The ManureEcoMine pilot installation: advanced integration of technologies for the management of organics and nutrients in livestock waste

Cristina Pintucci, Marta Carballa, Sam Varga, Jimena Sarli, Lai Peng, Johannes Bousek, Chiara Pedizzi, Maël Ruscalleda, Elena Tarragó, Delphine Prat, Giovanni Colica, Merijn Picavet, Joop Colsen, Oscar Benito, Marios Balaguer, Sebastià Puig, Juan M. Lema, Jesús Colprim, Werner Fuchs and Siegfried E. Vlaeminck

ABSTRACT

Manure represents an exquisite mining opportunity for nutrient recovery (nitrogen and phosphorus), and for their reuse as renewable fertilisers. The ManureEcoMine proposes an integrated approach of technologies, operated in a pilot-scale installation treating swine manure (83.7%) and Ecofrit® (16.3%), a mix of vegetable residues. Thermophilic anaerobic digestion was performed for 150 days, the final organic loading rate was 4.6 kgCOD m⁻³ d⁻¹, with a biogas production rate of 1.4 Nm³ m⁻³ d⁻¹. The digester was coupled to an ammonia side-stream stripping column and a scrubbing unit for free ammonia inhibition reduction in the digester, and nitrogen recovery as ammonium sulphate. The stripped digestate was recirculated daily in the digester for 15 days (68% of the digester volume), increasing the gas production rate by 27%. Following a decanter centrifuge, the digestate liquid fraction was treated with an ultrafiltration membrane. The filtrate was fed into a struvite reactor, with a phosphorus recovery efficiency of 83% (as orthophosphate). Acidification of digestate could increment the soluble orthophosphate concentration up to four times, enhancing phosphorus enrichment in the liquid fraction and its recovery via struvite. A synergistic combination of manure processing steps was demonstrated to be technologically feasible to upgrade livestock waste into refined, concentrated fertilisers.

Key words | ammonia stripping, biogas, co-digestion, nitrogen recovery, phosphorus recovery, piggery waste, resource recovery, ultrafiltration

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INTRODUCTION

Intensive agriculture is heavily dependent on the use of synthetic fertilisers for sustaining the increasing food and feed production requests. Total manufactured fertiliser consumption in the European Union (EU) was estimated at 11 million tonnes of nitrogen (N) and 1.1 million tonnes of phosphorus (P) in 2014 (Eurostat 2016). Consumption of P has raised concerns worldwide, since its depletion is estimated to occur by 2060–2110 (Cordell et al. 2009). For this reason, economically feasible processes to recover P through non-conventional P sources are of paramount importance for sustainable development of the human population (Kataki et al. 2016). In this context, manure represents an exquisite mining source, since its nutrient content is estimated to be in the range of 2.1–6.7 g N L⁻¹ and 0.2–1.6 g P L⁻¹ in pig waste (Mondor et al. 2008; Barret et al. 2015), and 2.6–5.3 g N L⁻¹ and 0.3–0.9 g P L⁻¹ (Barret et al. 2015) in cow manure, and as it is the major waste flow of nutrients through our economy (Coppens et al. 2016).

Despite this opportunity, it has been evaluated that only 7.8% of the manure produced annually in the EU-27 member countries is processed in some way (Foged et al. 2011). Current manure treatments are mainly related to removing N and P without advanced nutrient recovery, e.g. through anaerobic digestion (Page et al. 2014), biological nitrogen removal processes (Zhu et al. 2008) and composting of manure or manure digestate (Bernal et al. 2009). Over the past 10 years, several innovative technologies have been implemented for the processing of wastewater generated from diverse sectors. These technologies are characterised by high recovery efficiencies of refined nutrients, yet an important demonstration gap for manure treatment needs to be filled in order to upgrade manure to a secondary raw material. Struvite (MgNH₄PO₄·6H₂O) recovery is one of these technologies, which has been applied to several kind of wastes, including manure (Katakı et al. 2016). Struvite is a naturally occurring mineral that slowly releases nutrients at a rate suitable for crop uptake (Tao et al. 2016). ManureEcoMine proposes a synergistic combination of processing technologies for the recovery of refined manure nutrients, aiming at reducing the environmental impact of animal husbandry. Well known technologies such as thermophilic anaerobic digestion are coupled to nutrient recovery steps like ammonia stripping and struvite precipitation. Ammonia stripping is a relatively simple process already applied to several types of waste (Serna-Masa et al. 2014). Coupled with an anaerobic digester as a side loop process, it reduces ammonia inhibition of the digester biomas, thus allowing higher biogas production rates (GPR). Siegrist et al. (2005) demonstrated the feasibility of coupling an ammonia stripper to a mesophilic anaerobic digester working on slaughterhouse wastes, for reducing the free ammonia (FA) levels in the digester. However, no nutrient recovery was attained, since the FA in the stripped air was catalytically oxidised. In the ManureEcoMine process, the stripped ammonia is recovered through an absorption process using a strong acid such as sulphuric acid, leading to the recovery of ammonium sulphate ((NH₄)₂SO₄), which can be used as agricultural fertiliser (Yuan et al. 2016).

