INVENTORY

Techniques for nutrient recovery from digestate

Biomass for Energy

This report has been elaborated in the framework of the ARBOR Interreg IVB project, with financial support of the Interreg IVB programme, the province of West-Flanders and the Flemish Commmunity.

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ABBREVIATIONS

CHP: Combined heat and power generation
DAF: Dissolved air flotation
ED: Electrodialysis
KGW: Kitchen and garden waste
LF: Liquid fraction of the digestate
MAP: Magnesium ammonium phosphate (struvite)
MF: Microfiltration
N: Nitrogen
RD: Raw digestate before separation
RO: Reversed osmosis
SF: Solid fraction of the digestate
TMCS: Trans-membrane-chemosorption
UF: Ultrafiltration
WSA: Water sparged aerocyclone

I. Introduction

Because of the historic presence of intensive livestock production and the limited amount of arable land for manure disposal, nitrate pollution in certain European areas is considerable. The European Nitrate Directive, implemented in 1991, is intended to improve water quality in Europe by preventing pollution of ground- and surface water by leaching of nitrates from agriculture. Through the Directive member states were obliged to set up an action programme and define vulnerable zones. The Flemish action plan, for example, consists of an obligation to process manure. Manure processing is defined as treating manure in such a way that the nitrogen present is not brought back on Flemish soil after treatment, so that it is either exported or converted to nitrogen gas or a mineral fertiliser. The restrictions on nutrient application on the fields combined with the presence of intensive livestock, implies that anaerobic digestion plants in Flanders and other nutrient rich areas, who are often obliged to co-digest manure, have no other choice than to invest in expensive digestate processing techniques.

More recently, the focus in the development of manure and digestate processing techniques has switched from mere processing towards techniques that recover a maximal amount of nutrients (N, P, K) and produce dischargeable or re-useable water. This development is i.a. triggered by the increasing worldwide awareness of the depletion of phosphorus and potassium, which are nowadays extracted through mining. Another incentive is the volatile price of fossil-based mineral fertilizers. Estimates of the current phosphorus and potassium reserves are highly uncertain, but based on population growth and future nutrient demand, it is predicted that depletion will occur within 93 to 291 years for P and 235 to 510 years for K (Fixen and Johnston, 2012; Van Vuuren et al., 2010; Villalba et al., 2008; Smit et al.,2009). Geopolitical moves can however shift this date forward, making nutrient scarcity an imminent threat. These findings have generated awareness. The challenge for anaerobic digestion plants now is to achieve optimal recovery and recycling of nutrients from the digestate in a sustainable way.

ARBOR is an Interreg IVb-project that focusses on the acceleration of bio-energy development in North-West Europe. The goal of action 9 in work package 2 of the project is to make an inventory of existing nutrient recovery techniques from digestate in North-West Europe and to stimulate marketing of the end-products by means of i.a. physicochemical characterisations and field trials. This report gives an overview of the inventory made in the framework of the ARBOR project. It shows how digestate can be used as a sustainable source of nutrients. A distinction has been made between currently used digestate processing techniques and nutrient recovery techniques, the latter being in an earlier phase of development, but very promising with respect to the demand for more sustainability in agriculture.

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II. Digestate

a. Introduction

Digestate is the remaining product after biogas production in an anaerobic digester. It contains the non-digested resilient organic fraction, water, micro- and macro-nutrients. The composition of digestate varies strongly according to the input biomass. This chapter gives a short overview of how physicochemical characteristics change during the digestion process and how digestate composition is influenced by the biomass types that are digested.

b. Dry matter content

During the anaerobic digestion process part of the organic carbon is transformed into methane (CH_4) and carbon dioxide (CO_2). This implies that the organic matter and dry matter content decrease in the digestate. Digestate can contain up till 80% less organic matter than the ingoing streams. However, only easily degradable organic matter is decomposed. Complex organic matter, such as lignin, remains in the digestate, thus creating soil improving qualities. Analyses of Flemish digestate from different types of anaerobic digestion plants showed that larger slurry fractions resulted in lower dry matter content of the digestate. The dry matter content of dry anaerobic digestion with 100% KGW was 21%(WPA, 2006). Recent data showed a median DM content of 8.7% (Table 1).

c. Total nitrogen content

An input stream with a high N-level is pig slurry (on average 6.78 kg N/ton), in comparison to cattle slurry (3.75 kg N/ton) and maize (4 kg N/ton) (WPA, 2006). Recent data showed a median total N content of 4.2 kg N/ton (Table 1).

During the digesting process, organically bound nitrogen is released as ammonium, which is directly available for crop uptake. The higher the share of NH4^{+}-N, the higher the efficiency of the digestate as a nitrogen fertiliser.

Analyses showed that when digesting purely pig slurry 81.8% of the nitrogen is available as ammonium in the digestate. In co-digestion however, the share of ammonium in the digestate was not higher than 44-47%. In comparison: when using pig slurry as a fertiliser 64% of the nitrogen is available as ammonium. Digestates which have a low ammonium-content are mostly those originating from organic waste (including KGW). This relates to the fact that in waste there are very small amounts of ammoniacal nitrogen and most of it is to be released during the digesting process (WPA, 2006).

d. pH

During the digesting process volatile fatty acids are decomposed, which leads to an increase in pH. The pH is not so dependent on the type of input streams. The pH of slurry is on average 7.1 (WPA, 2006). Recent data showed a median digestate pH of 8.3 (Table 1). Thanks to the degradation of more than 90% of the volatile fatty acids the odour emissions are significantly lower during the application of digestate on the fields in comparison to pig slurry. However, the higher pH causes an increased risk for ammonia volatilisation. This is why injecting the digestate is strongly adivised (WPA, 2006).

e. Phosphate content

The phosphate content of digestate is entirely defined by the ingoing streams as no changes occur during the digesting process. Pig slurry has a high phosphate content of about 5 kg P_2O_5 /ton. By adding co-

products to pig slurry the phosphate content of the digestate is somewhat lowered (WPA, 2006). Recent data show a median total P_2O_5-content of 3.9 kg/ton (Table 1).

f. Heavy metals and impurities

During digestion the heavy metal content of the ingoing streams doesn't change. However, there is an upconcentration due to the decrease in dry matter content. This is of importance in e.g. digestate derived from mainly pig slurry where zinc and copper contents can sometimes be critical (WPA, 2006).

