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

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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 CH_4 production of 1.4 Nm^3 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 4 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 of 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.* 2011). For this reason, economically feasible processes to recover P through non-conventional P sources are of paramount importance for a sustainable development of human population (Kataki *et al.* 2016). In this context, manure represents an exquisite mining source, since its nutrient content is estimated in the range of 2.1–6.7 gN L^{-1} and 0.2–1.6 gP L^{-1} in pig waste (Mondor *et al.* 2008; Barret *et al.* 2013), and 2.6–5.3 gN L^{-1} and 0.3–0.9 gP L^{-1} (Barret *et al.* 2013) 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 yearly produced in the EU-27 member countries is processed in some way (Foged *et al.* 2011). Current manure treatments are mainly related to remove 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 characterized by high recovery efficiencies of refined nutrients, yet an important demonstration gap for manure treatment needs to be filled up in order to upgrade manure to a secondary raw material. Struvite ($MgNH_4PO_4 \cdot 6H_2O$) recovery is one of these technologies, which has been applied to several kind of wastes, including manure

(Kataki *et al.* 2016). Struvite is a naturally occurring mineral which 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 biomass 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 ($(NH_4)_2SO_4$), 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 laboratory. The aim of ManureEcoMine was to optimise individual technologies for manure processing, as well as to demonstrate its 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.

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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 potential co-substrate, and analysed for its composition together with swine manure. The substrates were stored indoor in separate buffer tanks which were loaded weekly. Before loading the buffer tanks, manure was sieved and 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, the average composition is showed in Table 1. Compared to the swine manure composition present in literature (Mondor *et al.* 2008; Barret *et al.* 2013), the livestock substrate used in the ManureEcoMine pilot plant had 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

		Pig manure ($n = 16$)	Ecofrit® ($n = 9$)	Feeding mixture ($n = 9$)
DM	g kg^{-1}	86.0 ± 11.0	191.4 ± 14.7	107.1 ± 25.9
ODM	g kg^{-1}	60.0 ± 8.0	144.9 ± 14.6	77.0 ± 9.3
COD	g kg^{-1}	83.4 ± 20.9	239.0 ± 14.5	114.7 ± 19.6
COD$_s$	g kg^{-1}	40.6 ± 16.7	111.8 ± 3.8	54.8 ± 14.1
TN	gN kg^{-1}	6.9 ± 1.2	6.7 ± 0.5	6.9 ± 1.1
NH$_4^+$-N	gN kg^{-1}	4.5 ± 0.6	1.6 ± 0.2	3.9 ± 0.5
TP	gP kg^{-1}	1.9 ± 0.4	2.4 ± 0.3	2.0 ± 0.4
PO$_4^{3-}$-P	gP kg^{-1}	1.7 ± 0.4	2.1 ± 0.2	1.7 ± 0.3

The composition of the feeding mixture was calculated starting from the composition of the raw materials (pig manure and Ecofrit®) daily fed in the anaerobic digester.
DM: dry matter; ODM: organic dry matter; COD: chemical oxygen demand; COD$_s$: chemical oxygen demand soluble; TN: total nitrogen; NH$_4^+$-N: ammonium nitrogen; TP: total phosphorus; PO$_4^{3-}$-P: orthophosphates. $n =$ number of replicates analysed.

Thermophilic anaerobic co-digestion

Thermophilic anaerobic co-digestion was performed in a 3 m^3, insulated, stirred, stainless-steel tank, at a constant temperature of $51 \pm 2 \,^{\circ}\text{C}$. The temperature was continuously measured on line. The digester was inoculated with thermophilic biomass (Ecofuels, Well, the Netherlands) and daily fed, with an influent flowrate increasing over time pursuing an increasing organic loading rate (OLR), composed by $83.7 \pm 14.4\%$ of swine manure and $16.3 \pm 14.4\%$ of Ecofrit®. Digestate was analysed daily for its composition, as dry matter (DM), organic dry matter (ODM), chemical oxygen demand (COD), TN, ammonium nitrogen (NH$_4^+$-N), TP, orthophosphates (PO$_4^{3-}$-P), pH, alkalinity, temperature and volatile fatty acids (VFA). For additional information, see supplementary material.