Several manure processes have been studied at pilot scale (Cavinato et al. 2010; Scaglione et al. 2013), yet combination of such technologies has not been demonstrated so far outside of the laboratory. The aim of ManureEcoMine was to optimise individual technologies for manure processing, as well as to demonstrate their synergistic combination at pilot scale.

In this work, the results of the ManureEcoMine pilot installation are presented. The plant was operated in the Netherlands for 6 months in 2015, treating a mixture of swine manure and vegetable waste.
MATERIALS AND METHODS

Manure and co-substrates

Swine manure was collected by the company Maatschap Van Alphen (Axel, The Netherlands) and processed together with a co-substrate largely available in the operation area (Zeeland-Flanders, The Netherlands) throughout the year. Ecofrit®, a mix of vegetable residues from supermarkets, was selected as a potential co-substrate, and analysed for its composition together with swine manure. The substrates were stored indoors in separate buffer tanks, which were loaded weekly. Before loading the buffer tanks, the manure was sieved and the Ecofrit® was shredded and sieved, in order to counteract clogging in the feed line. The characterisation of the feeding was evaluated on the shredded and sieved substrates, and the average composition is shown in Table 1. Compared to the swine manure composition present in the literature (Mondor et al. 2008; Barret et al. 2013), the livestock substrate used in the ManureEcoMine pilot plant had a higher concentration of both total nitrogen (TN) and total phosphorus (TP).

PILOT-SCALE INSTALLATION

The ManureEcoMine process carried out with the pilot installation is shown in Figure 1.

Table 1 | Feeding composition of the thermophilic anaerobic digester of the ManureEcoMine pilot installation

<table>
<thead>
<tr>
<th>Component</th>
<th>Pig manure (g kg⁻¹)</th>
<th>Ecofrit® (g kg⁻¹)</th>
<th>Feeding mixture (g kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DM</td>
<td>86.0 ± 11.0</td>
<td>191.4 ± 14.7</td>
<td>107.1 ± 25.9</td>
</tr>
<tr>
<td>ODM</td>
<td>60.0 ± 8.0</td>
<td>144.9 ± 14.6</td>
<td>77.0 ± 9.3</td>
</tr>
<tr>
<td>COD</td>
<td>85.4 ± 20.9</td>
<td>239.0 ± 14.5</td>
<td>114.7 ± 19.6</td>
</tr>
<tr>
<td>COD₄</td>
<td>40.6 ± 16.7</td>
<td>111.8 ± 3.8</td>
<td>54.8 ± 14.1</td>
</tr>
<tr>
<td>TN</td>
<td>6.9 ± 1.2</td>
<td>6.7 ± 0.5</td>
<td>6.9 ± 1.1</td>
</tr>
<tr>
<td>NH₄-N</td>
<td>4.5 ± 0.6</td>
<td>1.6 ± 0.2</td>
<td>3.9 ± 0.5</td>
</tr>
<tr>
<td>TP</td>
<td>1.9 ± 0.4</td>
<td>2.4 ± 0.3</td>
<td>2.0 ± 0.4</td>
</tr>
<tr>
<td>PO₄³⁻-P</td>
<td>1.7 ± 0.4</td>
<td>2.1 ± 0.2</td>
<td>1.7 ± 0.3</td>
</tr>
</tbody>
</table>

The composition of the feeding mixture was calculated starting from the composition of the raw materials (pig manure and Ecofrit®) fed daily into the anaerobic digester. DM: dry matter; ODM: organic dry matter; COD: chemical oxygen demand; COD₄: chemical oxygen demand solubile; TN: total nitrogen; NH₄-N: ammonium nitrogen; TP: total phosphorus; PO₄³⁻-P: orthophosphates. n – number of replicates analysed.

