NUTRIENT RECYCLING FROM BIO-WASTE AS GREEN FERTILIZERS

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INTRODUCTION

In the transition from a fossil to a bio-based economy, it has become an important challenge to maximally recuperate and recycle valuable nutrients coming from manure and digestate processing. Membrane filtration is a suitable technology to separate valuable nutrients in easily transportable concentrates which could potentially be re-used as green fertilizers, in the meantime producing high quality water. However, traditional membrane filtration systems often suffer technical problems in waste stream treatment. The aim of this study was to evaluate the performance of vibratory shear enhanced processing (VSEP) in the removal of macronutrients (N, P, K, Na, Ca, Mg) from the liquid fraction of digestates, reducing their concentrations down to dischargeable/re-usable water. In addition, the re-use potential of VSEP-concentrates as sustainable substitutes for fossil-based mineral fertilizers was evaluated.

MATERIAL AND METHODS

Site description and experimental set-up

The test site is a pilot scale biogas plant (3 545 kWel) located in Diksmuide, Belgium. It concerns an anaerobic digester with an influent feed consisting of animal manure, energy maize and residues from the food industry with a total capacity of 12 000 tons year\(^{-1}\) of fresh weight (FW). The digestate treatment process, operational since October 2007, is schematically represented in Figure 1.
The digestate (10% DW) is first separated in a liquid and thick fraction (19±3% DW) using a rotating drum, after adding polymer solution. The resulting thick fraction is then guided to a screw press for further dewatering, followed by a dryer, in order to obtain an exportable end-product at 76±1% DW. The liquid fraction is filtrated twice by a VSEP using RO-membranes. Each filtration step results in a concentrate and permeate flow. The permeate produced by the second filtration should meet the Flemish legislation criteria for discharge into surface waters. Because the VSEP-permeate is warm (45°C) and biologically inactive, it cannot be discharged in surface waters as such. It is guided to a lagoon for cooling, biological reactivation and further water polishing.

In 2008, samples of the process streams were taken during two sampling campaigns (August-September), and physico-chemically analyzed. During each sampling event, two homogenized samples (ten liters each) were taken of the different process streams on a different time of the day (= total of four samples per stream). The samples were collected in polyethylene sampling buckets and transported within 1 hour from the test site to the laboratory, carried in cooler boxes filled with ice. In the laboratory, the four replicate samples were stored cool (1-5°C) and kept separate for replicate analysis. Each sample was analyzed twice in order to detect the precision of the analytical method. The following process flows were sampled (Figure 1): raw digestate (1), thick (2) and liquid (3) fraction produced by the rotating drum, polymer solution (4), thick (5) and liquid (6) fraction produced by the screw press, permeate (7) and concentrate (8) produced by the first filtration step, permeate (9) and concentrate (10) produced by the second filtration step, and finally the exportable end-product (11). Moreover, the contents of nitrogen and phosphorus, as well as the chemical oxygen demand (COD) in the second compartment of the lagoon following membrane filtration were daily monitored at the test site during the experimental period (two months).

**Liquid Sample Analysis**

Conductivity and pH were determined potentiometrically using a WTW F537 conductivity electrode (Wissenschaftlich Technischen Werkstäten, Weilheim, Germany) and an Orion 520A pH meter (Orion Research, Boston, VS), respectively. Total nitrogen content was determined using a Kjeltec system 1002 distilling unit (Gerhardt Vapodest, Köningswinter, Germany) after digestion of the sample in a sulphuric–salicylic acid mixture. Finally, the captured ammonia in the distillate was titrated with 0.01 mol HCl l⁻¹ in the presence of a methyl red bromocresol green mixed indicator (Van Ranst et al., 1999). Total phosphorus content was determined using the colorimetric method of Scheel (Van Ranst et al., 1999) after wet digestion of the liquid samples (2.5 g sample+2 ml HNO₃ + 1 ml H₂O₂). The absorbance at 700 nm of samples and standards was determined using a Jenway 6400 spectrophotometer (Barloworld Scientific T/As Jenway, Felsted, UK). Calcium and magnesium were analyzed using ICP-OES (Varian Vista MPX, Palo Alto, CA, USA) after wet digestion (see above). Sodium and potassium of the digested samples (see above) were analyzed using a flame photometer (Eppendorf...
ELEX6361, Hamburg, Germany). The COD was determined photometrically using Dr. Lange standardized cuvette tests (Dr. Bruno Lange GmbH, Düsseldorf, Germany).