Ammonia stripping/absorption

Ammonia removal from manure digestate was operated 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 operation. Three different temperature levels ($55 \,^{\circ}\text{C}$, $60 \,^{\circ}\text{C}$ and $65 \,^{\circ}\text{C}$) were tested, and their effects on the process were assessed. For each test, samples at different points of 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 NH$_4^+$-N was analysed during each stripping batch. After ammonia stripping, the stripped digestate was recirculated back in the digester. The air deriving from the stripping process and containing high levels of ammonia, was circulated over a scrubber for the recovery of ammonia as (NH$_4$)$_2$SO$_4$. The scrubbing column was operated in counter current mode. H$_2$SO$_4$ (40% v/v) was used as scrubbing medium, which 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)

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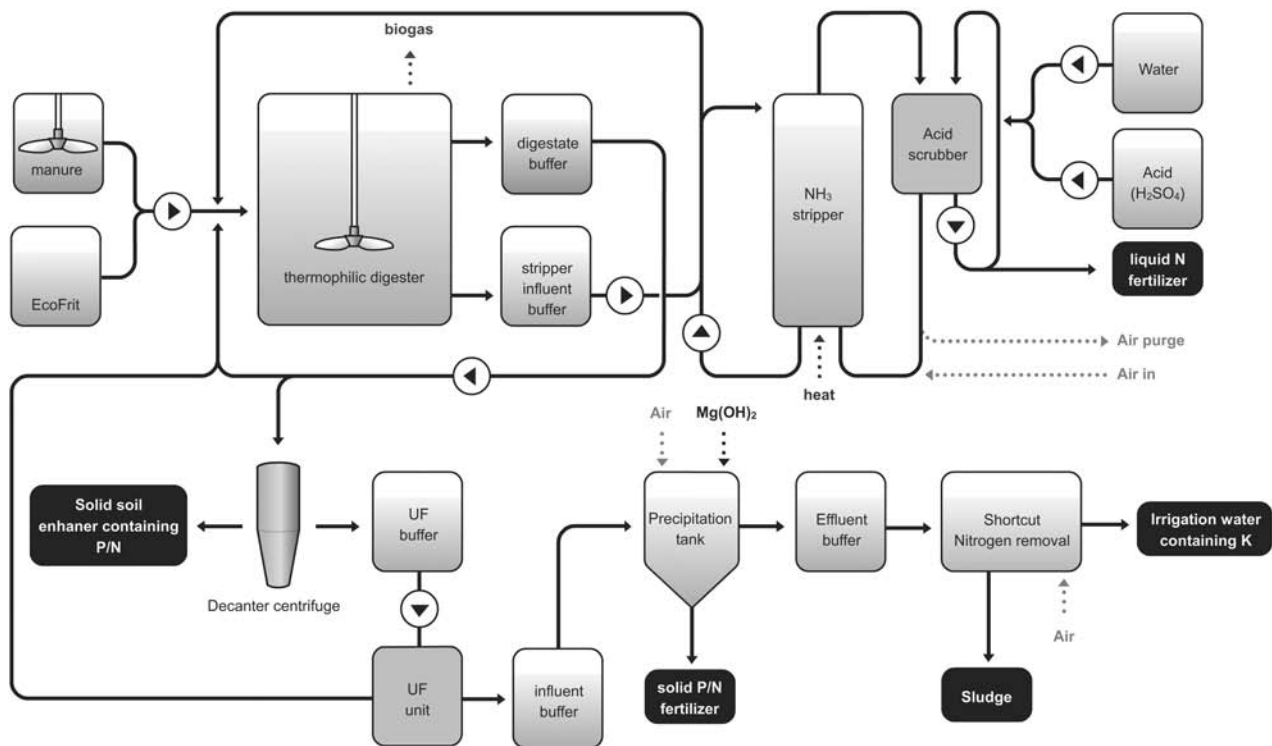
Figure 1 │ ManureEcoMine process scheme.

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, the total filtrating surface was 1.08 m^2. 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. 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% HNO$_3$ 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 (MgNH$_4$PO$_4$·6H$_2$O) 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, CO$_2$ was stripped out by aeration. To ensure that magnesium (Mg^{2+}) was not rate limiting the precipitation process, it was overdosed 60% over the stoichiometrically needed amount. Magnesium sulphate (MgSO$_4$) and magnesium hydroxide (Mg(OH)$_2$) were used separately for Mg^{2+} 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 MgSO$_4$ and Mg(OH)$_2$, respectively. For additional information, see supplementary material.