Thermophilic anaerobic co-digestion

Thermophilic anaerobic co-digestion was performed in a 3 m³, insulated, stirred, stainless-steel tank, at a constant temperature of 51 ± 2°C. The temperature was continuously measured on line. The digester was inoculated with thermophilic biomass (Ecofuels, Well, The Netherlands) and fed daily, with an influent flow rate increasing over time, pursuing an increasing organic loading rate (OLR) composed of 83.7 ± 14.4% swine manure and 16.3 ± 14.4% Ecofrit®. Digestate was analysed daily for its composition, as dry matter (DM), organic dry matter (ODM), chemical oxygen demand (COD), TN, ammonium nitrogen (NH₄-N), TP, orthophosphates (PO₄³⁻-P), pH, alkalinity, temperature and volatile fatty acids (VFA). For additional information, see supplementary material.

Ammonia stripping/absorption

Ammonia removal from the manure digestate was achieved through a side stream stripping unit. Air was supplied in the column at a flow rate of 75 L (air) L⁻¹ (digestate) h⁻¹. The percentage between recycled and fresh air was varied in order to identify the optimal recirculation ratio for the unit’s operation. Three different temperature levels (55°C, 60°C and 65°C) were tested, and their effects on the process were assessed. For each test, samples at different points in time (from 0 h to 24 h) were taken, in order to identify the best conditions with respect to ammonia removal and process duration. The concentration of TN and NH₄-N was analysed during each stripping batch. After ammonia stripping, the stripped digestate was recirculated back into the digester. The air deriving from the stripping process, containing high levels of ammonia, was circulated over a scrubber for the recovery of nitrogen as (NH₄)₂SO₄. The scrubbing column was operated in counter current mode. H₂SO₄ (40% v/v) was used as the scrubbing medium, and was sprayed from the top of the column. The ammonia-free air exited from the top of the column. A part of it was recovered (recirculated into the stripper), while the remaining air was released into the environment. The pH of the scrubbing liquid was maintained at 3.1 ± 0.1 by pumping fresh acid solution into the scrubbing system. For additional information, see supplementary material.

Decanter centrifuge

The digestate exiting the thermophilic digester was collected in a digester effluent buffer tank. Solid/liquid (S/L)
separation was performed using a decanter centrifuge (MD-60, Lemitec Gmbh). Tests were carried out to optimise the dewatering process. In each test, different parameters were changed: (i) hydraulic retention time (HRT) of 23.5 s, 28 s, 34 s, 35 s, 42.5 s, 46 s and 56.5 s, and (ii) g-force (716 g, 1,353 g, 1,500 g, 2,191 g and 3,231 g). For additional information, see supplementary material.

**Ultrafiltration**

The liquid fraction produced by the decanter centrifuge (centrate) was fed to an ultrafiltration (UF) system (UF F0701 Pilot skid, Likuid Nanotek). Ceramic membranes with 100 nm pore size were used, and the total filtering surface was 1.08 m². Through the pressure applied, the permeate passed the membrane pores, while the retentate was recirculated back into the influent buffer tank, concentrating the influent. When the UF performance was hindered (i.e. there was a drop in permeate flow), the concentrated retentate was sent back to the feed system of the digester. Membrane cleanings were performed according to the supplier’s guidelines, subsequently with 1% NaOH (v/v) and 0.5% HNO₃ solutions (v/v), intermediated by rinsing with water. For additional information, see supplementary material.

