Improving nutrient fixation and dry matter content of an ammonium-rich anaerobic digestion effluent by struvite formation and clay adsorption

Maria M. Estevez, Roar Linjordet, Svein J. Horn and John Morken

ABSTRACT

The anaerobic digestion (AD) of organic wastes that contain nitrogen leads to its mineralization, yielding a digestate rich in ammonium (NH_4^+), an important fertilizing nutrient. The applicability of AD digestate as fertilizer can be improved by fixating the nutrients and increasing its dry matter content. Methods for the fixation and recovery of the digestate's NH_4^+ and possible also PO_4^{3-} include struvite precipitation and adsorption in clay materials such as bentonite. These techniques were tested in batch experiments employing the liquid fraction of a digestate originating from the AD of a substrate mix containing lignocellulose, cattle manure and fish industrial waste. The concentration of NH_4^+-N in this digestate was 2,300 mg L^{-1}. Struvite precipitation conditions at a molar ratio of 1.2:1:1 (Mg^{2+}: NH_4^+:PO_4^{3-}) and pH 9.5 were best in terms of simultaneous removal of NH_4^+-N (88%), PO_4^{3-} (60%) and soluble chemical oxygen demand (44%). Bentonite adsorption gave comparably high removal levels for NH_4^+-N (82%) and PO_4^{3-} (52%). Analysis of the precipitates' morphology and elemental composition confirmed their struvite and bentonite nature. Dry matter content was increased from 5.8% in the AD digestate to 27% and 22% in the struvite and bentonite sludges, respectively.

Key words | ammonium, anaerobic digestion, bentonite, digestate, phosphate, struvite

Maria M. Estevez (corresponding author)
John Morken
Department of Mathematical Sciences and
Technology,
Norwegian University of Life Sciences,
P.O. Box 5003, 1432 Ås,
Norway
E-mail: *maria.magdalena.estevez@nmbu.no*

Maria M. Estevez
Roar Linjordet
Bioforsk,
Norwegian Institute for Agricultural and
Environmental Research,
Frederik A. Dahls vei 20, 1432 Ås,
Norway

Svein J. Horn
Department of Chemistry,
Biotechnology and Food Science,
Norwegian University of Life Sciences,
P. O. Box 5003, 1432 Ås,
Norway

INTRODUCTION

Several sectors have a marked impact on greenhouse gas (GHG) emissions, and among them is the livestock industry, which is responsible for approximately 18% of the global GHG emissions. These livestock-associated emissions include methane originating directly from domestic animals (ruminant enteric fermentation) or manures, and nitrous oxide emitted from grazed and arable lands where manure is applied as fertilizer (Massé *et al.* 2011). The livestock sector is also identified as the largest contributor to environmental degradation of land and water (Steinfeld *et al.* 2006). Livestock manures usually lose nearly 50% of their nitrogen content during storage, handling, and application, and the loss of ammonia leads to acid rain, water eutrophication, acidification of sensitive ecosystems, and decimation of biodiversity (Massé *et al.* 2011). Notably, phosphate (PO_4^{3-}) is another nutrient that gives rise to eutrophication (de-Bashan & Bashan 2004; Hjorth *et al.* 2010). Interest in sustainable livestock production practices is growing, as exemplified by recycling of organic matter and plant nutrients to help mitigate the environmental hazards described above. These efforts may make it possible to replace mineral fertilizers with nitrogen, phosphorus, potassium, and micronutrients that have been recycled within farms (Hjorth *et al.* 2010). Mined rock PO_4^{3-} is a relatively cheap source of phosphorus for fertilizing purposes, but this resource is not renewable and will eventually be depleted (de-Bashan & Bashan 2004; Gonzalez Ponce & Garcia Lopez de Sa 2007; Forrest *et al.* 2008). Accordingly, liquid effluents containing phosphorus could represent a renewable source of PO_4^{3-} fertilizer rather than an environmental contaminant.

Anaerobic digestion (AD) offers a solution to several problems associated with livestock production. Biogas is a renewable fuel that can be used to substitute fossil fuels and thus reduce GHG emissions, and the biogas digestate contains mineralized nutrients that are better balanced to meet crop requirements compared to raw manure (Massé *et al.* 2011). Further fixation of the mineralized nutrients from AD digestates will minimize nutrient losses to the

environment, and thus lower the risk of eutrophication. Capturing energy and reducing the need for chemical fertilizers can substantially decrease the carbon footprint of livestock food products (Massé *et al.* 2011).