Enhanced phosphorus recovery through acidification

Digestate acidification was performed adding H$_2$SO$_4$ (60% v/v) in the decanter centrifuge influent buffer tank. The

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acid was dosed at 0.02 and 0.04 $gH_2SO_4\,g^{-1}$ 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; LCK338; LCK014), ammonium (NH_4^+-N) (LCK302; LCK342), TN (LCK338; LCK238), TP (LCK350; LCK339) and orthophosphates (PO_4^{3-}-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 with a WTW pH meter 340 with a pH electrode SenTix 41-3. 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 company Avecom (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 let 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 $kgCOD\,m^{-3}\,d^{-1}$. After 5 days, the OLR was increased to 1.5 $kgCOD\,m^{-3}\,d^{-1}$, keeping the swine manure/Ecofrit® ratio unaltered and decreasing the HRT to 73 days. On day 17, the OLR was raised to 2.0 $kgCOD\,m^{-3}\,d^{-1}$ and then step-wise increased over time, reaching the final value of 4.6 $kgCOD\,m^{-3}\,d^{-1}$ on day 149, corresponding to an HRT of 22 days. The GPR varied accordingly, reaching the final value of 1.4 $m^3\,m^{-3}\,d^{-1}$. The biogas had an average composition of 65.9% CH_4 and 33.9% CO_2, thus giving for the highest OLR a methane production of around 1.4 $Nm^3\,m^{-3}\,d^{-1}$. 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 needed 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 (needed 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 both reactors (thermophilic digester and side-stream stripping column). Further investigations on 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 2 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 all the operation but their concentration was never alarming considering also the stable pH at 7.72 ± 0.07 (Figure S2). 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 $m^3\,m^{-3}\,d^{-1}$ at day 53 to increase again at day 55 (0.74 $m^3\,m^{-3}\,d^{-1}$). 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 of 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%.
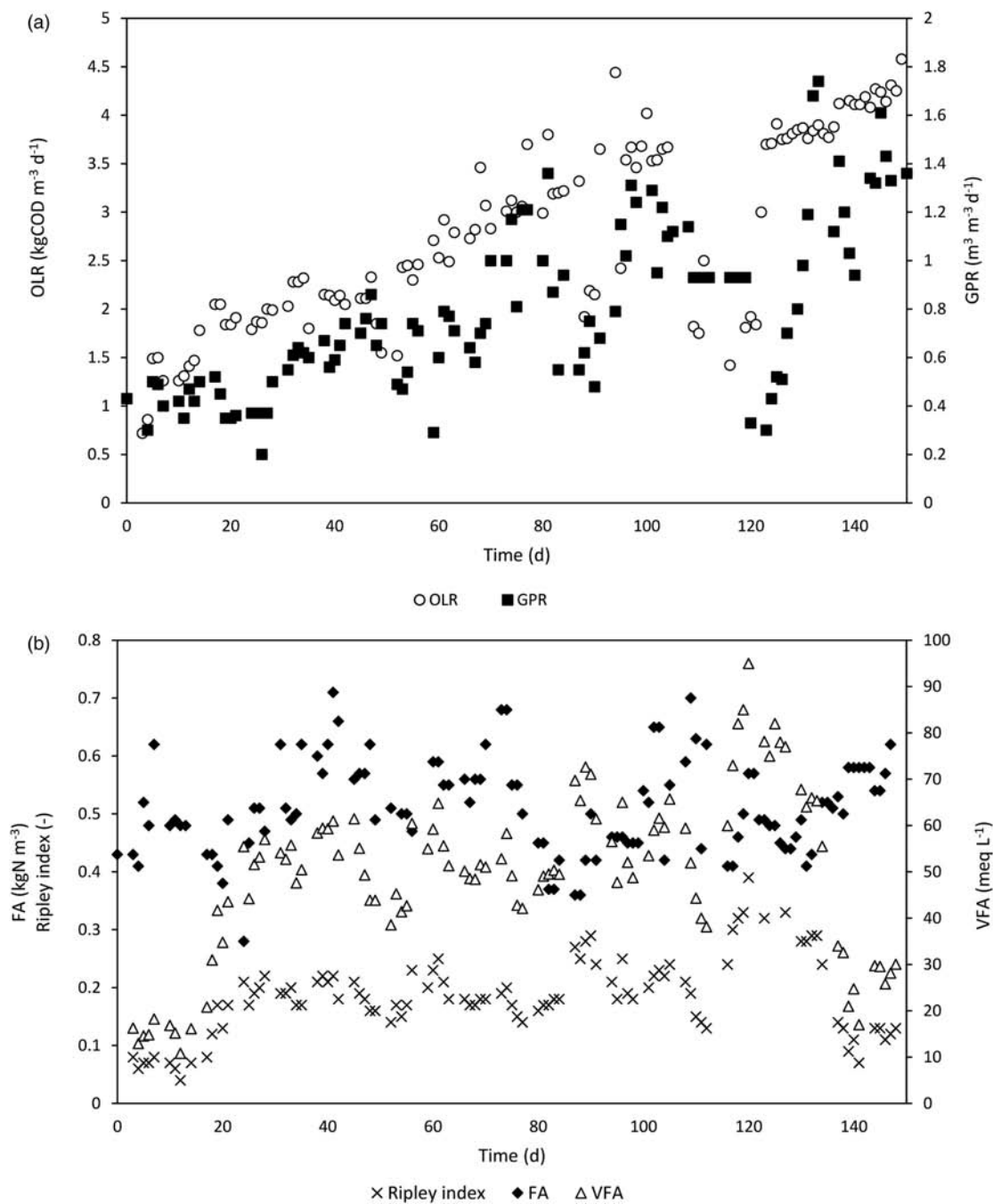
Figure 2 | Thermophilic anaerobic digestion: (a) Evolution of OLR and GPR; (b) Trends in FA concentration, VFA concentration and Ripley index.