**Struvite precipitation**

The UF permeate was used as substrate for the struvite (MgNH₄PO₄·6H₂O) reactor. To ensure flexibility in the reactor inflow, a struvite influent buffer tank was installed. The struvite reactor had a working volume of 100 L and was based on the one described by Tarrago et al. (2016). To reach the optimal pH (8.5) for struvite precipitation, CO₂ was stripped out by aeration. To ensure that magnesium (Mg²⁺) was not rate limiting the precipitation process, it was overdosed 60% over the stoichiometrically needed amount. Magnesium sulphate (MgSO₄) and magnesium hydroxide (Mg(OH)₂) were used separately for Mg²⁺ dosing, aiming to identify the optimal chemical for the process operation. In addition, centrate (without UF treatment) was also tested as influent for the struvite precipitation. In order to identify the optimal time for the struvite precipitation, batch tests were performed from 2.5 to 3.5 hours and from 3 to 6 hours, when dosing MgSO₄ and Mg(OH)₂, respectively. For additional information, see supplementary material.

**Enhanced phosphorus recovery through acidification**

Digestate acidification was performed adding H₂SO₄ (60% v/v) in the decanter centrifuge influent buffer tank.
The acid was dosed at 0.02 and 0.04 gH₂SO₄ g⁻¹ digestate, lowering the pH from 8 to 6 and 4, respectively. For additional information, see supplementary material.

Analytical procedures

Hach-Lange spectrophotometric tests were used to measure COD (LCK014; LCK514; LCK614), soluble chemical oxygen demand (CODs) (LCK14; LCK514; LCK358; LCK014), ammonium (NH₄⁻-N) (LCK302; LCK342), TN (LCK338; LCK238), TP (LCK350; LCK339) and orthophosphates (PO₄³⁻-P) (LCK350; LCK303) at the pilot plant site. DM and ODM were determined through gravimetrical analyses (CEN/TC 2003). Temperature and pH measurements were carried out using a WTW pH meter 340 with a SenTix 41-3 pH electrode. VFA and alkalinity measurements were carried out using the method of Kapp through 3 point titration (5; 4.3; 4) (Lahav & Morgan 2004). Analyses of the biogas composition were carried out by the Avecom company (Wondelgem, Belgium).

RESULTS AND DISCUSSION

Start-up of the thermophilic anaerobic co-digestion

The thermophilic anaerobic digester was operated for 150 days and its performance in terms of OLR and GPR is shown in Figure 2(a). After inoculation, the thermophilic biomass was left to acclimate to the new environment for 2 days without feeding. Later, a mixture composed of 84% pig manure and 16% Ecofrit® was fed to the reactor with a HRT of 170 days, in order to reach an OLR of 0.8 kg COD m⁻³ d⁻¹. After 5 days, the OLR was increased to 1.5 kg COD m⁻³ d⁻¹, keeping the swine manure/Ecofrit® ratio unaltered and decreasing the HRT to 73 days. On day 17, the OLR was raised to 2.0 kg COD m⁻³ d⁻¹ and then step-wise increased over time, reaching the final value of 4.6 kg COD m⁻³ d⁻¹ on day 149, corresponding to an HRT of 22 days. The GPR varied accordingly, reaching the final value of 1.4 m³ m⁻³ d⁻¹. The biogas had an average composition of 65.9% CH₄ and 33.9% CO₂. This quantity corresponded to an energy of 24 kWh d⁻¹ (if methane is used to recover heat only), which was enough to heat the feeding substrates up to 51°C and maintain a stable temperature in the digester (the total energy required was around 10 kWh d⁻¹). The heat excess could be used for the other applications within manure processing, e.g. digestate ammonia stripping (required energy 10–15 kWh d⁻¹, depending on the temperature used in the ammonia stripping process and amount of air purged). Dissipation losses were not considered in either reactor (thermophilic digester and side-stream stripping column). Further investigations of the heat reuse within the ManureEcoMine cycle were not considered in this study. The stability of the digestion was also monitored through parameters like VFA concentration, FA concentration and Ripley index (Ripley et al. 1986). The results are displayed in Figure 2(b).