There are both physicochemical and biological methods for removal of ammonium (NH_4^+) and PO_4^{3-} from a nutrient-rich AD liquid digestate. Biological techniques can remove the nutrients from wastewater but cannot recover them to obtain a useful fertilizer product, whereas several physicochemical methods can also achieve the latter (Zeng *et al.* 2006). The physicochemical methods applied most often for NH_4^+ recovery include reverse osmosis, air stripping, ion exchange, adsorption, evaporation and chemical precipitation (de-Bashan & Bashan 2004; Zeng *et al.* 2006; Hjorth *et al.* 2010; Gustin & Logar 2011). Chemical methods for the removal of ammonium include precipitation of ammonium salts, and, for phosphorus, precipitation with iron, aluminum, or lime (de-Bashan & Bashan 2004; Crutchik & Garrido 2011). These precipitated compounds will not recycle the nutrients in a form easily available for plants but instead generate sludges that need to be landfilled (Le Corre *et al.* 2009; Crutchik & Garrido 2011). On the other hand, when both nutrients are present, they can be recovered together as struvite (magnesium ammonium phosphate hexahydrate: $MgNH_4PO_4.6H_2O$), if the conditions for the precipitation of this compound are met. Struvite occurs in the form of white orthorhombic crystals that consist of regular tetrahedral PO_4^{3-}, distorted octahedral $Mg(H_2O)_6^{2+}$, and NH_4^+ groups retained by hydrogen bonds (Abbona & Boistelle 1979). For the precipitation of struvite to proceed, the three components must be present simultaneously at a stoichiometric molecular ratio (1:1:1) and the pH needs to be above 7.5 (de-Bashan & Bashan 2004; Crutchik & Garrido 2011). Other ions present such as calcium or carbonates may form amorphous precipitates that may inhibit the formation of struvite (Le Corre *et al.* 2009; Huchzermeier & Tao 2012). Impurities such as suspended solids may also interfere with struvite formation (Forrest *et al.* 2008).

Many studies have been carried out on precipitation of struvite for recovery of nutrients from municipal wastewaters (Suzuki *et al.* 2005; Forrest *et al.* 2008; Crutchik & Garrido 2011), some on AD effluents (Altinbas *et al.* 2002; Perera *et al.* 2007; Yetilmezsoy & Sapci-Zengin 2009), but few address recovery of nutrients from the co-digestion of livestock manure and other substrates. Since Mg^{2+} levels are usually low in wastewater, amendment of the molar ratio is normally done by adding MgOH (Le Corre *et al.* 2009). Production of struvite can occur either in batch, continuously stirring or fluidized bed reactor systems (Le Corre

et al. 2009). In Japan, full-scale production of struvite is performed in this last way, where by the influent is continuously fed but the precipitate is harvested sequentially allowing for longer solid retention times, and the product is sold as a commercial fertilizer (de-Bashan & Bashan 2004; Forrest *et al.* 2008; Le Corre *et al.* 2009). Struvite has been studied as a favorable slow-release fertilizer in different soil types (Li & Zhao 2003; Gonzalez Ponce & Garcia Lopez de Sa 2007; Yetilmezsoy & Sapci-Zengin 2009). Abbona & Boistelle (1979) have stated that bacterial action and particle size are the predominant factors determining the rate of phosphorus release from struvite to plants.

Removal of nutrients by adsorption into clay minerals is another method to consider since it has low cost and high competitiveness compared to biological and chemical treatments (Saltali *et al.* 2007; Eturki *et al.* 2012). Bentonites are smectite-type clays that rely on acid–base interactions for strong retention of molecules on their surfaces (Seredych *et al.* 2008) and can also act as ion exchange materials for the removal and recovery of ammonia from wastewater (Saltali *et al.* 2007; Eturki *et al.* 2012). Alkali metals and cations (typically Na^+ and Ca^{2+}) usually balance the high negative charge of the surface of a bentonite. In the sorption removal of PO_4^{3-}, inorganic hydroxyl metal polycations such as Al^{3+} and Fe^{3+} replace bentonite cations, acting as pillars that increase the interlayer spacing of bentonite (Yan *et al.* 2010). Clay minerals can be used as soil conditioners and not only provide nutrients to the soil but also improve its physico-chemical properties, reducing NH_3 volatilization, nutrients and water losses (Saltali *et al.* 2007).

Digestates from AD processes enriched in nutrients and dry matter content may become economically and environmentally attractive as fertilizers. In countries with long distances and winters such as Norway, where storage and transportation costs may be extensive, these materials may imply important benefits. This study focused on the digestate originating from the anaerobic co-digestion of three important Norwegian substrates: lignocellulosic biomass, cattle manure and industrial fish waste. The aim was to investigate NH_4^+ and PO_4^{3-} fixation of this digestate by struvite precipitation and adsorption into bentonite.

