

## Exploring technological alternatives of nutrient recovery from digestate as a secondary resource

E.M. Barampouti, S. Mai, D. Malamis, K. Moustakas, M. Loizidou \*

National Technical University of Athens, School of Chemical Engineering, Unit of Environmental Science & Technology, 9 Iroon Polytechniou Str., Zographou Campus, GR-15780, Athens, Greece



### ARTICLE INFO

**Keywords:**

Ammonia stripping  
Anaerobic digestion  
Biobased fertilisers  
Biogas residues  
Membrane-based technologies  
Nitrogen recovery  
Struvite

### ABSTRACT

The valorisation of anaerobic digestate in the context of circularity and sustainability is a very challenging issue, given its increasing production rate. The main aim of this paper was to study the established and emerging technological alternatives considering anaerobic digestate as secondary resource for nutrients recovery. Initially, after mapping the composition of digestate, elevated fluctuations of nutrients content were revealed. Nitrogen content ranged from 1.6 to 21% (dry base) and phosphorous from 0.1 to 3.5% (dry base), reflecting its potential to be used as feedstock in new value chains for the production of higher value bio-based fertilisers through a multi-stakeholder and zero waste approach in line with circular economy. The current state of knowledge that was collected was then synthesized into two scenarios under the concept of integrated biorefineries that would allow the production of bio-based products, ready to enter new supply chains.

### 1. Introduction

Anaerobic digestion (AD) of organic waste has been prioritized among waste treatment approaches, since “green energy”-biogas and anaerobic digestate, a material with potential fertilising capacity can be produced simultaneously. The financial opportunities offered by biogas utilisation boosted the number of biogas plants in Europe counting 17783 installations in 2017 (+11556 units since 2009) which corresponds to a total Installed Electric Capacity of 10532 MWe (+6374 MWe since 2010) [1]. Most of that growth derives from the increase in plants running on agricultural substrates (agricultural and plant residues and manure) which account for more than 70% of total EU biogas plants (12496 installations of 6631 MW in 2017) [1]. 80–90% of the feedstock introduced into AD ends up as digestate [2]. Its physicochemical composition presents high fluctuations and is regulated by the feed material and the AD operational conditions [3]. In 2016, fertilisers containing an average of  $15 \times 10^6$ t of nitrogen,  $3.8 \times 10^6$ t of phosphate and  $4 \times 10^6$ t of potassium were applied to  $173 \times 10^6$ ha of farmland in Europe [4]. Nevertheless, global food insecurity is imminent and agriculture is expected to play a crucial role in the effort to ensure security in the food supply chain. But, all efforts should be made without posing any environmental concerns [5]. Moreover, the need for efficient nutrient management, as demanded by limitations on direct land application of

digestate, along with the criticality of raw materials such as phosphorous, render nutrients recycling and recovery essential for all stakeholders involved such as farmers, technology providers and policy makers [3]. In this context, valorisation of digestate as a secondary nutrient resource is a promising exploitation option that can provide a two-fold benefit: (a) closing the loop in the biogas AD process by finding end-uses of the resulting digestate and (b) nutrients recycling which are much in need to the agricultural sector. In view of its fertilising properties, direct land application of digestate is the current practice [6].

However, biogas digestate is also associated with environmental impacts with varying outcomes. These impact and potential risks include amongst others water pollution through leaching (nutrients runoff - eutrophication,  $\text{NO}_3^-$  discharge to surface water and groundwater), soil contamination (toxic elements concentration e.g. heavy metals), threat to human health by food contamination (e.g. presence of pathogens) and volatile emissions to air estimated equal to 139 g  $\text{CO}_2\text{-eq}/\text{kg}$  digestate [6]. Other issues of concern in regard to biogas digestate management include inter alia (i) difficulties to manage due to its fertilising properties and high water content, (ii) increased transportation cost in cases where digestate cannot be applied locally and needs to be transported and marketed into applicable areas [7], (iii) limitations to the application on agricultural land due to Nitrate Vulnerable Zone (NVZ) legislation and EC Nitrates Directive (91/676/EEC), regional and

\* Corresponding author.

E-mail address: [mloiz@chemeng.ntua.gr](mailto:mloiz@chemeng.ntua.gr) (M. Loizidou).

seasonal restrictions and limitations to the time periods in the year when the digestate can effectively be spread to soil resulting in long, expensive storage periods and a negative economic value.

To this end, the main objective of this review is to map the digestate composition in light of its valorisation via nutrients recovery. Thus, the technological status quo in nutrients recovery from digestate is thoroughly discussed in view of controlling operational parameters, nutrients recovery efficiency and quality, cost and possible commercialization. This critical review shall aid all key actors to materialize the utmost objective of this paper; that is to use the state-of-the art as a solid foundation to the development of a sustainable integrated biorefinery aiming to turn digestate into a nutrients secondary resource.

## 2. Digestate characteristics

During AD, most of macro (N, P, K, S, Mg and Ca) and micronutrients (B, Cl, Cu, Fe, Mn, Mo, Ni and Zn) present in the feed are concentrated in the digestate [8,9]. Thus, the feedstock used, the configuration and the operating conditions of the digester regulate digestate's composition [10,11]. Nutrients profile for digestates deriving from various feedstocks have been mapped in regard to their dry matter, carbon, nitrogen, phosphorus, calcium, magnesium and potassium, contents along with sulphur and heavy metals contents (Table 1) and are further discussed below.