Ripley et al. (1986) reported that values of this index below 0.3 are an indication of stable digestion. Ripley index values were generally below or equal to the 0.3. Even though the Ripley index alone is insufficient to predict the stability of the system (Carballa et al. 2011), its trend can give an indication of the digestion performance. The VFA concentration increased noticeably between days 117 and 130, when the OLR was abruptly two fold higher, but then eventually diminished, reaching stable low values during the last days of operation. The presence of these intermediate digestion products was constant throughout the operation but their concentration was never alarming considering also the stable pH at 7.72 ± 0.07 (Figure S2, available with the online version of this paper). FA concentration varied between 0.4 and 0.7 kgN m⁻³, values that are below inhibition for a thermophilic biomass used to work with N-rich substrates (Rajagopal et al. 2013).

During the digester operation, several fluctuations can be identified (Figure 2(a) and 2(b)):

1. Days 45–55: decrease of the OLR of 35%, and consequent drop of the GPR. During this period, 4 batches of stripped digestate were recirculated in the digester and the OLR was reduced in order not to burden the digester operation. As a consequence, the VFA concentration decreased as well. The GPR decreased to 0.47 m³ m⁻³ d⁻¹ at day 53, to increase again at day 55 (0.74 m³ m⁻³ d⁻¹). FA values slightly decreased in the same period (14%), however always remaining in the range of 0.4–0.6 kgN m⁻³.

2. Days 85–95: in this period, the shredder pump of the feeding was upgraded and reinstalled. As a consequence, a 42% drop in the OLR occurred between days 88 and 89. The feeding issue was promptly solved, as can be seen by the increase in the OLR up to its former values (3.6 kgCOD m⁻³ d⁻¹) in the following days. As a consequence of the OLR drop, the GPR decreased by about 50%.
3. Days 105–122: this period was characterised by a reduced OLR (61% less than the value kept in the previous days). This drop was caused by issues with the feeding pump, eventually leading to manual feeding of the digester until day 120, and causing a further reduction in the OLR. The VFA content initially followed the OLR rate, with a steep decrease until day 110 (minimum value 38 meq L\(^{-1}\)) and a fast increase up to 95 meq L\(^{-1}\) at day 120. As a consequence, a 70% drop in the GPR was recorded.

4. Days 138–150: the last period of the anaerobic digester operation was characterised by a slight increase in the OLR (from 3.8 to 4.6 kg COD m\(^{-3}\) d\(^{-1}\)), which led to an increase in the GPR by 0.24 m\(^3\) m\(^{-3}\) d\(^{-1}\), reaching the final value of

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**Figure 2** | Thermophilic anaerobic digestion: (a) evolution of OLR and GPR; (b) trends in FA concentration, VFA concentration and Ripley index.
1.4 m$^3$ m$^{-3}$ d$^{-1}$. The Ripley index (0.12 ± 0.02) indicated stable operation over the last period of digester operation.

**Ammonia stripping/adsorption and its effect on anaerobic digestion**

**Optimisation of the stripping conditions**

In the ManureEcoMine pilot installation, ammonia stripping was implemented as a side-stream unit to the digester, with batches of digestate recirculated over the stripper. Optimised operational conditions (nitrogen removal in the stripper and recovery in the scrubber) were identified through tests carried out at the pilot plant. The ammonia stripping process was performed using air as the strip gas at different recirculation ratios: higher recirculation is beneficial in terms of energy savings. However, as demonstrated by Bousek et al. (2016), an increase of CO$_2$ content in the stripping gas leads to a considerable loss in terms of stripping performance. Therefore, an optimised operation point needs to be found in which both stripping efficiency and the heat required are within acceptable limits.

An important feature in the operation of the ammonia stripper is represented by the air supply needed for performing the ManureEcoMine treatment process. It is dependent on total air flow and the recirculation ratio. Tests employing different air circulation ratios were carried out aiming to reduce the input of fresh air. Figure 3(a) shows the ammonia stripping trends when operating at 25% and 75% air recirculation at 60°C. As expected, the lower the air recirculation, the higher the ammonia removal efficiency, corresponding to a 180 mgN L$^{-1}$ reduction when recirculating 75% of the air. This percentage was due to the higher amount of CO$_2$ present in the recirculated air. Anyway, the effect on the removal efficiency was limited: in a 6-hour batch, the stripping efficiencies were 39% and 35% when recirculating 25% and 75% air, respectively. Since the ManureEcoMine pilot installation aims to prove the feasibility of combined processes for manure processing in a nutrient-oriented perspective, it was considered that 75% air recirculation provided sufficient ammonia removal, along with energy saving for a reduced heat loss through the purging of air saturated with water vapour.