Impurities such as weed seeds and pathogens can be killed off during the digestion process. The extent to which this inactivation is sufficient depends entirely on temperature and residence time in the digester and on the type of organism.

Table 1: Composition of unprocessed digestate (VLACO, 2012)

		Unprocessed digestate		
		10-perc	median	90-perc
DM	**w%**	4.98	8.7	12.02
OM, fresh	**w%**	2.8	5.3	7.595
pH (water)	**-**	8.1	8.3	8.6
Ntot, fresh	**w%**	0.17	0.42	0.75
NH_4^+-N	**mg/l**	516	2148	3414
NO_3^--N	**mg/l**	3.1	5.85	10
C/N	**-**	3.89	6.58	13.67
Total P_2O_5	**w%**	0.14	0.39	0.65
Total K_2O	**w%**	0.20	0.35	0.50
Total CaO	**w%**	0.16	0.30	0.55
Total MgO	**w%**	0.03	0.09	0.20

III. Digestate processing techniques

a. Introduction

There is a diverse range of techniques suitable for digestate processing, but certainly not all of them can be considered as a nutrient recovery technique. There is no straightforward definition of a nutrient recovery technique**. In the current report we consider techniques that (1) create an end-product with higher nutrient concentrations than the raw digestate or (2) separate the envisaged nutrients from organic compounds, with the aim to produce an end-product that is fit for use in the chemical or fertiliser industry or as a mineral fertiliser replacement, as a nutrient recovery technique.** This makes it possible to re-use the present nutrients locally and close the nutrient cycle.

Digestate is often primarily separated into a liquid fraction (aqueous solution) and a solid fraction (resilient organic matter). The solid fraction offers limited possibilities to recover nutrients, since they are largely organically bound. Soluble N, P, K, and organics as well as mineral salts are present in the liquid fraction. These soluble nutrients show quite some potential for further extraction techniques.

In Figure 1 an overview is given. The techniques that are delineated as a nutrient recovery technique are indicated in green.

b. Description of commonly used processing techniques

Since the general digestate processing techniques are not the main focus of this paper, only a short general description is given in this chapter.

i. Mechanical separation

Separation techniques for manure are well-developed. Different types are available on the market, including drum filters, screw presses, filter belt presses and centrifuges.

The dry matter content of the solid fraction can be considered as an indicator of separation performance, with a percentage of preferably more than 25% to obtain a stackable and transportable product. For further processing of the liquid fraction, it is also preferable to have the lowest concentration of suspended solids as possible, since they can cause fouling and blocking of membranes in downstream filtration processes.

As P application to soils is restricted to 65-95 kg P_2O_5/ha and will further be reduced during the upcoming years, there is very limited possibility to market P for direct agricultural use in Flanders. This implies that the P-content in the liquid fraction should be as low as possible, to create a P-low but N-rich fertilizer. Hence, the P-concentration in the solid fraction is also an important parameter for a good separation.

In the Flemish project Nutricycle thorough separation of digestate by means of either a belt press or a centrifuge is being tested. Different conditioning processes to pretreat the raw digestate are used to achieve a more efficient separation. The main difference with classical separation is that the conditioning process before separation makes it possible to retain almost all suspended solids in the solid fraction, as well as up to 98% of the P and 94% of the COD. As with classical separation the NH_4^+-N fraction remains in the liquid fraction whilst the organically bound N is mainly present in the solid fraction (B. Aerts, pers.comm.). Although mechanical separation creates an end-