The typical range of pH in fresh digestate is 5.6–9. The pH is mostly influenced by the progress of AD bioreactions as well as by the composition of the AD feed [12–14]. pH tends to increase when volatile fatty acids are consumed and/or when basic cations ( $K^+$ ,  $Ca^{2+}$ ) [12] are released, whereas a decrease in pH occurs due to carbonates and phosphates precipitation phenomena [3,15].

Dry matter of digestate ranges from 1.5 to 45.7% and is strongly influenced by the respective content of the AD feedstock and its biodegradable fraction. It is basically regulated by the initial total solids content of feedstock, the easily degradable organic content and the type of AD process (dry or wet). Digestate deriving from agricultural feedstocks presents elevated dry matter content (6.41–24%) due to very low digestibility of the structural plant polymer; lignin. On the other hand digestate from highly biodegradable substrates (that have high fat, sugar or alcohol contents) present lower total solids content according to

**Table 1.** The organic fraction of digestate may even reach 77% on a dry basis [3]. According to Peng and Pivato [16], digestate with 35% solids content was observed after a dry AD process of organic fraction of municipal waste (OFMSW). Accordingly, digestate from the wet and dry-batch digestion of biowaste presented 24.8 and 34% dry matter respectively [17].

As far as nitrogen in digestate is concerned, elevated concentrations of total nitrogen (TN) (up to 21% d.b.) mainly in form of total ammoniacal nitrogen (TAN) (35–81%TN) have been reported [11,18]. This fact is probably due to the low assimilation of organic nitrogen degraded by anaerobic sludge. Especially digestates coming from protein rich substrates such as food waste presented 40% nitrogen content higher than digestate from manure [19,20]. Cattle slurry has lower  $NH_4^+$ -N and N-total contents than pig slurry, and this will also be the case for digestate [21]. Table 1 also reflects the variances in nitrogen content of other AD feedstocks such as agricultural, industrial and food waste.

Regarding phosphorous, the conditions prevailing in anaerobic digesters favour phosphates production and their precipitation as  $Mg_3(PO_4)_2$  and  $Ca_3(PO_4)_2$  [22]. Nevertheless, the digestate phosphate content is independent of the anaerobic bioprocess but solely affected by the feedstock composition [12,13].

As for heavy metals and trace elements, their range in various digestates is presented in Table 1. During AD process the heavy metal content of the influent streams does not change. Nevertheless, the heavy metals and trace elements in the feedstock accumulate in the AD process, leading to an even higher concentration in the digestate due to the decrease in dry matter content [12,19].

Furthermore, various pathogenic microorganisms may be detected in AD substrates. A thermophilic treatment (over 52 °C and 10 h), but not a mesophilic [11,23], could replace a sanitation process efficiently [3,24]. The extent to which the inactivation of pathogens is sufficient depends entirely on digester's operational conditions such as temperature and residence time and on the type of microorganism [12].

Besides the aforementioned major components of digestates, attention has been drawn on organic micropollutants and their detrimental consequences due to uncontrolled land disposal. Although some pesticides, detergents and pharmaceuticals are partly anaerobically biodegradable, nonylphenols, estrogens, linear alkyl benzene sulphonates and synthetic musks resist to anaerobic biodegradation [11].

**Table 1**  
Typical characteristics of digestate for various feedstock types for various references.<sup>a</sup>

	Sewage Sludge	Food Waste	OFMSW	Agricultural feedstock	Manure	Co-Digestion Manure + crops and/or industrial waste	Digestate
pH		7.9–8.3	8–8.3	7.5–8.4	7.3–8.6	5.6–8.3	7.5–9
Dry matter (DM) (%)	1.9	1.4–7.88	0.72–51.2	6.41–24	2.2–9.2	1.5–24	1.5–45.7
Organic matter (OM) (%DM)		38.0–73.3	62.1–75.0	69–77	67.8–75.0	62.1–77	38–77
Total N (%DM)	0.005	0.06–1.24	0.21–7.8	0.14–2.1	0.05–0.62	0.12–5.04	0.005–5.04
Total $NH_4^+$ (% DM)		0.05–0.85	0.17–2.75	0.04–1.71	0.255–1.01	0.15–0.68	0.052–2.75
$NH_4^+$ (% TN)		68–83	30–80	38–47.6	19–61	44–81	35–81
Total C (% DM)		0.44–3.56	0.20–17.72	1.92–18.48	0.59–5.07	0.41–11.6	0.41–25.2
C/N		2.87–8.8	0.95–2.71	8.8–13.7	8.17–11.8	9.4–17.06	1.3–29.8
Total P (%DM)	0.04	0.008–0.126	0.002–0.819	0.058–2.400	0.034–0.221	0.010–1.001	0.002–2.400
Total K (%DM)	0.00019	0.03–0.64	0.004–3.994	0.324–0.392	0.03–0.43	0.03–2.52	0.001–2.52
Total Mg (%DM)		0.0042–0.079	0.001–0.512	0.041–0.042	0.013–0.166	0.006–0.260	0.001–0.26
Total Ca (%DM)		0.014–0.410	0.036–2.56	0.077–3.1	0.044–0.846	0.01–1.56	0.01–3.1
Total S (%DM)		0.01–0.08	0.01–0.358	0.01–0.041	0.008–0.048	0.004–0.096	0.004–0.358
Mg (mg/kgDM)		<0.1					0.5–0.7
Heavy metals (mg/kgDM)							
As				29			29
Cd	0.12	0.3–1	0.9	0.05–10	0.1–1.03	0.1–1.03	0.1–10
Cr		6–40	6–188	0.5–55	14–364	14–364	6–364
Cu	0.15	14–80	13–55	1–29		14–681	14–681
Mn		0–201	<0.7		164–663	24–1100	0–1100