**Thick Sample Analysis**

Dry weight content was determined as residual weight after 48 h drying at 100°C. Conductivity and pH were measured using a WTW FS37 conductivity electrode (Wissenschaftlich Technischen Werkstätten, Weilheim, Germany) and an Orion 520A pH meter (Orion Research, Boston, VS), respectively, after equilibration for 1 h in deionized water at a 5:1 liquid/dry sample ratio and subsequent filtering (white ribbon, MN 640 m, Macherey–Nagel, Düren, Germany). Total nitrogen was determined using the Kjeldahl procedure (Van Ranst et al., 1999). For the determination of phosphorus, dry samples were incinerated at 450°C during 4 h in a furnace (Nabertherm, Lilienthal, Germany). The phosphorus content was then determined by the colorimetric method of Scheel (Van Ranst et al., 1999) after digestion of the residual ash (1 g ash + 5 ml 3 mol HNO₃ l⁻¹ + 5 ml 6 mol HNO₃ l⁻¹). Calcium and magnesium of the digested samples (see above) were analyzed by means of ICP-OES (Varian Vista MPX). Sodium and potassium of the digested samples (see above) were determined using a flame photometer (Eppendorf ELEX6361, Hamburg, Germany).

**RESULTS & DISCUSSION**

**VSEP performance in liquid digestate treatment**

Average macronutrient contents in the different process flows were analyzed. As expected, during the pre-treatment (rotating drum + screw press) most of the phosphorus (91%), calcium (96%) and magnesium (92%) was recovered in the separated thick fraction, which can be dried to an exportable, organic soil conditioner. In contrast, most of the nitrogen (57%), potassium (78%) and sodium (72%) ended up in the liquid fraction. The VSEP system aims to separate these valuable macronutrients into easily transportable concentrates, producing permeates low in nutrient contents that meet the Flemish legislation criteria for discharge into surface waters.

The permeate produced by one VSEP filtration step did not meet the Flemish discharge legislation criteria of 15 mg N l⁻¹ and 2 mg P l⁻¹. Nitrogen and phosphorus contents in the VSEP permeate produced by the 2nd filtration were low, although average concentrations were not below the discharge criteria. However, in the subsequent lagoon the average concentrations for nitrogen and phosphorus based on daily monitoring during the experimental period were 12±6 mg N l⁻¹ and 1.6±1.0 mg P l⁻¹, respectively, and thus met the discharge criteria. Furthermore, it was observed that the COD in the VSEP-permeates can reach high peaks related to the addition of citric acid (C₆H₈O₇) during acidic cleaning events. Nevertheless, the chemical oxygen demand in the lagoon (26±10 mg COD l⁻¹) was constantly below the Flemish discharge level of 125 mg COD l⁻¹ due to microbial breakdown of the organic matter and dilution with rainwater. Finally, it was observed that average concentrations of calcium, magnesium and sodium in the permeate pro-
duced by the 2nd filtration step were very low, in agreement with the low salt content (0.56 g salt kg\(^{-1}\) FW or 0.88 mS cm\(^{-1}\)) and total hardness (0.19 ± 0.12 D°H) of this process flow.

**Agricultural value of concentrates**

Membrane technology allows handlers to concentrate nutrients recovered in the liquid fraction of digestate in a small volume that can be transported to agricultural fields. Concentrates produced by the 1st membrane filtration step could potentially be re-used as inorganic fertilizers, rich in nitrogen and potassium. The nitrogen content was 7.3±1.6 kg N t\(^{-1}\) FW, comparable to that of conventional pig manure (5–10 kg N t\(^{-1}\) FW). The potassium content was 3.5±0.0 kg K\(_2\)O t\(^{-1}\) FW, which is lower than predicted literature data (6–12 kg K\(_2\)O t\(^{-1}\) FW), but slightly higher than that of conventional pig manure (3.3 kg K\(_2\)O t\(^{-1}\) FW). As expected, the amount of phosphorus in the concentrates was rather low, because most of the phosphorus ends up in the separated thick fraction during the pretreatment. Regarding the phosphorus restrictions that become more and more stringent in high-nutrient regions, the use of this phosphorus-poor fertilizer could benefit important advantages. Concentrates produced by the 2nd membrane filtration step were poor in macronutrients and have therefore little/no potential for re-use as a fertilizer. This flow is currently recycled within the process.