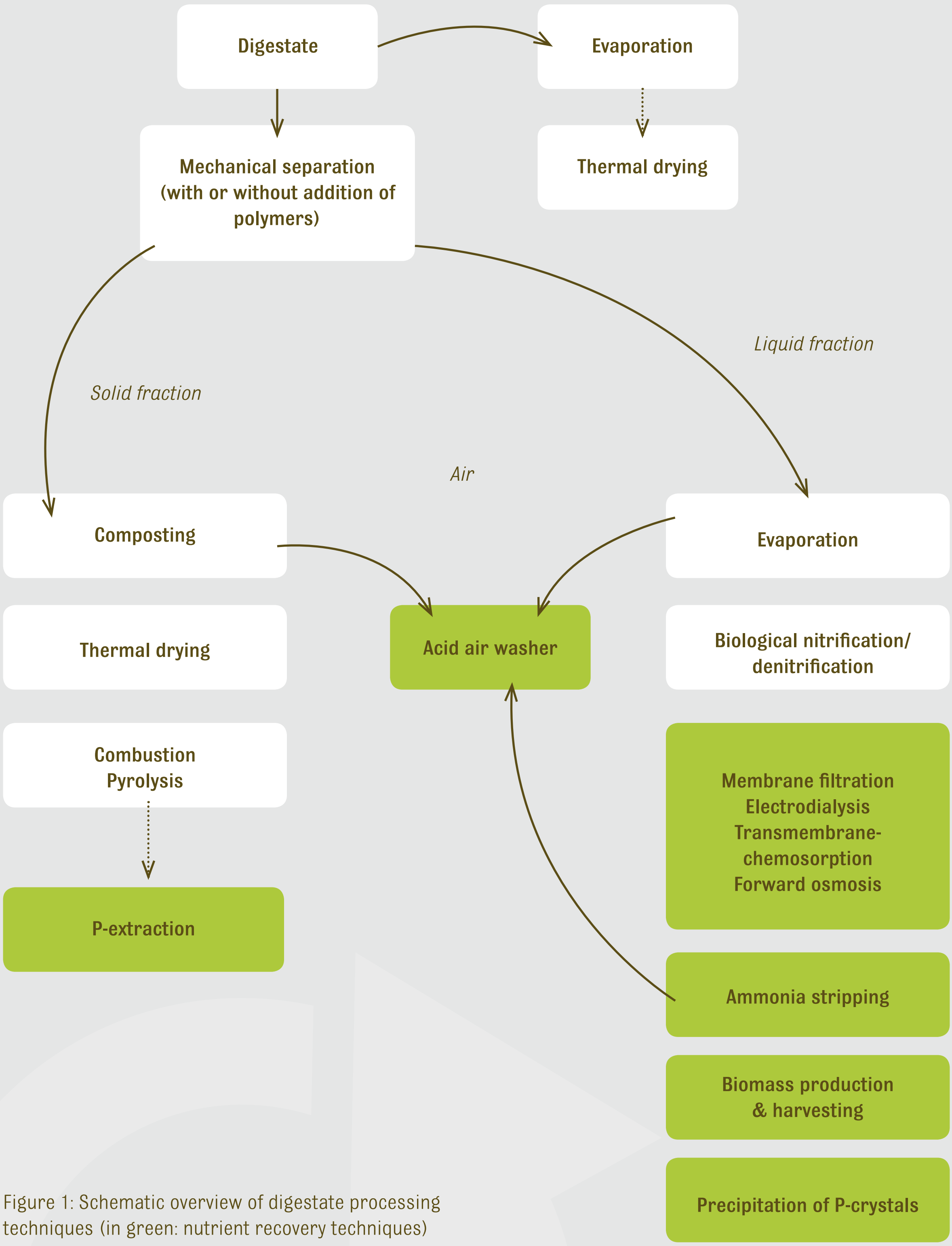


Figure 1: Schematic overview of digestate processing techniques (in green: nutrient recovery techniques)

Table 2: Median composition of solid and liquid fraction digestate after separation (VLACO, 2012)

		Solid fraction, median value	**Liquid fraction, median value**
DM	**w%**	25.5	6.55
OM, fresh	**w%**	17.3	3.25
pH (water)	-	8.7	8.4
Ntot, fresh	**w%**	0.60	0.38
NH_4^+-N	**mg/l**	766	2110
NO_3^--N	**mg/l**	7.5	5
C/N	-	14.8	3.77
Total P_2O_5	**w%**	1.02	0.25
Total K_2O	**w%**	0.42	0.32
Total CaO	**w%**	1.16	0.26
Total MgO	**w%**	0.32	0.03

product (i.e. the solid fraction) with higher nutrient concentrations than the raw digestate, it is not considered as a nutrient recovery technique because it is merely a first step that facilitates further processing.

ii. Composting of the solid fraction

The composting process is well-known and involves the conversion of organic matter into CO_2 and water by micro-organisms. The heat that is produced causes water to evaporate, which, together with the breakdown of organic matter, results in considerate mass- and volume reduction.

Before composting digestate is mixed with other input streams, such as wood shavings, straw, road shoulder grasses or dried chicken manure, to optimise the C/N ratio.

iii. Thermal drying

Anaerobic digestion sites often have to cope with a considerable amount of heat produced by the CHP. This heat is partially used for the digesting process and can also be used to heat nearby stables or houses. However, many installations have found that drying the raw digestate or the solid fraction is an economically viable way to use the extra heat thus creating an end-product which is strongly reduced in volume and stabilised in such a way that it is suitable for export. Because there is limited space in nutrient-rich areas to spread out a fertilizer with a high P-content, the dried digestate is almost always exported, either in its pure form or after pelletisation to reduce transport costs and facilitate logistics such as application to the field.

iv. Evaporation of the liquid fraction

Evaporation of digestate is commonly used to concentrate the nutrients in the liquid fraction and reduce digestate volume. A condensate is produced, which mainly consists of ammonia and some volatile compounds, but is salt-free. Acidification before evaporation ensures that the ammonia remains in the concentrate, but can cause foaming due to the release of carbon acid. Several evaporator types are on the market and used in large scale digesters. The produced concentrate remains fluid. To further increase the dry matter content, a drying step is needed (Lemmens et al., 2006).

v. Biological nitrification/denitrification

The main goal of the biological treatment is a reduction of the N-content and the BOD of the liquid fraction of the digestate. The process is an aerobic activated sludge process with a nitrification and a denitrification step. The sludge is recirculated, N_2 is blown into the air and the effluent is applied on the field by nearby farmers, whether or not after an evaporation step to reduce the volume. Sometimes a polishing step to create dischargeable water is applied to the effluent, for example constructed wetlands (Lemmens et al., 2006).

Table 3: Composition of thermally dried digestate (VLACO, 2012)

		Dried digestate		
		10-perc.	median	90-perc.
DM	**w%**	68.06	86.7	95.55
OM, fresh	**w%**	35.76	54.05	65.81
pH (water)	**-**	7.4	8.8	9.78
Ntot, fresh	**w%**	1.15	2.37	3.03
NH_4^+-N	**mg/l**	17.28	126	991
NO_3^--N	**mg/l**	5	10	106.5
C/N	**-**	9.71	12.80	21.98
Total P_2O_5	**w%**	2.28	3.52	5.42
Total K_2O	**w%**	0.90	2.44	4.74
Total CaO	**w%**	1.92	3.57	5.68
Total MgO	**w%**	0.52	0.95	2.05

IV. Nutrient recovery techniques for liquid fraction

a. Pressurised membrane filtration

i. Technique & end-product

The input stream for membrane filtration is either the liquid fraction of the digestate or a pre-processed stream, such as the condensate of the evaporator. The input stream is forced through the membrane by means of pressure. There are several types of membranes used in manure/digestate processing, which are categorised according to pore size: MF- (pores > 0,1 µm, 0,1-3 bar), UF- (pores > nm, 2-10 bar) and RO-membranes (no pores, 10-100 bar). In a MF-concentrate suspended solids are retained, while in a UF-concentrate also macromolecules are retained. Both filtration steps can be used as a pre-treatment for reversed osmosis, in order to prevent that either suspended solids or macromolecules block the RO-membrane. Another technique that can be used prior to RO is dissolved air flotation (DAF), a technique that consists of blowing small air bubbles through the liquid fraction, entraining suspended solids to the surface where they form a crust. This crust is then scraped off. When using DAF coagulants and flocculants are often added.

The permeate of RO, which consists mainly of water and small ions, can be discharged, if necessary after a 'polishing' step, or used as process water.

The biggest problem reported in membrane filtration is clogging and fouling of the membrane, which increases the hydraulic resistance. During MF and UF, this is mainly caused by suspended solids that form a cake on the surface of the membrane. Higher tangential velocities on the cross flow stream can prevent the membranes from blocking but imply higher operational costs. Waeger et al. (2010) stress that blocking of the pores is strongly correlated to particle size distribution.