Ammonia removal through stripping is affected by the temperature. To identify the best operating condition, three different temperatures (55°C, 60°C and 65°C) were tested in the pilot installation (Figure 3(b)). As expected, the results confirmed that the higher the temperature of the ammonia stripping process, the faster the ammonia removal. Ammonia removal efficiencies were 28%, 36% and 47% at 55°C, 60°C and 65°C, respectively, when stripping over a period of 6 hours. Operating the stripping for a longer time (12 h), resulted in an ammonia removal of 50%, 59% and 69% when at 55°C, 60°C and 65°C, respectively (Figure 3(b)). From these results, stripping for 12 h at 65°C appeared to be the better condition, however a stripping temperature of 55°C and a time of 6 hours were selected, avoiding possible negative local effects on the anaerobic digester, due to the recirculation of digestate at a temperature too high above that of the digester. Operating with full scale plants, this impact is considered to be negligible. A batch time of 6 h reduced the evaporation losses (3% when operating the stripper at 55°C for 6 h compared to 14% at 12 h and 21% at 24 h, at 65°C) (Figure S3, available with the online version of this paper).

**Effect of ammonia stripping on anaerobic digestion**

Ammonia side stripping was performed batch-wise, firstly identifying the optimal operational conditions, then coupling it to the thermophilic digester and recirculating the stripped digestate into the reactor. Between day 123 and day 137, treated digestate (137 kg) was daily recirculated into the digester, for a total amount of 2,055 kg (68.5% of the digester volume) over the indicated period. In order to avoid burdening the digester stability, the OLR was kept constant at a value of 3.8 ± 0.1 kg COD m$^{-3}$ d$^{-1}$. The effect of daily treated digestate recirculation into the digester is shown in Figure 2(a). In the reference period, VFA concentration decreased (33%) while the GPR had a 27% increase. In this time interval, the FA concentration decreased by 28% as a result of the recirculation of the treated digestate. At the same time, the Ripley index was on average 0.30, indicating possible system instability, probably due to the technical issues with the feeding pump that occurred before day 120. Finally, 57% of the COD was converted into biogas during the stabilised digester operation, corresponding to the phase in which digestate was recirculated over the ammonia stripping and scrubbing unit.

**Digestate S/L separation**

Besides volume reduction and simplified stream handling, the aim of the S/L separation process was to obtain a liquid fraction that could be used as influent for the struvite reactor. Ideally, the lower the solids content in the struvite reactor influent, the higher the purity of the recovered struvite. Therefore, a two-step S/L separation set-up (decanter centrifuge and UF with ceramic membranes) was implemented.
S/L separation with a decanter centrifuge

For the first S/L step a decanter centrifuge was used. The HRT and the gravitational force \((g)\) play a crucial role in the solids separation in waste material, thus parameter optimisation experiments were conducted. A minimal HRT value of 30 s was required to remove at least 60% of the solids, while a 68% reduction of total suspended solids (TSS) was obtained with 35 s HRT and 1,353 g (Figure S4, available with the online version of this paper). Based on these observations, several tests were carried out at an HRT of 35 s, varying the g-force (716 g, 1,353 g, 2,191 g and 3,231 g) and measuring the

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**Figure 3** | Ammonia stripper: (a) effect of air recirculation ratio on the ammonium content and removal at 60°C; (b) effect of temperature on the ammonium content and removal at air recirculation of 75%. Each variation was measured once.
retention in the solid fraction of several parameters (Figure S5, available with the online version of this paper). The higher the g-force, the more compounds were retained in the solid fraction. On the other hand, this did not affect the TN and NH₄⁺-N, indicating that a large fraction of nitrogen was dissolved. The high amount of TP and PO₄³⁻-P in the solid fraction was due to the fact that P in manure is generally bound to solids, thus its retention is parallel to the TSS.

In the ManureEcoMine installation, the operational settings chosen were 1,500 g and 46 s HRT, which enabled a 68% retention of TSS. At the tested conditions, the DM and ODM retentions in the solid fraction were 50% and 58%, respectively, with a retention of 82% and 84% of phosphate as TP and PO₄³⁻-P, respectively (Figure 4).