Although potassium is an important element for crop production, high ratios of potassium over nitrogen and phosphorus are not preferred in every agricultural sector. In particular, livestock farmers rather use potassium-poor fertilizers, because of the potential health risks for cattle (head illness) at high potassium fertilization (>50 t ha\(^{-1}\) year\(^{-1}\); Romheld and Kirkby, 2010). Also, high ratios of monovalent cations, such as K and Na, to divalent bases, such as Ca and Mg, may cause degradation of the soil structure, especially when soils are rich in clay. Hence, depending on the composition of the base fertilizer and the soil characteristics, more or less concentrate can be applied as mineral fertilizer, with a maximum advised dose of 70 kg K\(_2\)O ha\(^{-1}\) year\(^{-1}\) (Romheld and Kirkby, 2010). Furthermore, concentrates produced by the 1st membrane filtration could have higher salt contents (66 mS cm\(^{-1}\)) compared to conventional animal manure (30–50 mS cm\(^{-1}\)). This results in high salt/N ratios (±6) for this product. Too high salt contents can cause soil degradation and can dramatically reduce crop production. Therefore, when using concentrates in agriculture, it will also be important to pay attention to the salt doses per unit nitrogen that is applied to the soil. Extensive greenhouse and field testing will be required to investigate the impact of concentrates on soil and crop production.

**Economic value of concentrates**

Next to the potential ecological benefits, re-use of concentrates as a green fertilizer and/or soil conditioner in agriculture could also result in significant economic benefits. Nowadays, the anaerobic digestion plant has to pay high disposal or treatment costs for the off-set of the produced concentrates. In the meantime, prices for artificial mineral fertilizers are increasing and nutrient resources are depleting (Öborn et al., 2005; Vilalba et al., 2008). Re-use of valuable nutrients coming from digestate processing could therefore
also convert the digestate problem into an economic opportunity. The economic value of concentrates is calculated based on the current cost price for fossil based artificial fertilizers/soil conditioners (Table 1).

<table>
<thead>
<tr>
<th>Artificial fertilizer/Soil conditioner</th>
<th>Economic value (€ t⁻¹ FW)</th>
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<tbody>
<tr>
<td>Ammoniumnitrate (27% N)</td>
<td>165</td>
</tr>
<tr>
<td>Tripelsuperphosphate (46% P)</td>
<td>268</td>
</tr>
<tr>
<td>Potassium chloride (60% K)</td>
<td>365</td>
</tr>
<tr>
<td>Calciumoxide (71,5% Ca)</td>
<td>165</td>
</tr>
<tr>
<td>Kieserite (25% Mg)</td>
<td>260</td>
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The application of concentrates in agriculture could have a value of €6.3±1.1 t⁻¹ FW, if both nitrogen and potassium are appreciated by the agriculturist. If only nitrogen is appreciated, the economic value is €4.5±1.0 t⁻¹ FW, whereas it amounts to €1.8±0.1 t⁻¹ FW if only potassium is of relevance. Unlike as mineral fertilizers, these concentrates could also contain significant amounts of organic carbon (24±1%). Application of concentrates could therefore also have additional values in organic carbon recycling.

CONCLUSION

Removal efficiencies for N and P by two VSEP filtration steps were high, though not sufficient to continuously reach the Flemish legislation criteria for discharge into surface waters (15 mg N l⁻¹ and 2 mg P l⁻¹). Additional purification can occur in a subsequent lagoon, yet further optimization of the VSEP filtration system is advised. Concentrates produced by the 1st VSEP filtration step were rich in macronutrients and could potentially be re-used as a sustainable substitute for fossil-based mineral fertilizers. However, pot and field experiments are required to evaluate its impact on plant growth and soil quality. Re-use of nutrient rich concentrates produced by VSEP membrane filtration in a sustainable cradle-to-cradle approach, might so benefit the economic performance of anaerobic digestion in Flanders, thereby stimulating the production of bio-energy in frame of the 2020 objectives.

REFERENCES