MATERIALS AND METHODS

AD and digestate

The digestate was collected over a period of 4 months from a mesophilic ($37 \pm 1\,°C$) continuously stirred tank

reactor (CSTR) processing pre-treated lignocellulose, cattle manure and industrial fish waste in a volatile solids ratio of 40%, 40% and 20% respectively. The lignocellulosic substrate was Salix 'Tora' (*S. viminalis* 'Orm' × *S. schwerinii*) steam exploded at 210 °C for 10 min as previously described (Horn *et al.* 2011). The digester underwent recirculation of its own process water after being screened through sieves of 2.5 and 1 mm mesh pore size. A diagram of the process is shown in Figure 1. The sieved liquid digestate that was not recirculated within the process was collected and used for the nutrient fixation trials. Characterization of this fraction was performed so to evaluate its initial $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio, calculate the additions of chemicals required to reach stoichiometric ratio for struvite precipitation to occur, and to determine nutrient removal efficiencies. Determination of pH was done according to *Standard Methods* (APHA 1995) and Mg^{2+}, NH_4^+-N, total-N, PO_4^{3-}, total-P, and soluble chemical oxygen demand (COD) were analyzed with a Spectroquant® Pharo 100 spectrophotometer (Merck KGaA, Darmstadt, Germany) using Merck Spectroquant© Kits. When necessary, samples were diluted and/or centrifuged (6,000 rpm, 5 min) before being filtered through a 0.45 μm glass fiber filter. All analyses were performed in triplicate. Total solids (TS), volatile solids (VS) and total suspended solids (TSS) were analysed according to *Standard Methods* (APHA 1995).
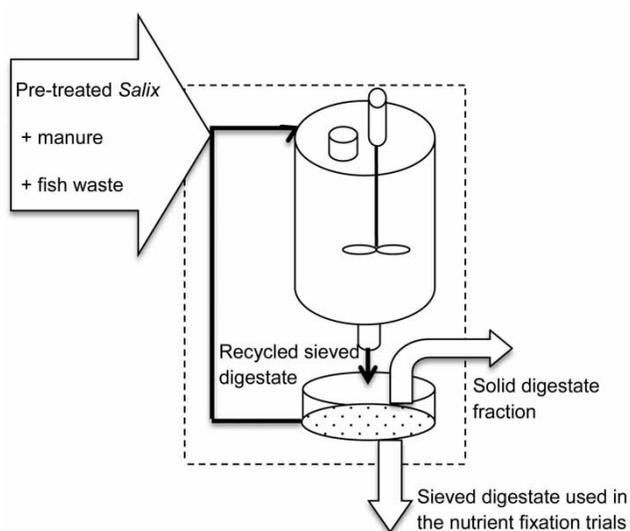

Figure 1 │ Diagram of the CSTR process with recirculation. The sieved digestate not being recirculated was the fraction to which struvite and bentonite trials were applied.

Removal of nutrients by struvite precipitation

Batch experiments of struvite precipitation were performed on the liquid sieved digestate. Precipitation according to Equation (1) was analyzed for the molar ratios ($Mg^{2+}:NH_4^+:PO_4^{3-}$) 1:1:1 and 1.2:1:1, with duplicate trials for each ratio.

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O(s)$$
(1)
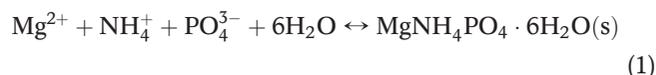
According to the characterization of the digestate (Table 1) corresponding quantities of $MgCl_2.6H_2O$ as Mg^{2+} source and KH_2PO_4 as additional PO_4^{3-} were added to 300 mL of sieved digestate so to reach each ratio. For 1:1:1, 7.5 g and 5.2 g were added while for 1.2:1:1, 9 and 5.2 g were added, respectively. The content was agitated at 300 rpm for 15 min and left to settle for 15 min before being divided into four aliquots of 45 mL. The pH of these aliquots was adjusted to 7, 8, 9, and 9.5 with 1 N NaOH solution, and kept covered to avoid any NH_3 volatilization. For the samples that showed a visible sedimentation of precipitate, determination of NH_4^+-N, PO_4-P and soluble COD in the supernatants after a 24 h settling period were followed spectrophotometrically as described above. In some cases, analysis was only possible after 48 h settling time. Precipitate samples were washed three times with ultra-pure water (Millipore Direct-Q 3 Ultrapure Water System, Billerica, MA, USA) and left to dry at 40 °C for 48 h. Morphological analysis of the precipitates was performed by scanning electron microscopy (SEM) (Zeiss EVO 50 EP, Carl Zeiss SMT, Cambridge, UK) and elemental composition was determined with an energy-dispersive X-ray spectrometer (EDX) (INCA Energy 350, Oxford

Table 1 │ Characteristics of the sieved (liquid) fraction of the biogas digestate used for the nutrient fixation trials

Parameter	Concentration
pH	7.5 ± 0.2
Mg^{2+} (mg L^{-1})	110.0 ± 5.5
Total-N (mg L^{-1})	3150.0 ± 353.6
NH_4^+-N (mg L^{-1})	2300.0 ± 115.0
Total-P (mg L^{-1})	61.1 ± 3.1
PO_4-P (mg L^{-1})	56.0 ± 3.0
Soluble COD (mg L^{-1})	4380.0 ± 219.0
TS (% weight)	4.7 ± 0.7
VS (% weight)	4.2 ± 0.3
TSS (% weight)	1.4 ± 0.2

Instruments Analytical, UK). Samples for the SEM-EDX analysis were prepared in carbon coatings and analyzed at acceleration voltage of 30 kV.