**Centrate filtration with ceramic UF membranes**

Since struvite precipitation is affected by the solids content, an additional separation step was included in the ManureEcoMine process scheme prior to struvite recovery. Operating the UF module at the best efficiency point, permeate fluxes between 15 and 30 L h⁻¹ m⁻² were obtained, with a resulting cross flow velocity of 4 m s⁻¹. The permeate flux reduced significantly during the process operation, probably as result of membrane fouling due to digestate cake accumulation. Regularly timed backwashes of the membranes allowed restoration of the flux.

Through the UF step, DM and ODM retentions from the liquid stream into the solid fraction (retentate) of 40% and 52%, respectively (Figure 4), were attained. Similar results were obtained in terms of TP and PO₄³⁻-P, for which a reduction in the effluent of 57% and 50% resulted, respectively. These results confirmed those of the decanter centrifuge, indicating that most of the phosphorus present in the centrate was attached to the now retained solids. Moreover, precipitates were present on the membranes (possibly struvite or calcium phosphates), therefore not all soluble PO₄³⁻-P was able to pass through the membranes.

The overall S/L separation (decanter centrifuge and membrane UF) led to a solids retention of 69% and 78% of DM and ODM, respectively, but on the other hand it resulted in a low P concentration in the final liquid stream, which had 7% and 8% of TP and PO₄³⁻-P present in the centrate, respectively.

**Struvite recovery from permeate and centrate**

The UF permeate was used as influent to the struvite reactor. Batch tests were performed dosing MgSO₄ or Mg(OH)₂ as the varying Mg²⁺ source. When dosing Mg(OH)₂, P recovery as TP and PO₄³⁻-P increased with the batch duration (Figure S5): the precipitation efficiency increased by 30% (both for TP and PO₄³⁻-P recovery) when doubling the
precipitation time (from 3 h to 6 h). Similar results were obtained dosing MgSO\(_4\) (Figure S6, available with the online version of this paper).

Small amounts of DM, ODM and COD (on average 7%, 13% and 29%, respectively) were co-precipitated with the struvite (Figure 5). However, organic contamination in the struvite could contribute positively to its fertilising effects (Palm et al. 1997).

Regarding ammonium, on average, significant removal of around 80 mM NH\(_4^+\)-N was observed. In molar quantities, around 3.5 mM of P was removed, thus not all N was removed via struvite formation. Based on the assumption that all removed phosphate was recovered as struvite, more than 80% of NH\(_4^+\)-N (and TN) was removed in a different way, i.e. by air stripping. To reduce this nitrogen loss, the off-gas generated during the struvite batches may be circulated into the ammonia scrubber, thus increasing the amount of nitrogen recovered as (NH\(_4\))\(_2\)SO\(_4\).

Additional tests were performed using manure centrate as the influent of the struvite reactor (Figure S7, available with the online version of this paper). In this case, the precipitation efficiency was reduced to 15% and 19% as TP and PO\(_4^{3-}\)-P, respectively. This reduction could be attributed to the higher concentration of solids in the centrate than in the permeate. The content of DM and ODM in the centrate was 1.8 and 2.9 times higher than in the permeate, respectively. The presence of suspended particles in the influent used for struvite precipitation can act as the nuclei for heterogeneous nucleation (Liu et al. 2013). Nevertheless, higher quantities (>1,000 mg L\(^{-1}\)) could interfere in struvite precipitation, thus the solids present in the centrate were preventing the formation of struvite.

### Increased P recovery by acidification

The low P concentration (97 ± 4 mgPO\(_4^{3-}\)-P L\(^{-1}\)) in the digestate liquid streams (centrate and permeate) represented a limitation for efficient phosphorus recovery in the pilot installation. To counteract the high P retention in the solid fraction during S/L separation, acidification of the manure digestate can be implemented in the ManureEcoMine technology structure. Preliminary laboratory tests performed on manure digestate confirmed that the phosphorus release into the centrate increased as the pH decreased from 8 to 4 (Figure S8, available with the online version of this paper). Digestate acidification was implemented at pilot level, and the pH was reduced to 6 prior to decanter centrifuge separation. The pH reduction to 6 was found to be most favourable for the release of orthophosphate in the centrate, considering the high increase in phosphate and the reduced acid dose compared to pH 4. At pH 6, the concentrations of TP and PO\(_4^{3-}\)-P in the centrate increased by 2.7 and 4 fold, respectively, compared to non acidified centrate. As a consequence, the retention of phosphorus in the liquid fraction after centrifugation increased up to 64% and 74% for TP and PO\(_4^{3-}\)-P (Figure 6).