The efficiency of RO-membranes can decrease because of several reasons: 1) low-soluble salts can precipitate on the membrane surface (scaling), 2) suspended solids can adsorb to the membrane surface (fouling) or 3) bacteria can colonise the membrane (biofouling). Scaling can be prevented by regulating pH and using anti-scalants. Once too many pores are blocked however, the membrane should be cleaned using chemicals such as NaOH and H_2SO_4. Bio-

Figure 2: Cross flow membrane filtration
(www.filterswater.com)

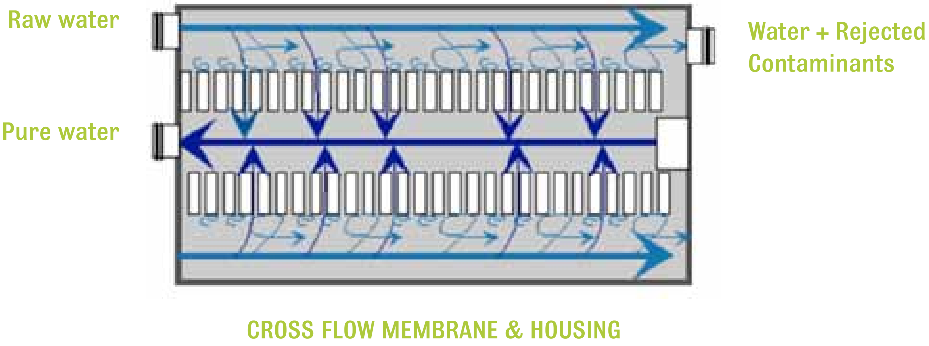


Table 4: Average composition of the mineral concentrate in the pilot plants in the Netherlands (Velthof, 2011)

Installation	A	B	C	D	E	F	H
DM (g/kg)	29.1	39.3	40.2	25.8	19.4	33.9	113
OM (g/kg)	10.5	18.2	19.3	7.81	6.32	13.7	70.7
Ntot (g/kg)	6.41	7.17	8.92	5.26	4.16	8.12	11.0
NH_4^+-N (g/kg)	5.92	6.86	7.77	4.72	3.56	7.13	10.5
P (g/kg)	0.20	0.01	0.34	0.11	0.08	0.26	0.27
K (g/kg)	7.08	6.75	8.44	6.81	5.53	8.08	15.7

fouling is very hard to remove and should be avoided at all times.

In the Netherlands a large research project is ongoing since 2008 with the permission of the European Commission on the RO-concentrate of 8 different manure/digestate processing installations. In this research project, called 'pilot mineral concentrates' the agronomic, economic and environmental effects of the production and use of mineral concentrates as mineral fertiliser replacement is investigated (Velthof, 2011). The 8 installations use as a pre-treatment to RO either an ultrafiltration or a dissolved air flotation step (Table 4).

As seen in Table 4 the average composition varies considerable between installations. This can only partially be explained by differences in ingoing type of slurry. The pretreatment probably has an effect on the composition of the concentrate as well. The installations using a combination of a centrifuge and ultra filtration (A and H) and the ones using a combination of a sieve belt press and flotation (B, C and F) have higher nutrient contents in their installation than the ones using a screw press and flotation (D and E) (Velthof, 2011).

ii. Stage of development

This technique is developed on full-scale, but is not implemented frequently yet. There are some manure and digestate processing plants in Europe implementing this technique. Examples of commercially available techniques are: VP Systems (NL), AquaPurga International (NL), Wehrle Umwelt GmbH (DE), A3 Watersolutions (DE), ...

b. Ammonia stripping and scrubbing

i. Technique and end-product

Ammonia is stripped by blowing air or steam through the liquid fraction in a packed tower. For optimal ammonia removal, the pH of the liquid fraction should be around 10 and the temperature around 70°C (Lemmens et al., 2006). However, Liao et al. (1995) observed that at a pH of 9,5 and 10,5 ammonia removal efficiency was directly dependent upon the air and liquid influent temperatures, whereas at a pH of 11,5 and a temperature of 22°C there was no appreciable improvement with a rise in air and influent temperatures. This led them to the conclusion that a pH of 10,5 is most optimal, as very high levels of nitrogen removal were obtained without incurring problems of excess lime. It was confirmed by Gustin and Marinsek-Logar (2011) that a high pH has the most significant effect on stripping, whilst temperature had the least significant effect. However, according to Bonmatí and Flotats (2003) complete ammonia removal without pH modification is possible at a temperature of 80°C.

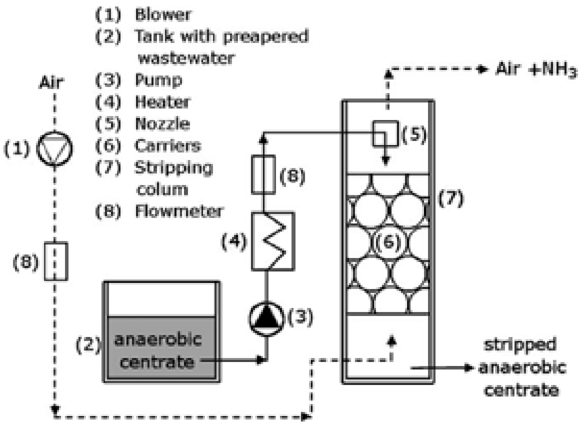


Figure 3: Ammonia stripping tower (Gustin and Marinsek-Logar, 2011)

During aeration of the digestate, there is quite a large risk of scaling and fouling of the packing material. To avoid scaling, one can install a lime softening step before stripping, which removes a large part of the Ca, Mg, carbonic acids and carbonates and increases the pH. To avoid fouling, it is important that during separation as many suspended solids as possible are retained in the solid fraction. Nonetheless, it is unavoidable that the packing material will have to be cleaned periodically.

The stripgas, which is charged with ammonia and volatile organic matter, is then put in contact with a strong acid solution (H_2SO_4), which produces ammonium sulphate (chapter VI.a).

A combination of the ammonia stripping technique and struvite precipitation (chapter IV.c) was studied by Quan et al. (2010). Both processes were taking place simultaneously in a water sparged aerocyclone reactor (WSA, Fig. 4). The wastewater containing ammonia is pumped into the water jacket and then sparged towards the centerline of the WSA through the porous section of the inner tube wall, thus forming a large gas–liquid contact area. The transfer of ammonia from liquid to air is high because of the very small amount of liquid.