<sup>a</sup> Sewage sludge: [26]; Food waste: [11,16]; OFMSW: [16,19,26]; Agricultural feedstock: [11,19,26,34,38]; Manure: [19,115,116]; Co-Digestion Manure + crops and/or industrial waste: [33,34,38,116–118]; Digestate: <u>[8,10,17,36]</u>.

### 3. Technological approaches for nutrients recovery from digestate

In this paper, nutrients recovery from digestate is the ultimate goal of this study (Fig. 1), whereas technological alternatives focused on digestate treatment and management as waste or energy production source are out of the scope.

#### 3.1. Solid-liquid separation

Separation of digestate in two distinct fractions (solid – liquid) is currently applied on site for a more efficient land application [25]. Nevertheless, it is also the initial stage of digestate valorisation schemes [11,26–28] aiming to improve its handling, cease degradation reactions composition process, reduce its volume and thus transportation costs [26,29–34].

After the separation, the solid fraction of digestate (about 20–25% TS) contains concentrated levels of organic material [27], organic nitrogen and phosphorus (Table 2). More specifically, it contains 40–80% of its dry matter and 40–90% of the phosphorus while just 20–25% of the nitrogen (Fig. 2) when conventional techniques are employed. In contrast, the liquid fraction is characterised by lower dry matter, phosphorous and organic carbon contents but is rich in ammonium nitrogen and potassium (Table 2). For the separation of digestate, numerous technological approaches have been proposed, determining the characteristics of the respective fractions (Fig. 2).

Screw press, centrifuge and screening drum press [26,30,31] are the most commonly used in full scale application whereas belt press [11,27,42], bow sieve, double circle bow sieve [31] have also been reported. Screw presses are the usual configuration selected for the treatment of fibrous substrates while decanting centrifuges are used for non-fibrous feedstocks [37]. In terms of cost, a screw press ( $0.54 \text{ €}/\text{m}^3$  digestate [43]) is cheaper than a centrifuge ( $3.68 \text{ €}/\text{m}^3$  [44]) (capital and operational cost). Total cost for centrifugation coupled with an ultrafiltration system has been reported for full scale plant between 4 and  $12 \text{ €}/\text{m}^3$  [27] when ultra-filtration costs around  $6.05 \text{ €}/\text{m}^3$  [43].

In order to further increase nutrients recovery, advanced mechanical technologies have been developed [42]. Additives such as  $\text{Al}_2\text{SO}_4$ ,  $\text{FeCl}_3$ ,  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{Ca}(\text{OH})_2$ , polymers and flocculants [45] usually improve separation via molecular intercrossing as is evident in Fig. 2 [11,46]. More specifically, the addition of precipitating agents ( $\text{FeCl}_3$  and  $\text{CaCO}_3$ ) increased the separation efficiency of the suspended solids from 46% to 75% according to Meixer et al [45]. Functionalized chitosan has been recognised as another advanced additive [31,47]. Garcia et al. [48] reported that separation by screening alone was not effective (TSS removal

**Table 2**  
Composition of digestate's liquid and solid fractions on wet basis [33–36].

	Liquid fraction	Solid fraction
pH	7.8–7.9	7.7–8.5
TS (%)	3.3–6.6	19.3–24.7
Total C (% DM)	2.64–3.15	9.0–10.1
Total N (% DM)	0.32–0.51	0.33–0.65
Total $\text{NH}_4$ (% DM)	0.17–0.3	0.13–0.3
$\text{NH}_4$ (% Total N)	40–80	26–49.4
Total P (% DM)	0.03–0.1	0.08–0.25
Total K (% DM)	0.29–0.52	0.25–0.48
Total Mg (% DM)	0.03–0.05	0.09–0.10
Total Ca (% DM)	0.04–0.06	0.16–0.19

efficiency 60%) while mixing with chitosan before screening substantially increased separation over 95%.

Furthermore, aiming to further increase separation efficiency, some processes integrate two sequential separation technologies [26,49]. A screw press–centrifuge working at relatively low flow rates ( $4.5 \text{ m}^3/\text{h}$ ) could provide higher N and P recoveries (45–80%) but with considerable expenses ( $3.68 \text{ €}/\text{m}^3$ ;  $4.43 \text{ €}/\text{kg P}$  and  $2.34 \text{ €}/\text{kg N}$ ) while a run-down screen screw press system working at high flows ( $0.3 \text{ m}^3/\text{min}$ ) could achieve P and N recoveries of 20 and 15% respectively with lower operational costs ( $1.03 \text{ €}/\text{m}^3$ ;  $4.96 \text{ €}/\text{kg P}$  and  $1.96 \text{ €}/\text{kg N}$ ) [26].