Removal of nutrients employing bentonite

Removal of nutrients by adsorption in silicate clay was evaluated in batch trials employing commercial sodium bentonite (Alfa Aesar®, CAS number: 1302-78-9). Effects of varying the dosage of adsorbent added to the sieved digestate samples at constant pH (7.51) and room temperature (22 °C) were analyzed. Trials were performed in triplicate by adding 1.5, 3, 4, 6, and 9 g of bentonite to 50 mL aliquots of digestate. The mixtures were agitated at 600 rpm for 5 min and left to settle 24 h. Supernatants were analyzed for NH_4^+-N, PO_4-P and soluble COD as described previously. Morphological and compositional study of the precipitates was performed by SEM-EDX analysis as previously stated.

RESULTS AND DISCUSSION

Removal of nutrients by struvite precipitation

The digestate employed possessed high ammonium content (2,300 mg L^{-1}) while its PO_4-P content was rather low (56 mg L^{-1}) (Table 1).

Thus, KH_2PO_4 was added as a PO_4^{3-} source in order to reach stoichiometry for the struvite to precipitate. Additionally, $MgCl_2.6H_2O$ was added as a Mg^{2+} source and NaOH was used to increase the pH. Figure 2 shows the final concentrations of NH_4^+-N and PO_4-P in the supernatant after struvite precipitation for both the 1:1:1 and 1.2:1:1 ratios. Sedimentation after 24 h was not clear for the pH 7 and 8 at molar ratio 1:1:1. Thus a longer settling time of 48 h was used in this case, which showed a clearer phase separation for all pHs.

Generally, removal of NH_4^+ did not change with pH; in all cases reduction efficiencies were between 83 and 89%. For all pHs except pH 9.5, the 1.2:1:1 ratio gave better removal of NH_4^+. Positive PO_4^{3-} reduction with respect to the digestate's initial content (56 mg L^{-1}) was observed for the ratio 1.2.1:1 at the two highest pHs (Table 2). Soluble COD removal was clearly best at 1.2:1:1 ratio (Table 2). Overall, for both ratios, the best simultaneous removal of NH_4^+ and PO_4^{3-} occurred at pH 9 and 9.5 (Figure 2 and Table 2). The ratio 1.2:1:1 at pH 9.5 gave the best simultaneous reduction efficiencies for the three parameters.

Other studies of AD digestates containing lower NH_4^+ levels than reported here showed NH_4^+-N reductions in the same range (Altinbas *et al.* 2002; Yetilmezsoy & Sapci-Zengin 2009), when pH was between 9 and 9.2 and stoichiometric ratios of 1:1:1 and 1.5:1:1 were used. Perera *et al.* (2007) stated that best precipitation conditions for both NH_4^+ and PO_4^{3-} removal from swine waste AD digestate were pH 9 and molar ratio $Mg^{2+}:NH_4^+:PO_4^{3-}$ of 1:1:1.

Imaging and X-ray analysis confirmed the struvite nature of the precipitate. Orthorhombic mono-crystals were observed (Figure 3) and the EDX spectrum showed elemental analysis consistent with struvite (Wang *et al.* 2010) (Table 3). Calcium (Ca) has been shown to interfere in the precipitation of struvite, competing for phosphate to form calcium phosphates (Crutchik & Garrido 2011;
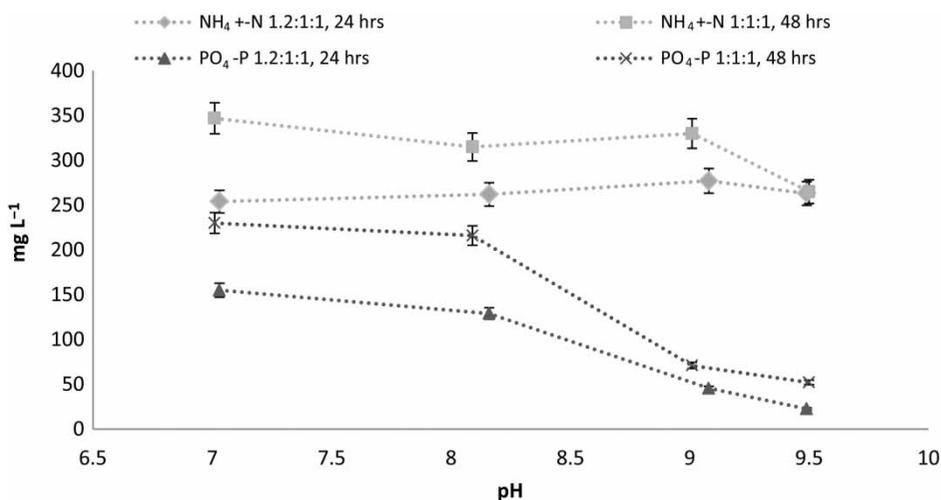
Figure 2 | Effect of pH on the final supernatants' concentrations of NH_4^+-N and PO_4-P after 24 h settling time for ratio 1.2:1:1 and 48 h settling time for ratio 1:1:1. Initial concentration of NH_4^+-N: 2.3 g L^{-1}. Initial concentration of PO_4-P after stoichiometric ratio adjustment: 12 g L^{-1}.