They claim that the WSA, in comparison to the traditionally used packed towers, is characterized by good mass transfer performance and self-clean function and is suitable for air stripping of wastewater with suspended particles at a temperature of 30°C and a pH > 11.

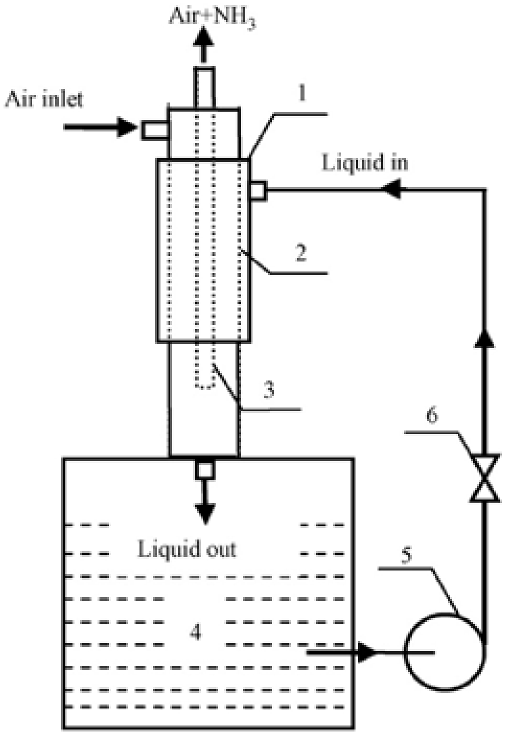
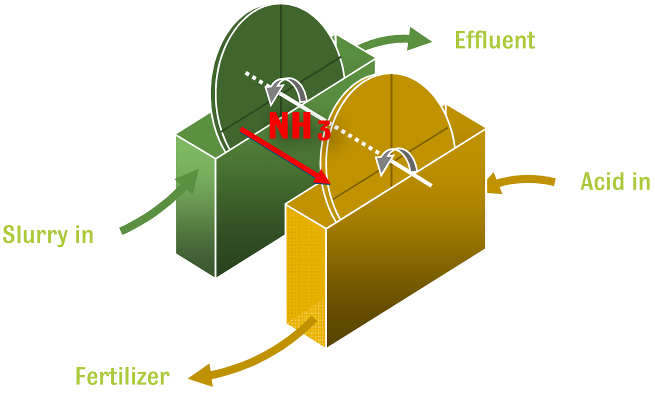


Figure 4: Water sparged aero cyclone reactor (Quan et al., 2010)

The Dutch company Dorset developed another type of ammonia stripping system for manure and digestate without air recirculation or ventilation. The system consists of rotating disks that are partly submerged in either the liquid manure or the receiving sulphuric acid solution. The rotating disks are close to each other so the ammonia coming from the gas phase is absorbed at the other disc with the sulphuric acid (Dorset GM).

Figure 5: Dorset LGL Ammonia Stripper (*www.dorset.nu*)



ii. Stage of development

Ammonia stripping is developed on a full-scale but not yet frequently used for digestate and manure treatment. In the ongoing Flemish MIP-project Nutricycle, Waterleau (BE) is testing ammonia stripping from digestate on a pilot scale. The process will be followed closely to evaluate how pH increase can be obtained and scaling can be avoided. Waterleau has experience with classical ammonia stripping systems. During the project the goal is to find out what the most suitable type of ammonia stripper for digestate treatment is and what the optimal process parameters are.

Other commercially available stripping techniques for digestate in Europe are AMFER by Colsen (NL) and ANAStrip by GNS (DE).

c. Precipitation of phosphorus

i. Technique and end-product

Several ions can be added to a solution containing soluble phosphate (orthophosphate) to induce a precipitation reaction forming phosphate salts. Addition of calcium to a phosphate solution will form calcium phosphate. By adding magnesium or potassium and adjusting pH to 9-11, $MgNH_4PO_4.6H_2O$, $K_2NH_4PO_4.6H_2O$ or $MgKPO_4.6H_2O$ precipitates. Struvite is considered to be a slow-release fertilizer.

The research on struvite is excessive in determining how to avoid struvite scale formation in piping and equipment of wastewater treatment plants. In the recent years however, interest is shifting to the potential of struvite for P-recovery from waste streams, slurries and digestate. Several research institutes mention the use of special reactors with seeding material to form large and pure pellets. An important bottleneck could be the formation of fine particles that are hard to separate. This can be avoided by adjusting reactor design and process parameters (Anonymous, 2006). Wang et al. (2006) confirm that proper seeding materials increase crystal size and improve settling ability. The University of Ghent is currently evaluating how chemical modelling can predict optimal struvite crystallizing parameters.

Struvite is mostly formed by adding MgO. However, adding $MgCl_2$ is also a possibility. Main advantage of $MgCl_2$ is that its production requires less energy. Main disadvantages are a slower and less complete reaction as well as the presence of chloride ions in the remaining solution. This implies that this solution can only be valorised as a fertiliser for crops that are tolerant for chloride ions, e.g. grass (Sanders, 2010).

Researchers at the Fraunhofer Institute for Interfacial Engineering and Biotechnology in Germany have patented an electrochemical process to precipitate struvite without the addition of salts or bases. The mobile pilot plant consists of an installation with a magnesium anode and a metallic cathode. The electrolytic process splits the water molecules into negatively charged hydroxyl ions at the cathode. At the anode an oxidation takes place: the magnesium ions migrate through the water and react with the phosphate and ammonium in the solution to form struvite.

Besides from the addition of Mg or K, $Ca(OH)_2$ can also be added. Because of pH and temperature increase ammonia is stripped out of the solution and should be scrubbed with an acid air washer. Quan et al. (2010) examined the coupling of $CaNH_4PO_4.4H_2O$ precipitation and ammonia stripping in a water sparged aerocyclone reactor on lab scale.