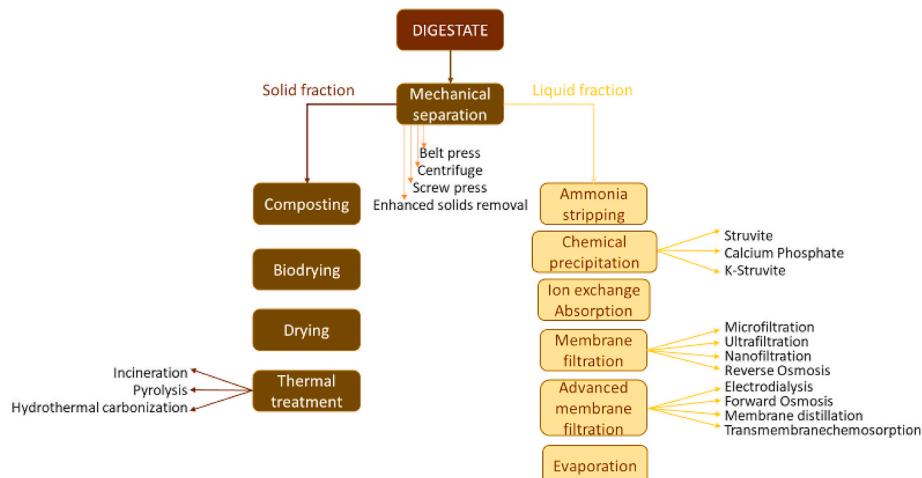
Similarly, Xia et al. [50] proposed a two-step sand and pebble filtration apparatus for the passive solid and liquid separation of anaerobically digested manure (15–92 g/L TS), achieving a mean TS content of 5.5 g/L and 793 mg/L after sand and pebble filtrations respectively [50,51].

#### 3.2. Processing of liquid fraction of digestate

##### 3.2.1. Ammonia stripping

A technology for the recovery of nitrogen from the liquid fraction of digestate is ammonia stripping [25,27,36,42,52–54].

Ammonia stripping takes place in a desorption column [55,56]. The most common mass transfer design is packed towers, as they provide increased mass transfer area [53], but in practice they are easily fouled [40,57]. Selecting the most suitable technique is usually site-specific. Scaling problems are also common [25]. To prevent them, prior to stripping, a  $\text{CaO}$  softening stage must be included that can remove most of magnesium, calcium and carbonates by increasing pH. To prevent fouling, a high efficiency solid–liquid separation step is essential [3,36,40,58,59]. Other configurations reported are bubble diffusers, spray towers, aspirators and surface aerators. Furthermore, novel gas/liquid contactors (semibatch jet loop vessel) have been proposed [60].



**Fig. 1.** Schematic overview of techniques available for the recovery of nutrients.

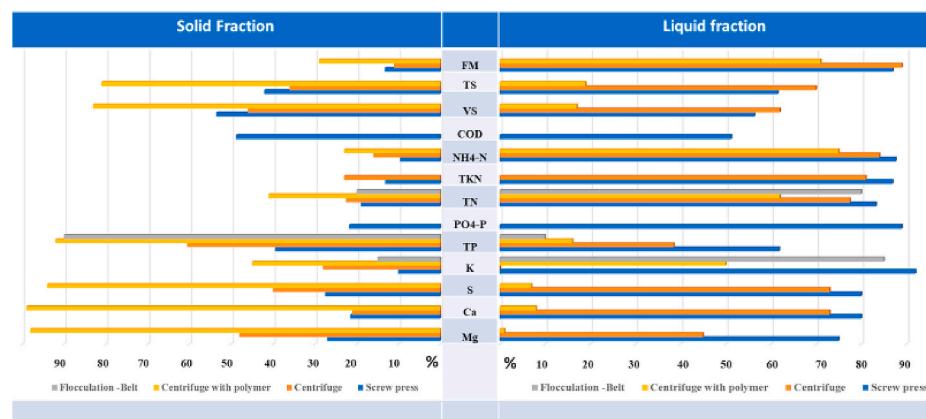


Fig. 2. Distribution of main components after applying different solid-liquid separation techniques on weight basis [3,26,34,37–42].

Ukwuani and Tao [61] used an alternative vacuum thermal stripping process treating digestate from manure. Stirred tank reactors also provided encouraging results [40]. Another ammonia stripping system developed by the Dutch company Dorset consists of rotating disks partially underwater in the liquid fraction of digestate or in  $H_2SO_4$ . The distance between the disks is small and thus gaseous  $NH_3$  is absorbed from the  $H_2SO_4$  of the other disc [36,62].

In the study of Limoli et al. [25], a low-cost ammonia stripping configuration imposing turbulence was assessed for high TS digestate from manure. Working at pH 10, elevated ammonium removal efficiencies were obtained without causing scaling or fouling. Coupling post-sanitation and  $(NH_4)_2SO_4$  production through stripping of digestate resulted in 80% removal efficiency with a positive energy balance [63].

The efficiency of  $NH_3$  stripping is governed by numerous factors like  $NH_4-N$  content of substrate, hydraulic loading, packing [53], retention time, air and liquid flow rates [64], air to liquid ratio [25], mass transfer area, etc., but mostly temperature and pH [54,59,64–66]. Typically, temperatures over 20 °C and pH over 9 are preferable [25]. Nevertheless, there are several papers reporting the optimum temperature around 70 °C and pH in the range of 10–11.5 [55,67]. However, at 80 °C the ammonia nitrogen could be fully recovered independently of pH [59].