Table 2 │ Reduction levels (%) in the supernatants' concentrations of NH_4^+, PO_4^{3-} and soluble COD, after 24 h

		NH_4^+ % reduction	PO_4^{3-} % reduction	Soluble COD % reduction
Ratio 1:1:1[a]	9.0	87.9 ± 2.3	–	8.40 ± 0.7
	9.5	89.5 ± 2.5	–	27.0 ± 2.0
Ratio 1.2:1:1	9.0	83.5 ± 6.2	18.6 ± 6.2	31.9 ± 3.0
	9.5	88.2 ± 0.6	59.8 ± 6.3	44.4 ± 8.2

[a]pH values of 9.0 and 9.5 were the only ones showing visible sedimentation after 24 h for the ratio 1:1:1.

Huchzermeier & Tao 2012). In our precipitates, some amorphous precipitation as calcium phosphates or carbonates may be present since small levels of Ca were detected by EDX (Table 3) and amorphous agglomerates were observed together with the struvite crystals. Amorphous phosphates should be minimized since they are insoluble salts with very low phosphorus bioavailability for crops and plants (Crutchik & Garrido 2011). The presence of high levels of carbon (C) and oxygen (O) seen on the EDX spectra may originate from lignocellulosic material whose fibers were observed in the SEM images (Figure 3). The carbon to oxygen ratio (C/O) concurs with the ratio observed for steam-exploded lignocellulosic fibers (Vivekanand *et al.* 2013). Generally, pre-treated material contains less O than untreated lignocellulosics due to the formation of pseudo-

lignin from sugars during the pretreatment (Estevez *et al.* 2012; Vivekanand *et al.* 2013). Additionally, lignin will accumulate due to degradation of sugars during AD. Lignin accumulation has been shown to correlate with increased C/O ratios (Vivekanand *et al.* 2013).

Costs of struvite production depend on the quantities of reagents employed, where the Mg^{2+} source and the base used to adjust the pH are most important. Costs can be reduced if MgOH is employed for both purposes (Le Corre *et al.* 2009). In our case, due to low PO_4^{3-} content, additional PO_4^{3-} was needed to reach stoichiometry. For effluents containing high levels of PO_4^{3-} it should be a target to recover it together with the ammonium. Studies have shown that use of phosphate rock fertilizer is still more economical than production of struvite, but when considering the latter the reduced costs of sludge disposal and pipe-scaling cleaning due to struvite incrustations, the improved availability of a non-renewable resource and the reduced nutrients losses to the environment, struvite production was proven to be feasible (Forrest *et al.* 2008; Le Corre *et al.* 2009; Molinos-Senate *et al.* 2011).

Removal of nutrients employing bentonite

The efficiency of NH_4^+ ions removal by adsorption into bentonite clay increased with the amount of bentonite
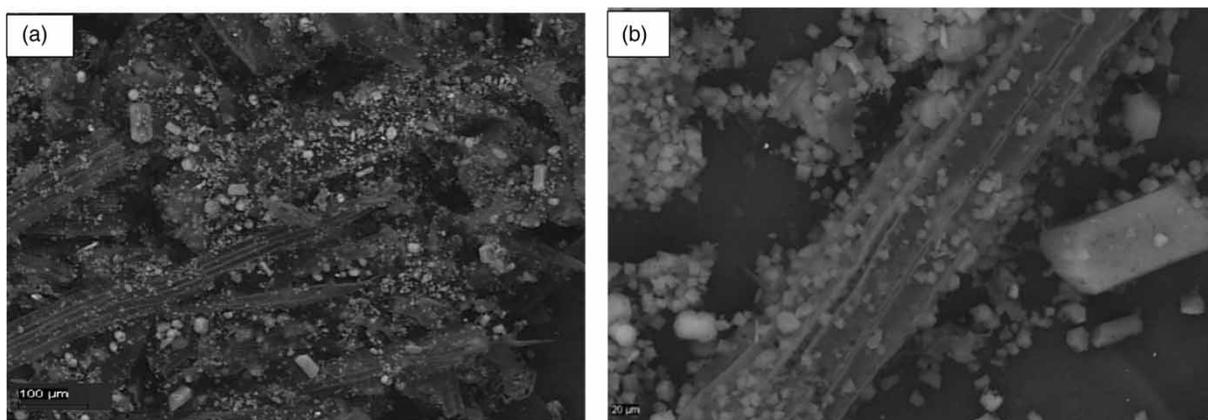
Figure 3 │ SEM images of the struvite precipitate at (a) 100 μm and (b) 20 μm.