Schoumans et al. (2010) mention that a significant P fraction is organically bound and present as phytates and lipids and may not end up directly as precipitates. They suggest an initial hydrolysis step in which organic compounds such as esters, amides and phospholipids will break down into smaller compounds. Daumer et al. (2010) investigated a process to be able to recover the P that is bound in the organic matter by using acidification combined with solid/liquid separation. Pig slurry was acidified with formic acid and separated, resulting in a liquid fraction that contained the dissolved P. Formic acid was chosen as a reagent instead of the cheaper sulphuric acid, to avoid enriching the effluent with undesirable compounds (chloride or sulphate), which increase salinity. They concluded that the struvite product could be economically competitive with mineral fertilizer as superphosphate in less than 10 years.

ii. Stage of development

Current use of struvite precipitation is mostly limited to treatment of industrial and municipal wastewater. There is one full-scale system operating on calf slurry in the Netherlands. A pilot plant is installed at research centre De Marke (NL) by Fermtech Systems for the treatment of cattle slurry digestate. The liquid fraction of the digestate goes to a crystallisation reactor where struvite is formed and a NK-effluent remains which can be used as a fertiliser on the dairy farm (van Zessen, 2012).

Examples of commercial struvite forming processes:

- NuReSys (BE)
- DHV Crytalactor (NL)
- ANPHOS by Colsen (NL)
- PHOSPAQ by Paques (NL)
- Nutritec by Sustec (NL)
- PRISA (GE)
- Process Berliner Wasserbetriebe/AIRPREX (GE)

Examples of commercial calciumphosphate forming processes:

- Phostrip (GE)
- FIX-Phos/P-ROC: calciumsilicatehydrate containing particles are added to sludge that release Ca^{2+} which triggers the formation of calciumphosphates (GE)

d. Biomass production and harvest

i. Technique and end-product

The Flemish RENUWAL-project (2013) investigated economical and practical feasibility of growing algae on the liquid fraction of pig slurry. This seemed practically feasible if a polymer was added that precipitated the suspended solids, thereby allowing light penetration. However, the liquid fraction of pig manure does not have the most optimal N/P-ratio for nutrient removal. The economical study showed that the energy consumption of the algae production plant made it hard to make the installation economically feasible, even if the algae were sold to the animal feed industry.

Figure 6: Algal growth on decolored slurry (RENUWAL, 2013)

Besides algae, macrophytes have also been studied to recover nutrients from digestate. Xu and Shen (2011) studied the use of duckweed (*Spirodella oligorrhiza*) for nutrient recovery from anaerobically digested pig slurry.

The produced algae/macrophytes can serve as feedstock for chemical industry and biofuel industry or can be used as animal feed (provided that the necessary amendments in legislation are made) or spread out as a fertilizer on the fields. For bulk products the cost of producing algae is too high in comparison with other types of biomass (Muylaert and Sanders, 2010).

ii. Stage of development

There is one algae pilot pond in the Netherlands that is fed with the evaporation gases (containing NH_3) from the liquid fraction of the digestate.

In ACRRES there is a pilot algae pond installed which is currently fed with artificial fertiliser. However, if future legislation allows the marketing of algae fed on digestate in feed industry, pilot scale experiments could be performed at that site. For algae and duckweed there are no restrictions for use in feed, however if they are grown on a medium containing animal manure, the biomass will also be defined as animal manure, unless it can be marketed free of manure particles (A. Kroon and R. Schipperus, pers. comm.).

e. Other techniques

i. Forward Osmosis

During the last couple of years there has been an increased interest in forward osmosis as opposed to reversed osmosis. In forward osmosis there is also a semipermeable membrane, but no external pressure. The water flow is obtained by imposing an osmotic pressure by means of a draw solution such as NaCl. The potential advantages over pressure-driven processes are low energy consumption, reduced cleaning, low costs and high water flux.

Forward osmosis can be an interesting technique for use in wastewater treatment, food processing and seawater desalination, but also for the concentration of digested sludge. Some critical challenges are membrane fouling, new membrane development and draw solute design. Evolutions in the near future will show how promising this technique could be in manure/digestate processing (Shuaifei et al., 2012).

ii. Electrodialysis

During electrodialysis ammonia in the diluate solution is transferred by electromigration to an adjacent solution by an ion-exchange membrane under the driving force of an electrical potential. This means that the main ionic compounds in the liquid digestate (in the diluate cells) i.e. NH_4^+, K^+ and HCO_3^- are transferred and concentrated.

Mondor et al. (2007) studied the use of electrodialysis as a pre-treatment to RO. Different types of ED membranes were evaluated based on the NH_4^+ transfer rate and membrane stability. The result of the total treatment suggested that the use of ED and RO membranes to recover and concentrate ammonia is potentially interesting but that the process must include an approach to minimise ammonia volatilization. Ippersiel et al. (2012) used ED as a pre-treatment step to ammonia stripping without pH modification. Total ammonia nitrogen in the concentrate solution reached approximately seven times the concentration in the swine manure. The maximum achievable total ammoniacal nitrogen concentration in the concentrate solution was limited by water transfer toward the concentrate solution by osmosis and electro-osmosis.

In the Netherlands a pilot plant was installed at Dairy Campus in Leeuwarden, where digestate is treated by means of membrane electrolysis. Ammonium and potassium are captured in gas scrubbers by means of CO_2 as ammonium carbonate and potassium carbonate. The remaining nitrogen will be captured in an acid air washer. In 2013 extensive research will be performed on the fertilising value of the end-products (van Zessen, 2012).

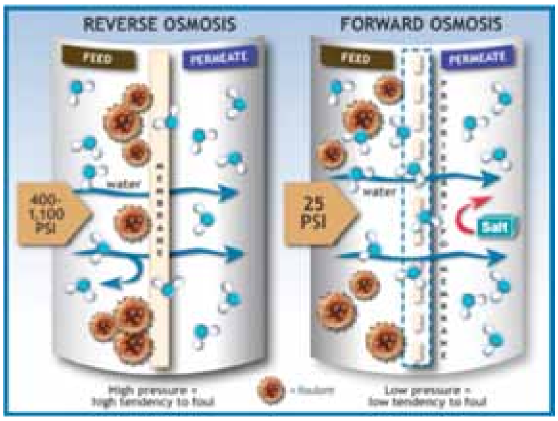


Figure 7: Schematic representation forward osmosis (*www.htiwater.com*)

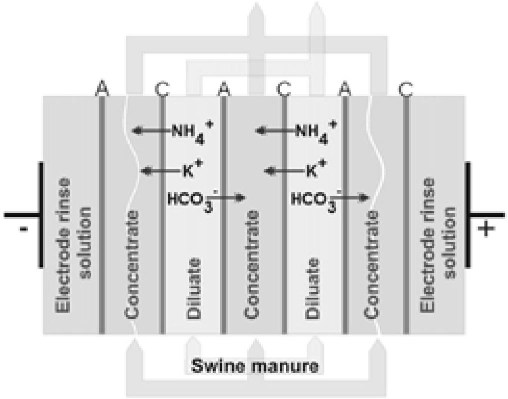


Figure 8: Electrodialysis cell, A: anionic membrane, C: cationic membrane (Ippersiel et al., 2012)

iii. Transmembranechemosorption

This process is used in pig slurry treatment systems in the Netherlands, where the ammonia is stripped and removed using TMCS. Ammonia is brought in the gaseous phase by means of a pH increase. The ammonia diffuses through a hollow-fibre membrane with gas-filled pores and is captured at the other side of the membrane in a sulphuric acid solution.

