solids g/L
VSS	volatile suspended solids g/L
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
EMP	electron microprobe
FTIR	Fourier transform infrared spectroscopy
Raman	Raman spectroscopy
XRD	(micro) X-ray diffraction
IAP	ion activity product
K_{sp}	solubility product
OCP	octacalcium phosphate $Ca_8(HPO_4)_2(PO_4)_4{}^*5H_2O$
pK_a	logarithmic acid dissociation constant
TSP	triple superphosphate

struvite (Doyle and Parsons, 2002), its use as a fertilizer (Gaterell et al., 2000), and commercializing its use as a fertilizer (Ueno and Fujii, 2001). However, the presence of ammonium, magnesium and poorly water soluble phosphate in struvite limits its use as a raw material in the phosphorus industry (Driver et al., 1999). Instead, ongoing efforts are made to create new fertilizer markets for struvite (Ostara, 2009). Recovery of calcium phosphate is often considered more attractive as it has the effective composition of phosphate rock, and can therefore be processed in the phosphorus industry using the existing infrastructure.

Calcium phosphate is recovered from municipal wastewater and animal manure either by using the incinerated sludge ash where phosphorus is concentrated, or by precipitating calcium phosphate pellets in a Fluidized Bed Reactor (FBR) fed with a concentrated stream such as flushed manure (Harris et al., 2008) or a side stream of the sludge treatment (Schipper et al., 2001). The incinerated sludge ash has high heavy metal concentrations, in particular copper, zinc and iron, and cannot be processed together with phosphate rock. The calcium phosphate pellets from a FBR have lower levels of impurities and can be used by the phosphorus industry. The drawback of this technology, however, is the high consumption of chemicals to increase the solution supersaturation and to adjust the pH.

In order to minimize the operation costs, phosphorus recovery technologies should be integrated into the existing wastewater treatment processes in a way that no or a minimum amount of chemicals is needed. For example, phosphorus could be recovered in the activated sludge process without chemical additions through accumulation of hydroxyapatite (HAp) ($Ca_{10}(PO_4)_6(OH)_2$) by Polyphosphate Accumulating Organisms (PAO) in an Enhanced Biological Phosphorus Removal (EBPR) process (Mañas et al., 2011). To avoid the need for further processing of HAp into a water soluble form, calcium phosphate could be recovered in a more soluble hydrated form or as amorphous calcium phosphate (ACP) ($Ca_x(PO_4)_y{}^*nH_2O$) (Dorozhkin and Epple, 2002). Recovered calcium phosphate hydrate could find a niche market as a fertilizer product when the use of processed fertilizers is prohibited, such as in organic farming, provided that the level of heavy metals can be controlled.

Source separated domestic wastewater streams, such as vacuum collected black water, are ideal for phosphorus recovery due to high phosphate concentrations and relatively low heavy metal concentrations compared to municipal wastewater with industrial effluents and manure (Winker et al., 2009). In the study of de Graaff et al. (2010), phosphorus was recovered by precipitating struvite from the effluent of an Upflow Anaerobic Sludge Blanket (UASB) reactor operated on vacuum collected black water. No studies, however, have investigated the recovery of calcium phosphate within the anaerobic treatment of black water. Although de Graaff (2010) reported supersaturation of HAp in black water and retainment of 39% of the incoming phosphorus in the sludge bed of the UASB reactor, no precipitation of calcium phosphate granules was observed.

This study introduces a novel approach to phosphorus recovery by precipitation of calcium phosphate granules in anaerobic treatment of black water. The chemical composition and mineralogy of the produced granules from both lab- and demonstration-scale UASB reactors are investigated by quantitative elemental analysis and direct spectral analyses. The amount of phosphorus recovered with these granules is quantified and the simultaneous phosphorus and energy recovery in the black water UASB reactor is discussed.

2. Materials and methods

2.1. *UASB reactor and black water collection*

A 50 L lab-scale UASB reactor was operated for 988 days on vacuum collected black water at a hydraulic retention time (HRT) of 8.8 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. Black water was collected with jerry cans every two weeks from 32 houses in the Decentralized Sanitation and Reuse (DESAR) demonstration site in Sneek, the Netherlands (Zeeman and Kujawa-Roeleveld, 2011), and was stored at 4 °C before feeding to the reactor. 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 DESAR demonstration site (Kujawa-Roeleveld et al., 2012).

2.2. *Influent, effluent and sludge bed sampling and analyses*

Influent and effluent samples (0.5–1 L) were collected from the lab-scale UASB reactor once a week (74 samples) and