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 of 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 were characterised by a slight increase of the OLR (from 3.8 to 4.6 kgCOD m^{-3} d^{-1}), which led to an increase of the GPR by 0.24 m^3 m^{-3} d^{-1}, reaching the final value of

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$1.4 \, \mathrm{m^3 \, m^{-3} \, d^{-1}}$. The Ripley index ($0.12 \pm 0.02$) indicated stable operation over the last period of digester operation.

Ammonia stripping/adsorption and its effect on anaerobic digestion

Optimization of the stripping conditions

In the ManureEcoMine pilot installation, ammonia stripping was implemented as 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 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 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 a 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 operative condition, 3 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 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 higher temperature than 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).

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 $3.8 \pm 0.1 \, \mathrm{kgCOD \, m^{-3} \, d^{-1}}$. 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 in average 0.30, indicating possible system instability, probably due to the technical issues with the feeding pump occurred before day 120. Finally, 57% of the COD was converted in 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 which 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.
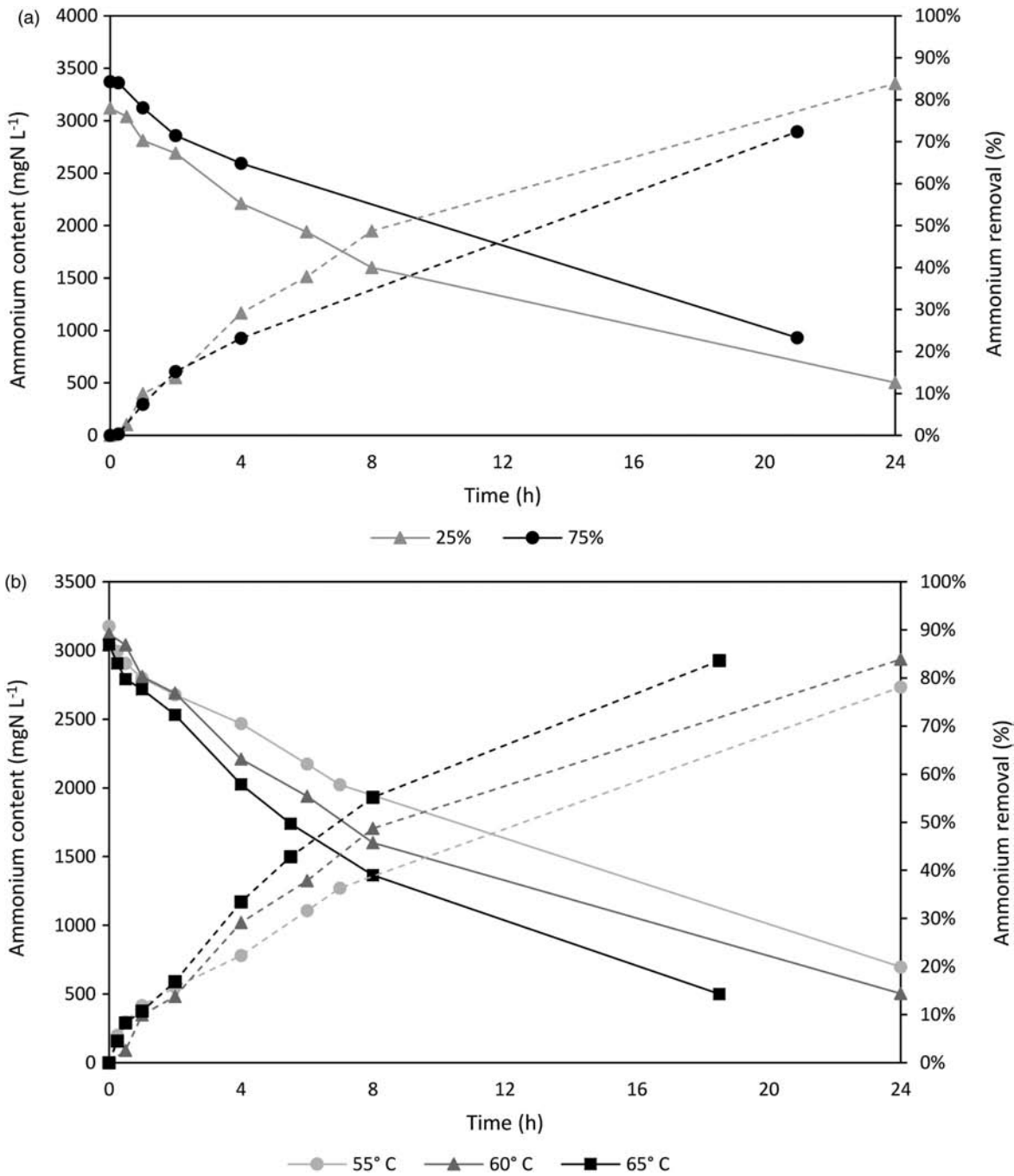
Figure 3 │ Ammonia stripper: (a) Effect of air recirculation ratio on the ammonium content and removal at 60 °C; (b) effect of temperature on the ammonium content and removal at air recirculation of 75%. Each variated condition was measured once.

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 optimization 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). Based on these observations, several tests were carried out at HRT of 35 s, varying the g-force (716 g, 1,353 g, 2,191 g and 3,231 g) and measuring the retention

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in the solid fraction of several parameters (Figure S5). 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 NH_4^+-N, indicating that a large fraction of nitrogen was dissolved. The high amount of TP and PO_4^{3-}-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 PO_4^{3-}-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) by 40% and 52%, respectively (Figure 4), were attained. Similar results were obtained in terms of TP and PO_4^{3-}-P, which reduction in the effluent resulted by 57% and 50% respectively. These results confirmed the ones 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 PO_4^{3-}-P was able to pass through the membranes.

The overall S/L separation (decanter centrifuge and membranes 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 PO_4^{3-}-P present in the centrate, respectively.