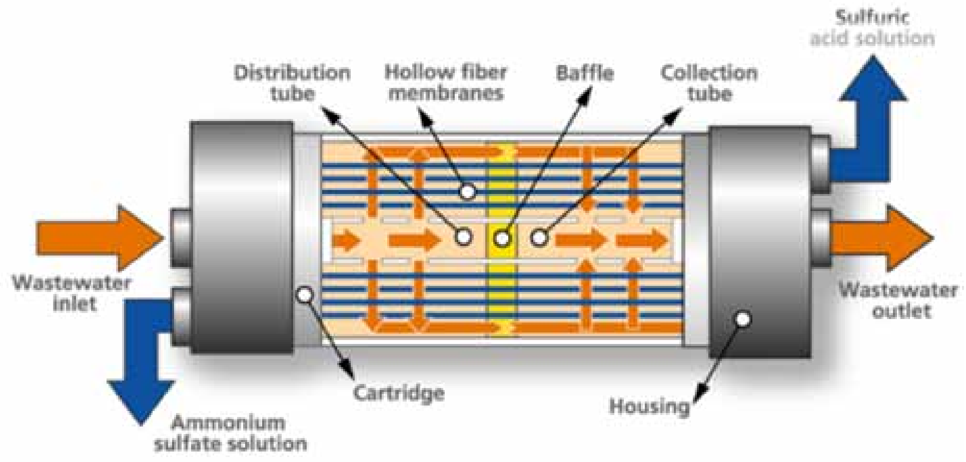


Figure 9: Schematic overview TMCS (*www.sustec.nl*)

V. Nutrient recovery techniques for solid fraction

a. Extraction of phosphorus

i. Technique & end-product

Extraction of phosphorus has been tested extensively for dried or dewatered sludge and ashes from sludge incineration. However, tests on dried fraction, ashes or biochar from digestate are absent in literature.

Digestate is considered a waste stream that is eligible for recycling as soil conditioner, which makes it not eligible for conversion to energy by combustion according to Flemish waste legislation. On the other hand, animal manure, which is not subject to the waste legislation, can be combusted, taking into account the emission standards (Art. 4.5.2., VLAREMA, 2012). The goal of combustion could be to produce electricity from the released energy and to recover nutrients (mainly P) from the ashes. Also a strong reduction in volume is obtained and pathogens are killed. However, a thorough flue gas cleaning system is indispensible, which makes small-scale combustion difficult. The remaining ashes after combusting digestate/manure contain up to 20-25% P_2O_5, next to K- , Al-, Mg- and Si-compounds and possibly also some heavy metals such as Cu, Zn and Cd. Several companies have designed different processes to extract phosphorus from combustion ashes (Schoumans et al., 2010). These techniques can be subdivided into thermochemical and wet-chemical techniques.

Pyrolysis exposes the digestate to a temperature of 150-900°C in the absence of oxygen. Organic matter fractionates into syngas, bio-oil and biochar (Lemmens et al., 2006). Preliminary pyrolysis tests on digestate revealed that oil yield and quality (very viscous) were suboptimal (K. Smets, pers. comm.). Experiments with pyrolysis of manure cakes have been conducted. The fraction of nutrients recovered in biochar is larger than in ashes and the plant-availability of the nutrients tends to be higher, especially for phosphorus (Schoumans et al., 2010).

ii. Stage of development

Techniques for phosphorus extraction from sewage sludge or sludge incineration ash are existing on full scale or demonstration scale. However, techniques to recover phosphorus from digestate ashes/biochars are less frequently mentioned. Some examples of P-recovery processes in Europe (CEEP, 2012):

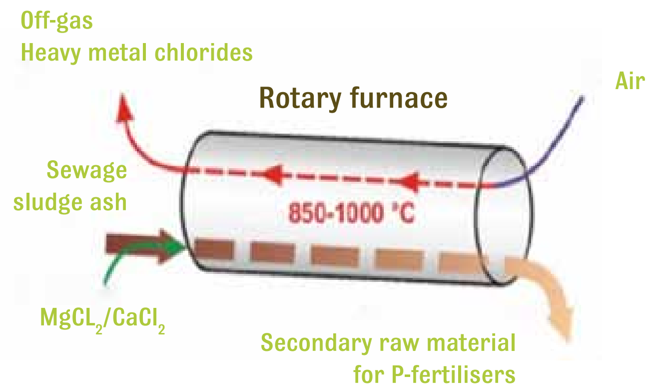


Figure 10: Schematic overview of a possible P-recovery process (*www.outotec.com*)

P-recovery from dried or dewatered sludge

- **PHOXNAN/LOPROX:** phosphorus recovery from sewage sludge by a hybrid process of low pressure wet oxidation and nanofiltration at acidic pH (GE)
- **Seaborne:** wet chemical (acid and temperature) extraction of P from dewatered/dried sludge followed by struvite precipitation (GE)

- **LEACHPHOS:** phosphorus extraction and contaminant reduction by leaching with mineral acids, followed by precipitation of calcium phosphate (CH)
- **Mephrec:** Metallurgical Phosphorus Recovery, thermal treatment of dried sludge (GE)

P-recovery from ash

- **Sephos process:** wet chemical extraction of phosphorus (GE)
- **PASH process:** leaching of phosphorus (GE)
- **ECOPHOS:** production of phosphoric acid from ash (BE)
- **RecoPhos project:** high temperature, reducing extraction of P and heavy metals from ash (DE, AT, CH, FR, BE)
- **SUSAN/ASH DEC (Figure 10):** ash is treated at c. 1000°C with a chlorine donor, to separate heavy metals and generate a bioavailable mineral phosphate (DE, AT, FI, NL)
- **ICL Amfert:** use of ash to produce mineral fertilisers (NL)

VI. Nutrient recovery techniques for gaseous streams

a. Acid air washer

i. Technique & end-product

Thermal drying, composting and evaporation result in emissions of dust particles, water vapour, ammonia and odour compounds. Air treatment is obligatory before emission to the environment. Often an acid air washer is used, which captures the NH_3 in sulphuric acid by means of a packed tower where sulphuric acid is sprayed with nozzles over the packing material and treatment air is blown into the tower in counterstream.