Biological acidification could represent an economically friendly way to increase the soluble P content in digestate. Studies on this process are lacking in the literature, however...
Hjorth et al. (2015) have demonstrated the feasibility of using glucose on raw manure for bioacidification: pH reduction was achieved through conversion of carbohydrates to lactic acid by indigenous lactic acid producing bacteria. To reduce the costs, residues with high carbohydrate content (e.g. fruit processing waste) could be used as a glucose source for bioacidification.

Overall process considerations

The complete ManureEcoMine cycle enabled the recovery of nutrients as fertilisers while upgrading swine manure from waste to resource. The overall mass balance of the process has been assessed considering the optimised settings identified during the MEM pilot testing, and summarised in Figure 7(a).
The main constraint of the ManureEcoMine manure process was represented by the P retention during S/L separation, which can be overcome by digestate acidification prior to the decanter centrifuge (Figure 7(b)). Acidification of manure digestate allowed a considerable reduction (68%) of TP in the solids (centrifuge cake and UF retentate), and a consequent increase (87%) of P recovered as struvite, compared with the non-acidified process. However, the impact on the buffer capacity of the stream is related to P recovery through struvite and successive final biological removal.

The final step of the ManureEcoMine technology is planned as biological nitrogen removal, i.e. nitrification/denitrification, after the struvite recovery unit. Scaglione et al. (2013) reported that 80% N can be removed from liquid digestate of swine and poultry manure mixed with agricultural wastes using a sequencing batch reactor (SBR) nitrification/denitrification. To provide the biological process with the needed COD/N ratio in the influent stream, external C sources can be added to the influent. As an example, Kulikowska & Bernat (2013) performed nitrification/denitrification on landfill leachate in an SBR fed with sodium acetate and glycerine. Glycerine generated as a by-product, e.g. from oil production industries, could be dosed during nitrification/denitrification to reduce the operational costs. When implementing a short-cut biological N removal, i.e. nitrification/denitrification, in the ManureEcoMine process (Figure 7(b)), the 21% of the TN fed into the process is biologically converted into N₂, with an 80% reduction of the TN present in the final irrigation water.

The overall ManureEcoMine process offers an opportunity to recover refined fertilisers, as opposed to a baseline manure treatment scenario targeting a nutrient-poor effluent, e.g. based on centrifugation, composting of the P-rich solid fraction, and N removal from the liquid fraction (nitrification/denitrification). ManureEcoMine, including manure digestate acidification and final shortcut nitrogen removal, would cost about three times more than the baseline scenario (EUR/ton manure treated), in a preliminary estimation of capital and operational expenditures. However, if the fertilisers can be marketed at 2 €/kgP (struvite) and 0.85 €/kgN (ammonium sulphate), the current prices of synthetic fertilisers, then the overall cost balance would be only slightly higher than the baseline scenario.

CONCLUSIONS

The ManureEcoMine manure processing approach allows the reduction of the environmental burden associated with nutrients leaching into surface water, by reducing and recovering nitrogen and phosphate. The overall process was demonstrated at pilot scale for 6 months, where swine manure and Ecofrit® were daily fed into the installation. Ammonia side stream stripping associated to a thermophilic anaerobic digester reduced the likelihood of ammonia inhibition, while increasing the GPR when recirculating batches of digestate over a stripper. Struvite precipitation enabled the recovery of phosphorus from the pilot plant’s effluent after the UF. Through digestate acidification, phosphorus release into the centrate was achieved and resulted in an important optimisation of the process. ManureEcoMine showed as a valuable approach for the recovery and upgrading of manure nutrients as agricultural fertilisers and crop enhancing products.

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