Struvite recovery from permeate and centrate

The UF permeate was used as influent of the struvite reactor. Batch tests were performed dosing $MgSO_4$ or $Mg(OH)_2$ as varying Mg^{2+} source. When dosing $Mg(OH)_2$, P recovery as TP and PO_4^{3-}-P increased with the batch duration (Figure S5): the precipitation efficiency increased by 30% (both for TP and PO_4^{3-}-P recovery) when doubling the
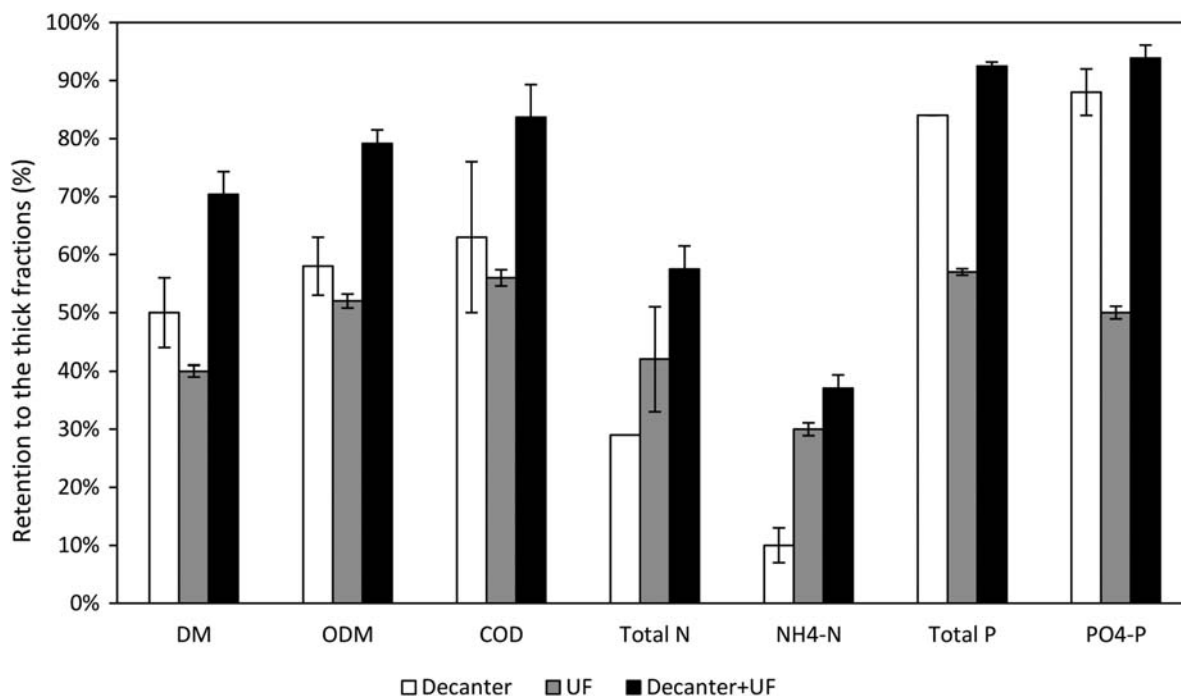

Figure 4 | S/L separation: Retention efficiencies of solids, organics and nutrients in the thick fraction using the decanter centrifuge (HRT: 46 s; g-force: 1,500 g; $n = 4$), the UF membrane ($n = 2$) and the two systems in row ($n = 3$).

precipitation time (from 3 h to 6 h). Similar results were obtained dosing $MgSO_4$ (Figure S6).