Table 3 │ EDX analysis of elemental composition of the generated struvite precipitate

Element	C	O	Mg	Al	Si	P	S	K	Ca
Weight %	58.02	36.38	2.56	0.10	0.06	2.18	0.02	0.26	0.42
Atomic %	66.14	31.13	1.44	0.05	0.03	0.96	0.01	0.09	0.14

added to the 50 mL digestate aliquots, up to a level of 76–82% (Table 4). Regarding removal of PO_4^{3-} and soluble COD, results showed that about 40–50% of the initial concentration was removed. COD removal followed a similar trend as NH_4^+-N (not shown), while the PO_4^{3-} removed was slightly more the lower the doses of bentonite applied (Table 4).

SEM and EDX analysis confirmed bentonite product (Eturki *et al.* 2012) with high content of silicium (Si) and aluminum (Al), and very low concentrations of sodium (Na) in the precipitate, indicating it was exchanged by ammonium (Figure 4, Table 5). C and O content gave a lower C/O ratio than for struvite. Bentonite consists mainly of oxides of Al and Si (Seredych *et al.* 2008; Eturki *et al.* 2012), explaining the higher O content in the clay than in the struvite precipitate.

The high removal of NH_4^+ confirmed that bentonite is highly selective for NH_4^+ ion adsorption (Ayari *et al.* 2007; Eturki *et al.* 2012). Maximum cation exchange capacity for the NH_4^+ in this trial was estimated on 65 meq per 100 g dry bentonite.

For the removal and recovery of NH_4^+-N from AD effluents, bentonite use seems a good strategy since no chemical amendment is required, and it will generate a natural product that could better comply with organic fertilizer requirements. According to the Norwegian Food Safety Authority (2012), clay materials are approved to be used as organic fertilizers in Norway. Furthermore, natural bentonite is a low-cost mineral whose deposits are widespread in Europe.

Dry matter content

Dry matter of the obtained nutrient-rich materials was analyzed and results are presented in Table 6. Values were higher than in all the different fractions of AD digestate obtained after sieving. Production of such type of nutrient-concentrated digestates may benefit handling costs for the final AD effluent to be used as fertilizer, by decreasing storage volume requirements and transport costs.

In order to assess the applicability of the generated materials as organic fertilizers, they must be analyzed for heavy metals and pathogens and comply with specifications regarding their content (Norwegian Food Safety Authority 2012). EDX analysis did not detect heavy metals in the struvite and bentonite materials.
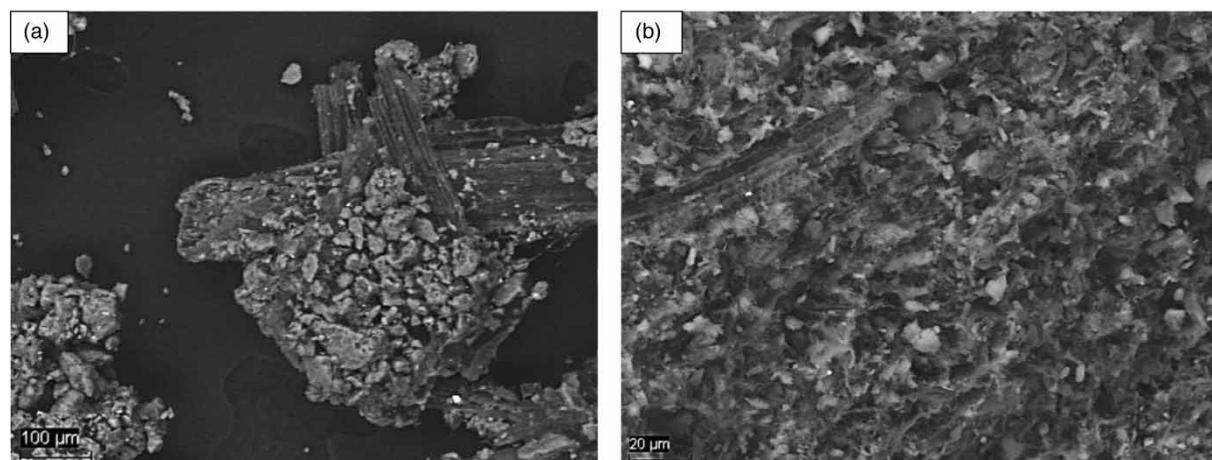
Table 4 | Final supernatants' concentrations and reduction levels (%) of NH_4^+-N and PO_4-P at constant pH (7.51) and room temperature (22 °C) after 24 h settling time

Dosage of bentonite per 50 mL digestate (g)	NH_4^+		PO_4^{3-}	
	Conc. (mg L^{-1})	% reduction	Conc. (mg L^{-1})	% reduction
1.5	706.0 ± 70.0	69.3 ± 3.6	30.0 ± 1.5	46.4 ± 2.3
3	662.0 ± 40.0	71.2 ± 1.7	27.0 ± 1.4	51.8 ± 2.6
4	543.5 ± 46.0	76.4 ± 2.0	36.0 ± 1.8	35.7 ± 1.8
6	558.0 ± 28.0	75.7 ± 3.4	32.0 ± 1.6	42.9 ± 2.1
9	404.5 ± 90.0	82.4 ± 7.0	34.0 ± 1.7	39.3 ± 2.0

Figure 4 | SEM images of the bentonite at (a) 100 μm and (b) 20 μm.