Laureni et al. [68] applied a stripping tower to raw digestate at 50 °C and lower air consumption achieving 80% and 95% ammonia stripping efficiencies at pH 8.5 and 9.5, respectively. Furthermore, elevated nitrogen removal efficiencies (93%) were obtained in a packed tower treating the liquid fraction of digestate at 50 °C, pH 10.5 and elevated air consumption [69].

According to Norddahlet al. [57] And Quan et al. [66] for an economically viable recovery, a pH around 11–12 is necessary [57,66]. By increasing pH from 8 to 11 a subsequent increase in the recovery efficiency (from 80 to 92%) was induced [65]. 87% efficiency was achieved by Bonmatí and Flotats [59] at 80 °C and pH 9.5.

Nitrogen as  $(NH_4)_2SO_4$  was recovered with 90% efficiency from anaerobically digested dairy manure [58] and it was suggested to be used as concentrated nitrogen fertiliser. The scheme also produced electricity and biogas. Similarly, Ledda et al. [35] used animal digestate to recover nitrogen as  $(NH_4)_2SO_4$  from an integrated process scheme utilizing ultrafiltration, reverse osmosis, and “cold ammonia stripping”. The scheme recovered 71% nitrogen with 1.8  $m^3$  concentrated  $(NH_4)_2SO_4$  obtained for every 100  $m^3$  of treated digestate [53]. Ammonia recovery efficiencies of 80–90% for full scale plant have also been reported by “cold ammonia stripping” operating at 20 °C by regulating pH with lime at 12–12.5 [27].

The stripping of ammonia in the presence of carbon dioxide can achieve 40–50% N recovery rates producing a 35% ammonium sulphate solution without requiring alkali chemicals or stripping towers [42].

During ammonia stripping, ammonium sulphate is usually recovered when  $H_2SO_4$  is used as a scrubbing means. This end-product stands as a

chemical platform with market value used for the production of bio-fertilizers and other products [3,26,36,55,64,70] in line with the circular economy concept [54]. Nevertheless, market penetration is lower because of the fluctuation in S and N contents (61–100 kg S/t; 30–100 kg N/t), corrosive and acidic characteristics (elevated conductivities: 100–150 mS/cm; pH 2.5–7) along with farmers mistrust in its fertilising attributes [36,71]. Due to sulfuric acid, the pH of the acidic air scrubber water may reach 2, which is very low for use as a fertiliser. The low pH could cause corrosion to application instruments, leaf burning, and soil acidification after long-term application. Thus, it is advisable to neutralize the acidic pH [72]. Sulfuric acid has been traditionally used for this purpose but nitric acid is usually preferred. The higher nitrogen content of  $NH_4NO_3$  render it a higher value bio-product [27,52]. The chemical demand constitutes a major concern in ammonia stripping, since large amounts of chemicals need to be consumed and thus they have a fair share in the cost [3,55,64,73,74].

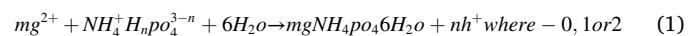
The ammonia stripping effluent still contains nutrients and thus it may be utilized in the agricultural sector after pH regulation, usually obtained by use of  $H_2SO_4$  [25,54].

The cost of nitrogen recovery may range from 2 to 7€/kg N removed. The operational costs may be mainly accredited to the acid (1.5 L  $H_2SO_4$ /kg  $NH_3$ ) and energy (0.057Wh/m<sup>3</sup> air) needs [36]. If ammonium sulphate penetrates in the market, the potential revenues may range from 90 to 120€/t fresh digestate, rendering the process economically viable [36].

Advances in ammonia stripping of digestate from lab-scale to full-scale have been successfully performed. In USA, 9–10 full scale plants operate recovering ammonia from digestate. There are also several full scale stripping systems in Europe producing mainly ammonium sulphate. Ammonia efficiency reaching 98% may be achieved by these configurations, although 80–90% is usually achieved in an effort to cut down the expenses [36,44,64].

### 3.2.2. Chemical precipitation

**3.2.2.1. Struvite.** One alternative to recover P and/or N from digestate is to induce the formation of struvite  $[Mg(NH_4)_4PO_4 \cdot 6H_2O]$  [64]. At elevated pH, in the presence of ammonium, magnesium and phosphate ions, struvite crystals presenting an orthorhombic pyramidal crystal lattice [51] are produced [42]:



Struvite formation takes place in two stages: crystal birth and growth [75]. These stages are influenced by various criteria including pH [76], supersaturation [77], temperature, presence of other ions ( $Ca^{2+}$ ), agitation energy [78], reaction time as well as  $Mg^{2+}:PO_4^{3-}$  ratio [79–81].

Digestate valorisation via struvite as a bio-based fertiliser prevents eutrophication phenomena by eliminating N and P run-off and mitigates

$\text{N}_2\text{O}$  emissions as a slow release product. In addition, digestate could stand as a secondary phosphorous resource, eliminating depletion of phosphate rock [81,82].

Equimolar concentrations of  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$  and  $\text{Mg}^{2+}$  are required for struvite precipitation although in general magnesium ion concentration in digestate is the lowest of the three [29,83]. For this reason, a magnesium source has to be supplemented to induce struvite.  $\text{Mg}(\text{OH})_2$  and  $\text{MgO}$  are among the most used  $\text{Mg}^{2+}$  precursors at different degrees of purity [84]. However,  $\text{MgCl}_2$  could be preferable given that its production demands little energy. Nevertheless, the reactions are not as fast and  $\text{Cl}^-$  remain in the solution. Hence, this end-product could be applied in Cl-tolerant crops [12]. Other  $\text{Mg}^{2+}$  sources have also been tested e.g. bittern [85], struvite pyrolysis recycling [86], magnesite pyrolysis [87] and byproducts from magnesite's calcination [26,88].