Small amounts of DM, ODM and COD (in 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. 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 $(NH_4)_2SO_4$.

Additional tests were performed using manure centrate as influent of the struvite reactor (Figure S7). 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). Digestate acidification was implemented at pilot level, the pH was reduced to 6 prior to decanter centrifuge separation. The pH reduction to 6 was found most favourable for the orthophosphate release 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 folds, respectively, compared to not 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 literature, however
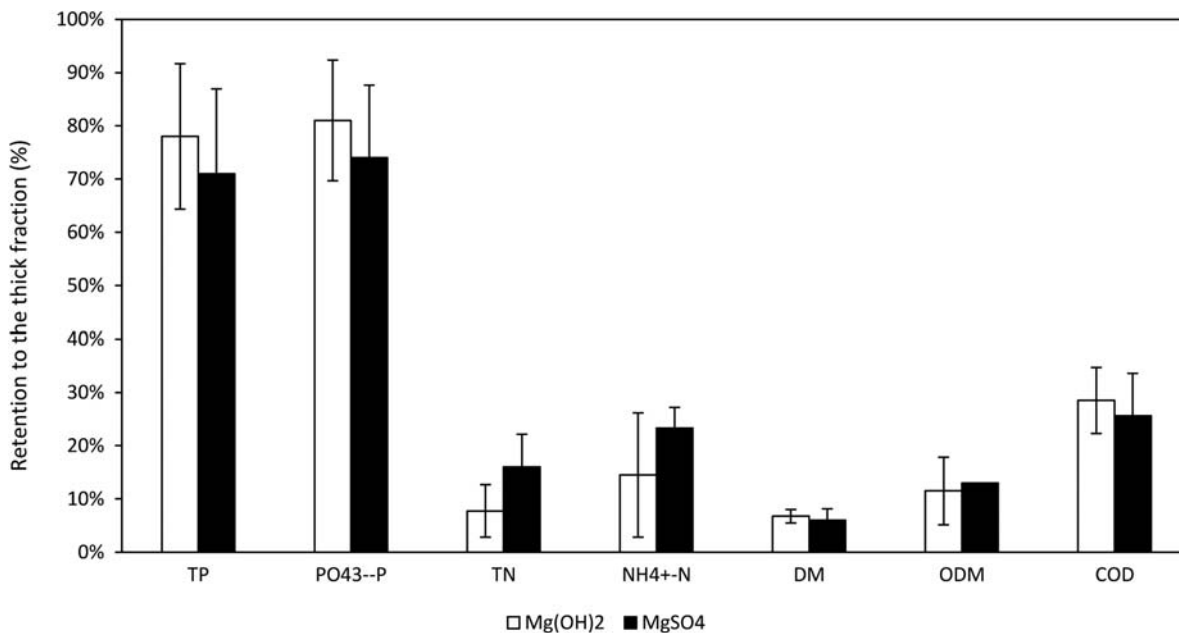