Table 5 │ EDX analysis of the elemental composition of the generated bentonite material

Element	C	O	Na	Mg	Al	Si	P	Fe	K	Ca
Weight %	36.49	42.69	0.22	1.12	3.73	10.07	0.45	2.33	0.79	1.68
Atomic %	47.55	41.78	0.15	0.72	2.17	5.61	0.23	0.65	0.32	0.65

Table 6 │ Dry matter concentration of the different digestate fractions and produced sludges

		Dry matter (% weight)
Struvite sludge		26.93 ± 4.35
Bentonite sludge		21.73 ± 2.54
AD digestate:	Total[a]	5.76 ± 0.29
	Sieved liquid fraction[b]	4.65 ± 0.68
	Solid fraction[c]	11.69 ± 0.71

[a]Total AD digestate refers to the raw effluent coming from the AD process.
[b]Sieved liquid fraction refers to the permeate fraction obtained after sieving the total AD digestate through 2.5 and 1 mm mesh-size sieves.
[c]Solid fraction refers to the concentrate fraction obtained after sieving the total AD digestate.

CONCLUSIONS

Up to 89% of the digestate's initial NH_4^+-N content $(2,300 \text{ mg L}^{-1})$ was possible to remove as struvite, but since the levels of PO_4^{3-} in the digestate were low, addition of PO_4^{3-} was required for struvite to precipitate. Nonetheless, removal levels reached 60% of the initial PO_4^{3-} content (56 mg L^{-1}), and soluble COD removal levels were up to 44% at conditions of pH 9.5 and molar ratio 1.2:1.1. Bentonite showed high affinity for NH_4^+ ions exchange, with removal efficiencies of up to 82%, while PO_4^{3-} was removed by up to 52% of its original content. The nature of the nutrient-rich sludges produced was confirmed by morphological and elemental analyses.

The dry matter content was improved from 5.8% in the AD digestate to 26.9% and 21.7% in the struvite and bentonite sludges, respectively. When both nutrients are present in high concentrations, struvite may be a good method to reach high recovery efficiencies. Bentonite adsorption is a cheap process that can be applied to ammonium-rich digestates and produce a natural product that could be approved as organic fertilizer. This fertilizer will provide good properties regarding not only nutrient release and availability in soil but also water retention. Producing materials with high dry matter and plant-available nutrient content, which are possible to employ as soil amendments, is one of the major challenges that faces the biogas industry.

REFERENCES

Abbona, F. & Boistelle, R. 1979 Growth morphology and crystal habits of struvite crystals ($MgNH_4PO_4.6H_2O$). *Journal of Crystal Growth* **46**, 339–354.

Altinbas, M., Öztürk, I. & Aydin, A. F. 2002 Ammonia recovery from high strength agro industry effluents. *Water Science and Technology* **45** (12), 189–196.

APHA 1995 *Standard Methods for the Examination of Water and Wastewater*, 19th edn. American Public Health Association/ American Water Works Association/Water Environment Federation, Washington, DC, USA.

Ayari, F., Srasra, E. & Trabelsi-Ayadi, M. 2007 Effect of exchangeable cations on the physicochemical properties of smectite. *Journal of Surface Engineering and Applied Electrochemistry* **43** (5), 369–378.

Crutchik, D. & Garrido, J. 2011 Struvite crystallization versus amorphous magnesium and calcium phosphate precipitation during the treatment of a saline industrial wastewater. *Water Science and Technology* **64** (12), 2460–2467.

de Bashan, L. & Bashan, Y. 2004 Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003). *Water Research* **38**, 4222–4246.

Estevez, M. M., Linjordet, R. & Morken, J. 2012 Effects of steam explosion and co-digestion in the methane production from *Salix* by mesophilic batch assays. *Bioresource Technology* **104**, 749–756.

Eturki, S., Ayari, F., Jedidi, N. & Dhia, H. B. 2012 Use of clay mineral to reduce ammonium from wastewater. Effect of various parameters. *Surface Engineering and Applied Electrochemistry* **48** (3), 276–283.

Forrest, A. L., Fattah, K. P., Mavinic, D. S. & Koch, F. A. 2008 Optimizing struvite production for phosphate recovery in WWTP. *Journal of Environmental Engineering* **134**, 395–402.