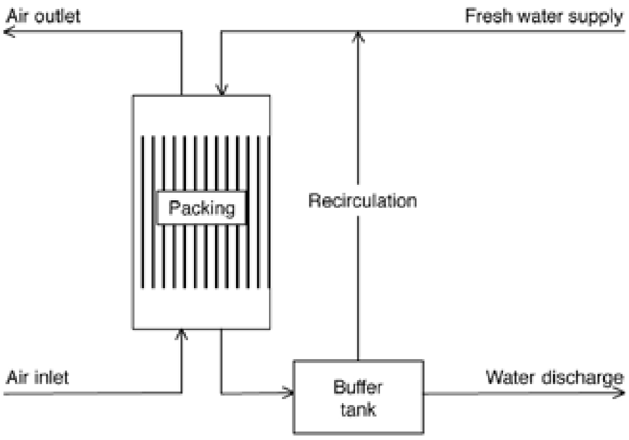
Ammonium sulphate is produced and the wash water is recycled until it is saturated and the removal efficiency of ammonia cannot be guaranteed anymore. At that point the ammonium sulphate solution should be removed and fresh sulphuric acid added. The reject solution is variable in N-content and pH, due to the variable efficiency of acid air washers. The supplier of the acid air washer defines a certain flow of reject wash water that guarantees a minimal ammonia reduction of 70%.

The $(NH_4)_2SO_4$ solution contains between 30-70 kg N/tonne. The pH is often acid, unless an alkaline step is incorporated. The pH varies between 3-7.

ii. Stage of development

This technique is developed on full-scale. It is frequently used in manure processing and digestate processing activities, as well as for pig stables. Examples of technique developers in NWE are: CB groep (BE), Inno+ (NL), Dorset Farm Systems (NL), ...

Figure 11: Acid air washer
(Melse and Ogink, 2005)



VII. Overview of end-products

NUTRIENT RECOVERY TECHNIQUE	STARTING FROM	END-PRODUCT(S)	CHARACTERISTICS OF END-PRODUCTS
Reversed osmosis	UF/MF/DAF-permeate	RO-concentrate (NK-fertilizer) + Permeate	**Concentrate**: Ntot: 7.3 g/kg[1] Ktot: 2.9 g/kg[1] Ptot: 0.42 g/kg[1]
NH3-stripping & scrubbing	(Decarbonated) LF	$(NH_4)_2SO_4$ solution + K-rich effluent	$(NH_4)_2SO_4$ solution: N-content[2] : ± 100 kg/m^3 pH: 3-7
P-crystallisation	(Acidified) RD/LF	$MgNH_4PO_4.6H_2O$ $K_2NH_4PO_4.6H_2O$ $MgKPO_4.6H_2O$ $CaHPO_4$ $Ca_5(PO_4)_3OH$ $CaHPO_4.2H_2O$	12,42% P 10.21% P 11.45% P 22.11% P 18.50% P 17.59% P
Biomass production	Diluted LF	Biomass	Further research needed
Forward osmosis	UF/MF/DAF-permeate	FO-concentrate (NK-fertilizer) + Permeate	Further research needed
Electrodialysis	(Filtrated) LF	NK-fertilizer + Permeate	Further research needed
TMCS	Tested on urine	NK-fertilizer + Permeate	Further research needed
P-extraction	Ashes/biochar/SF	Depends on technique	Depends on technique
Acid air washer	Strip gas	$(NH_4)_2SO_4$ solution	$(NH_4)_2SO_4$ solution : N-content 30-70 kg/m^3, pH 3-7

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[1] Vaneeckhaute et al., 2012

[2] R. Parduyns, pers.comm.

VIII. Conclusions

In nutrient rich areas it has become inevitable for anaerobic digestion plants to invest in a digestate processing technique as only a small fraction of the digestate can be spread out on land. Because of increased attention for nutrient recycling and the possible depletion of phosphorus, digestate should be considered a valuable source of nutrients and treated accordingly.

Defining nutrient recovery techniques is not as straightforward as it seems. This report proposes the following definition: techniques that create an end-product in which nutrients are present in a higher concentration than before processing or those that separate the envisaged nutrients from organic compounds, with the aim to produce an end-product that is fit for use in chemical or fertiliser industry or as a mineral fertiliser replacement.

From the discussed nutrient recovery techniques, only acid air washers, membrane filtration plants and ammonia stripping plants are currently working at full scale at anaerobic digestion plants in Flanders. However, they may need further technical fine-tuning, especially towards energy saving and decreasing the use of chemicals. Moreover, adjusting the process in a way that the characteristics of the end-products can be made client-specific and more predictable, is an important concern. A breakthrough in full-scale plants is to be expected for phosphorus precipitation. In the long run also electrodialysis, forward osmosis, TMCS and biomass production could become part of commonly used digestate processing techniques. The extraction of phosphorus from ashes or biochars seems less promising, because it is questionable if combustion/pyrolysis of digestate is a sustainable treatment option and if this should be encouraged. However, extraction techniques could also be applied on the (dried) solid fraction of digestate.

For all techniques described it is essential to put attention on their marketing value towards industrial or agricultural end-users. To be economically profitable, the price allocated to the recovered nutrients should be in accordance to the market price of N, P and K in mineral fertilizers. Obtaining the regulatory status of “mineral fertiliser” is considered to be very important to achieve successful marketing of these products for agricultural use.

Acknowledgements

This paper has been elaborated in the framework of the ARBOR Interreg IVB project, with financial support of the Interreg IVB programme, the province of West-Flanders and the Flemish Commmunity.

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