Figure 5 | Struvite precipitation: average removal efficiencies to the thick fraction for nutrients, organics and solids, dosing $MgSO_4$ (white bars) ($n = 3$) and $Mg(OH)_2$ (black bars) ($n = 4$).
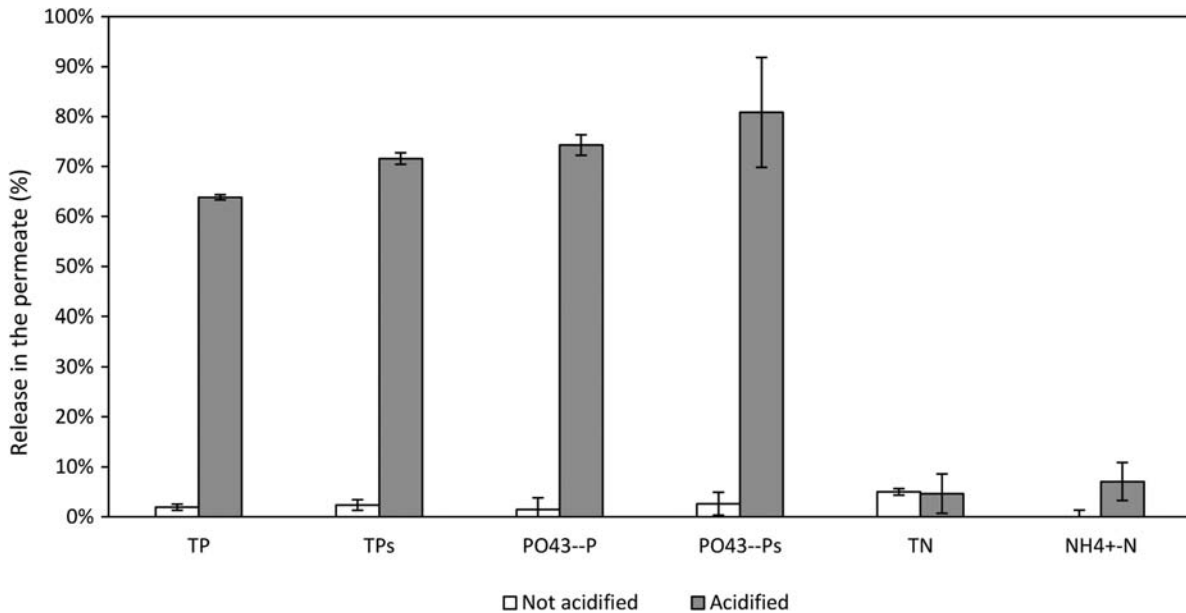
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Figure 6 │ Digestate acidification tests: Increments of unfiltered phosphorus (TP and PO_4^{3-}-P), soluble phosphorus (TPs and PO_4^{3-}-Ps) and nitrogen (TN and NH_4^+-N) upon acidification of the   **Q7**
digestate centrate (originally at pH 8, white bars) to pH 6 (grey bars) (n = 3).