During struvite formation in digestates, a high consumption of alkali is required, given the buffer capacity of the medium. The buffer capacity is mainly due to the ionic equilibria  $\text{H}_2\text{CO}_3/\text{HCO}^{-3}/\text{CO}_2^{-3}$  and  $\text{NH}_3/\text{NH}_4^+$ . Low-rate aeration reduces alkali needs due to  $\text{CO}_2$  stripping [89] with a subsequent pH increase [29].

The molar ratio of  $\text{Ca}^{2+}:\text{PO}_4^{3-}$  ought to be below 0.5 for efficient and pure struvite formation [27,52]. Inhibition of calcium could be overcome by the addition of oxalic acid or EDTA increasing however the cost of chemicals [64,90]. In a full scale plant, struvite was recovered by Moerman et al. [91] from digested dairy manure when the  $\text{Ca}^{2+}:\text{PO}_4^{3-}$  ratio was decreased from 2.69 to 1.36. Huchzermeier and Tao [92] induced calcium carbonate precipitation to the same substrate by reducing  $\text{Ca}^{2+}$  (46–74%); nonetheless low efficiency in struvite formation was achieved. Low efficiencies were also reported even at high  $\text{PO}_4^{3-}:\text{NH}_4$  and/or  $\text{Mg}^{2+}:\text{NH}_4$  ratios [93]. Except for struvite, other P-precipitates were also identified by Song et al. [65] when treating pig manure digestate ( $\text{MgHPO}_4$ ,  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{MgKPO}_4$ ,  $\text{K}_2\text{NH}_4\text{PO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ ,  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{CaHPO}_4$ ) [64].

Typically, the struvite nucleation lasts around 30 min, but possible impurities may elongate this period along with crystal growth [29,78]. Struvite formation from cattle manure digestate resulted in 83% of P recovery after 40–60 min with  $\text{PO}_4^{3-}:\text{NH}_4$  and  $\text{Mg}^{2+}:\text{PO}_4^{3-}$  ratios 1.25 and 23, respectively [94]. Lower N and P recovery efficiencies (58% and 55% respectively) were reported for the same feedstock at a much lower  $\text{Mg}^{2+}:\text{PO}_4^{3-}$  ratio (1.5) after 50 min [81].

It has been reported that struvite precipitation improves the efficiency of the solid-liquid separation of digestate and thus in some cases it may come as an earlier step of treatment [55].

Air-agitated and fluidised bed configurations have been commonly applied for struvite crystallization [64,75,78]. The process may take place either in one or two-stage reactors where separation of crystals takes place in another reactor [3].

Struvite has been efficiently applied as slow-release fertiliser on several crops especially for those that need magnesium, like sugar beet [95], given its high nutrient value per unit weight [75] preventing fertilization issues (e.g. nutrients runoff and crop burn) [10,51]. Yet, despite the possible heavy metal content of digestate that is trapped in struvite, it is unlikely to exceed limit concentrations for land application [26].

The production cost of struvite ranges from 270 to 2060€/t struvite [53,54] while its price ranges from 600 to 2500€/t [52]. The contribution of chemicals may reach 75% of the production cost [3]. To ensure economic viability of recovered fertilisers, market prices of P and N of mineral ones should be taken into consideration.

There are several established processes for struvite recovery as well as struvite-based products commercially available [27,54]. Nevertheless, technical challenges such as chemical demand, end-products purity and process stability hinder the market penetration of the process.

An advanced electrochemical process that delivers struvite without adding bases or salts has been patented in a configuration including a metallic cathode and a magnesium anode [54]. Struvite formation recovering 15% of the N, 90% of the P and 80% of the K from dairy

digestate was achieved in a process combining microwave irradiation with advanced oxidation processes [42]. Similarly, Quan et al. [66] introduced the coupling of  $\text{NH}_3$  stripping and  $\text{CaNH}_4\text{PO}_4 \cdot 4\text{H}_2\text{O}$  formation in a water-sparged aerocyclone reactor achieving high efficiencies. Combination of struvite precipitation with AD in a single vessel may decrease costs and ammonia inhibitions achieving elevated efficiencies (P:90%, N:50%). Nevertheless, increased  $\text{Mg}^{2+}$  dosages may invoke inhibitions due to pH or cations [26].

P recovery in the liquid fraction could be boosted by an acidic pre-treatment step of the whole digestate. Schoumans et al. [96] proposed a hydrolytic stage, where degradation of organo-phosphoric substances took place. Similarly, the liquid fraction of acidified with formic acid pig manure digestate presented elevated phosphates concentrations [97].

**3.2.2.2. K-struvite.** K-struvite ( $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ ) may be recovered from digestates as well when potassium ion concentration exceeds the respective of ammonium, given struvite and K-struvite solubility constants [27]. In Netherlands four large scale plants are producing K-struvite from calf manure digestate [98].