Gonzalez Ponce, R. & Garcia Lopez de Sa, M. E. 2007 Evaluation of struvite as a fertilizer: a comparison with traditional P sources. *Agrochimica* **51** (6), 301–308.

Gustin, S. & Marinsek Logar, R. 2011 Effect of pH, temperature and air flow rate on the continuous ammonia stripping of the anaerobic digestion effluent. *Process Safety and Environmental Protection* **89**, 61–66.

Hjorth, M., Christensen, K. V., Christensen, M. L. & Sommer, S. G. 2010 Solid-liquid separation of animal slurry in theory and in practice. A review. *Agronomy for Sustainable Development* **30**, 153–180.

Horn, S. J., Nguyen, Q. D., Westereng, B., Nilsen, P. J. & Eijsink, V. G. H. 2011 Screening of steam explosion conditions for glucose production from non-impregnated wheat straw. *Biomass Bioenergy* **35**, 4879–4886.

Huchzermeier, M. P. & Tao, W. 2012 Overcoming challenges to struvite recovery from anaerobically digested dairy manure. *Water Environment Research* **84**, 34–41.

Le Corre, K. S., Valsami-Jones, E., Hobbs, P. & Parsons, S. A. 2009 Phosphorus recovery from wastewater by struvite crystallization: a review. *Critical Reviews in Environmental Science and Technology* **39**, 433–477.

Li, X. Z. & Zhao, Q. L. 2003 Recovery of ammonium-nitrogen from landfill leachate as a multi-nutrient fertilizer. *Ecological Engineering* **20**, 171–181.

Massé, D. I., Talbot, G. & Gilbert, Y. 2011 On farm biogas production: a method to reduce GHG emissions and develop more sustainable livestock operations. *Animal Feed Science and Technology* **166–167**, 436–445.

Molinos-Senate, M., Hernandez-Sancho, F., Sala-Garrido, R. & Garrido-Baserba, M. 2011 Economic feasibility study for phosphorus recovery processes. *AMBIO* **40**, 408–416.

Norwegian Food Safety Authority 2012 Mattylsynet. http://www.mattilsynet.no/om_mattilsynet/gjeldende_regelverk/veiledere/veileder_b_utfyllende_informasjon_om_okologisk_landbruksproduksjon.2651/BINARY/Veileder%20B.%20Utfyllende%20informasjon%20om%20%C3%B8kologisk%20landbruksproduksjon (accessed December 2013).

Perera, P. W. A., Han, Z. Y., Chen, Y. X. & Wu, W. X. 2007 Recovery of nitrogen and phosphorous as struvite from swine waste biogas digester effluent. *Biomedical and Environmental Sciences* **20**, 343–350.

Saltali, K., Sari, A. & Aydin, M. 2007 Removal of ammonium ion form aqueous solution by natural turkish (yildizeli) zeolite for environmental quality. *Journal of Hazardous Materials* **141**, 258–263.

Seredych, M., Tamashausky, A. V. & Bandosz, T. J. 2008 Surface features of exfoliated graphite/bentonite composites and their importance for ammonia adsorption. *Carbon* **46**, 1241–1252.

Steinfeld, H., Gerber, P., Wassenaar, T., Castel, V., Rosales, M. & de Haan, C. 2006 *Livestock's Long Shadow: Environmental Issues and Options*. Food and Agriculture Organization, Rome, Italy.

Suzuki, K., Tanaka, Y., Kuroda, K., Hanajima, D. & Fukumoto, Y. 2005 Recovery of phosphorous from swine wastewater through crystallization. *Bioresource Technology* **96**, 1544–1550.

Vivekanand, V., Olsen, E. F., Eijsink, V. G. H. & Horn, J. S. 2013 Effect of different steam explosion conditions on methane potential and enzymatic saccharification of birch. *Bioresource Technology* **127**, 343–349.

Wang, C., Hao, X., Guo, G. & van Loosdrecht, M. C. M. 2010 Formation of pure struvite at neutral pH by electrochemical deposition. *Chemical Engineering Journal* **159**, 280–283.

Yan, L., Xu, Y., Yu, H., Xin, X., Wei, Q. & Du, B. 2010 Adsorption of phosphate from aqueous solution by hydroxy-aluminum, hydroxy-iron and hydroxy-iron aluminum pillared bentonites. *Journal of Hazardous Materials* **179**, 244–250.

Yetilmezsoy, K. & Sapci-Zengin, Z. 2009 Recovery of ammonium nitrogen from the effluent of UASB treating poultry manure wastewater by map precipitation as a slow release fertilizer. *Journal of Hazardous Materials* **166**, 260–269.

Zeng, L., Mangan, C. & Li, X. 2006 Ammonia recovery form anaerobically digested cattle manure by steam stripping. *Water Science and Technology* **54** (8), 137–145.