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 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).
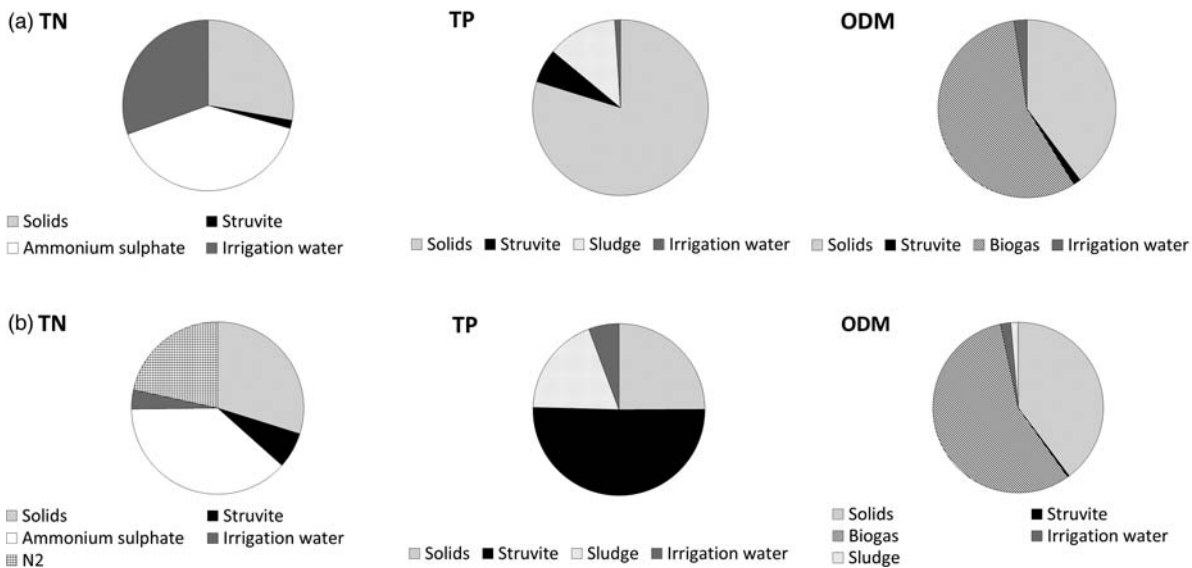

Figure 7 │ ManureEcoMine manure process overview: destiny of TN, TP and ODM in the actual process (a) and implementing manure digestate acidification and final biological nitrogen removal as nitritation/denitritation (b).

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The main restraint 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 retentate), and a consequent increase (87%) of P recovered as struvite, compared with the not-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. nitritation/denitritation, 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) nitritation/denitritation. 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, Q2 Kulikowska & Bernat (2013) performed nitritation/denitritation on landfill leachate in an SBR fed with sodium acetate and glycerine. Glycerine generated as by-product e.g. from oil production industries could be dosed during nitritation/denitritation to reduce the operational costs. When implementing a short-cut biological N removal, i.e. nitritation/denitritation, in the ManureEcoMine process (Figure 7(b)), the 21% of the TN fed into the process is biologically converted into N_2, with a 80% reduction of the TN present in the final irrigation water.

The overall ManureEcoMine process offers an opportunity to recover refined fertilizers, 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 folds more than the baseline scenario (EUR/ton manure treated), in a preliminary estimation of capital and operational expenditures. However, if the fertilizers can be marketed at 2 €/kgP (struvite) and 0.85 €/kgN (ammonium sulphate), 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 nutrient 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 likeliness of an ammonia inhibition, while increasing the GPR when recirculating batches of digestate over 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.

ACKNOWLEDGEMENTS

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Author Queries

Q1   Cordell *et al*. (2009) has been changed to Cordell *et al*. (2011) as per the reference list.

Q2   Kulikowska and Bernart (2013) has been changed to Kulikowska & Bernat (2013) as per the reference list.

Q3   Please provide the Editor names for Palm *et al*. (1997).

Q4   Sverdrup & Ragnarsdottir (2011) is not cited in the main text. Please confirm where it should be cited, or delete the reference.

Q5   Please provide volume number and page range for Tarrago *et al*. (2016).

Q6   Please provide publisher name and location for Zhu *et al*. (2008).

Q7   Please check whether the caption of the Figure 6 is appropriate.