**3.2.2.3. Calcium phosphate recovery.** Phosphorous could be recovered from digestate as calcium phosphate. Adding calcium hydroxide to the liquid fraction of digestate at 70 °C invokes a pH rise to 10, and subsequent fast (5min) precipitation of phosphorus as  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  or  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  [27].  $\text{CO}_2$ -stripping may be performed prior to precipitation preventing competing  $\text{CaCO}_3$  sedimentation. A removal efficiency of 50–60% P is usually achieved but efficiencies as high as 80–100% P have also been reported [36]. There are several processes commercially available for calcium phosphate recovery. Capital costs have been estimated around 2300–2900€/kg P/d while the  $\text{Ca}(\text{OH})_2$  demands define operational cost [36].

### 3.2.3. Ion exchange and adsorption

Extraction of nutrients (up to 100% P and 83% N) from the liquid fraction of digestate via ion exchange and adsorption takes place in column beds filled with solid sorbents, such as zeolites, resins and clays [64,99,100]. The sorbents may be thermally or chemically modified. Intermolecular forces govern adsorption and ionic ones the ion-exchange process. Batch or continuous processes by multiple columns may be applied [36]. Regeneration may be performed with  $\text{HNO}_3$ ,  $\text{NaCl}$  washing, or even biologically, depending on sorbent and end-products.

Zeolites have been extensively studied as adsorption agents for nutrients removal [36]. The adsorption capacity of natural zeolite is 19 g  $\text{NH}_4^+$ /kg and of Na-zeolite 21 g/kg while the removal efficiency ranges between 71 and 91% [101]. Adsorption of phosphorous by zeolites can be achieved but with lower efficiencies at pH 6.5–7.0 [102]. By applying at full scale an acidic gel cation exchange resin column after filtration and reverse osmosis, 27.6 g  $\text{NH}_4^+$ -N/L resin was extracted (99% efficiency) while 91.7% of the cation exchange capacity was achieved after regeneration with 3 bed volumes of 2 mol/L hydrochloric acid [103].

Fouling phenomena because of the high suspended solids content of liquid fraction of the digestate, the competition of foreign ions along with the reduction of exchange capacity after regeneration cycles are the main bottlenecks of this technological approach. Nevertheless, due to the porosity of zeolites, the ammonium release from zeolites is slow rendering ammonium-loaded clinoptilolite a slow-release fertiliser [36].

The applicability of ion exchange with zeolite in practice for the treatment of the liquid fraction of digestate still remains to be demonstrated, as does the use of the nutrient-enriched clinoptilolite or other regenerated N-solutions as a fertiliser. Nevertheless, the ion-exchange process may be used as an intermediate step in the digestate treatment train. In this context, coupling of zeolite and struvite precipitation for the production of a slow release fertiliser has been demonstrated as part of an integrated scheme [36].

The chemical cost for zeolite is higher than struvite precipitation and ammonia stripping since zeolite demands are higher than MgO and lime respectively [44]. Nevertheless, low energy needs and cost personnel are required due to the operation simplicity of ion exchange and adsorption processes [64].

### 3.2.4. Membrane-based separation

Membrane-based separation has been presented as an alternative nutrient recovery option.

**3.2.4.1. Pressure-driven membrane.** Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are the most prominent techniques [53,55] allowing nutrients concentration in the liquid fraction of digestate into bio-based fertilizers along with the production of high quality water [104]. MF (pores  $>0.1\text{ }\mu\text{m}$ , 0.1–3 bar) and UF ( $0.01 < \text{pores} < 0.2\text{ }\mu\text{m}$  (colloids), 2–10 bar) remove suspended solids (MF) and macromolecules (UF) by a porous membrane, while dissolved compounds ( $\text{NH}_4^+ \text{-N}$ ) remain in the permeate [104]. In order to further purify the permeate, nanofiltration and reverse osmosis are applied [40]. Separation efficiencies of 5–23%  $\text{NH}_4^+ \text{-N}$  and 97–98% P were achieved by NF [105]. In RO, dissolved solids are retained via a semi-permeable membrane at 10–100 atm [99] achieving 99–100% recoveries [106] and producing a permeate free of other pollutants. The energy needs of RO-systems are estimated around 4–6 kWh/m<sup>3</sup> [36].

A tubular RO membrane configuration recovered 95% of TN of the liquid fraction of anaerobically digested manure. At pH 8.0, TAN removal was 75–96%, while at pH 4 almost 100% efficiency was reported [107]. When cleaning the membranes, the flux was fully recovered [106].

The separation efficiency may be improved by the addition of surfactants, and water-soluble polymers (chitosan, polyethylenimine and polyacrylamide) able to complex with metals [53,104].

Total removal of pathogens (e.g. E-coli) and parasites (e.g. Nematode) has been reported by UF and MF [104]. When anaerobically digested manure was treated by UF (0.01  $\mu\text{m}$ ) coliforms and suspended solids were completely removed while COD remained unaffected [108].

The quality of permeate render it suitable for direct disposal or for other water uses such as irrigation, cleaning etc. [27,99].

MF and UF usually precede NF and RO in order to relieve fouling issues. Nevertheless, fouling remains the major challenge in membrane processes. Intermittent backwashing by air or water and increased tangential velocities on the cross-flow stream could lead to fouling mitigation. Ultrasonication may be applied for UF membrane cleaning. In case physical methods are insufficient, chemical means such as acidic or alkaline media, surfactants, chelants, oxidants, enzymes, or mixtures should be used to recover the capacity of the membranes [64].

Scaling due to low-solubility salt precipitation and biofouling due to bacteria colonization on the membranes may reduce their efficiency. Regulation of pH along with antiscalants could mitigate scaling phenomena, whereas biofouling cannot be removed easily [109].

Even though pressure-driven membrane processes are well-established waste treatment techniques, their potential on digestate has not been fully demonstrated yet in large scale [36]. Vibrating shear enhanced processing (60–90 Hz) has been proposed at pilot scale for manure digestate treatment, reducing cleaning needs [36]. RO combined with ammonia stripping has been employed for the treatment of liquid digestate [57].

Energy needs and economic viability are still crucial issues for membrane-based techniques aiming at nutrients recovery [36,40].

**3.2.4.2. Non-pressure membrane technologies.** Non-pressure membrane technologies are also being developed aiming to overcome conventional membrane filtration drawbacks.

Electrodialysis (ED) manages to concentrate ions ( $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{HCO}_3^-$ ) of liquid digestate by using an ion exchange membrane and applying

electrical potential [63]. Higher ammonium concentrations (up to 16–21 g/L) have been reported by ED rather than RO [64]. Apart from lab-scale ED, the treatment of digestate by membrane electrolysis in pilot scale in Netherlands recovering ammonium and potassium carbonates has been reported [12].

Bipolar membrane electrodialysis is an advanced technique, that, based on principles of ED and using a bipolar membrane, promotes water dissociation in  $\text{H}^+$  and  $\text{OH}^-$ . The derived products (acid and base) can be applied in various applications. Shi et al. [64] proposed an acid to substitute conventional chemical reagents used for acidification and cleaning of digestate, instead of a basic medium for ammonia stripping process. In the framework of a selective electrodialysis process, mono-selective membranes could achieve  $\text{PO}_4^{3-}$  retention, fact that would be advantageous for the following struvite precipitation. Fouling is also a serious operational problem for electrodialysis techniques. The  $\text{Cl}_2$  produced in the anode is considered as a reagent able to reduce fouling, but cracking and pitting phenomena on membranes are the main bottlenecks for its use [64].

Bioelectrochemical systems are alternative membrane configurations for nutrients recovery. Total recovery of ammonia from anaerobic digestate could be achieved by microbial fuel cells application. Despite the low energy needs of this configuration, full scale plants have not been established yet [26].

Nitrogen recovery through the application of membrane distillation is a promising option for anaerobic digestate, since ammonium could be concentrated in the permeate up to 18.3 g/L (pH > 9.68 and 45 °C) [64]. The fouling issues for this approach are not as important as for the other membrane-based processes. Regeneration with citric acid for 1.5 h was applied after 72 h of continual membrane operation by Kim et al. [110].

Holloway et al. [111] reported that in a reclamation facility in Nevada high water flow and nutrient condensation were achieved by applying forward osmosis on the liquid fraction of digestate. The process low energy demands and cleaning may lead to improved economics. However, fouling issues and issues related to the customised design of membranes and draw solution still exist [12].

Trans-membrane-chemosorption is another system for ammonia recovery demonstrated for pig manure digestate.  $\text{NH}_3$  is recovered after diffusion via hollow fibre membranes and captured in  $\text{H}_2\text{SO}_4$  [12].

### 3.2.5. Evaporation

Evaporation as an established management approach, concentrates (50%) the liquid fraction of digestate producing an aqueous stream rich in ammonia and volatile compounds [40] (Fig. 3). Ammonia content may be reduced if an acidic pretreatment is applied prior to evaporation. For further concentration, drying is recommended [12]. The high thermal energy needs of evaporation (300–350 kWh/t evaporated water) could be covered by waste heat of anaerobic plants [40].

Another option reported for the condensation of the liquid fraction of digestate is vacuum evaporation. Chiumenti et al. [112] reported that a single stage vacuum evaporation achieved 5-fold condensation. The

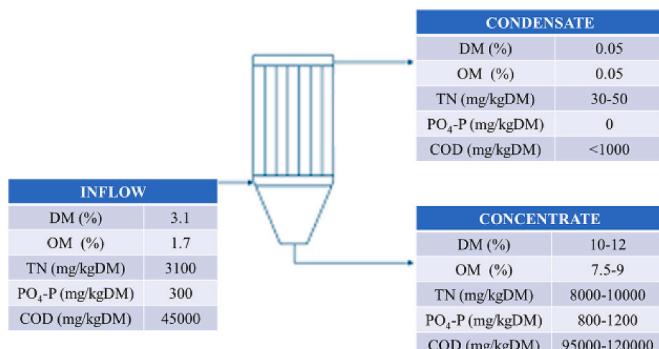


Fig. 3. Efficiencies of a typical evaporating system treating digestate.

addition of a second evaporation step led to a concentrate with 59% TS. Nitrogen distribution in the two fractions was regulated by pH; 97.5% was maintained in the concentrate at pH 5. Nitrogen balance was influenced by digestate pH. Low energy demands of vacuum evaporation should be taken into account.

### 3.3. Processing of solid fraction of digestate

The current practice for the solid fraction of digestate is direct land application. However, new pathways for resource-efficient management are proposed and discussed below.

#### 3.3.1. Composting

Low C/N ratios and bio-degradability along with high moisture are the main bottlenecks in solid fraction digestate composting [113]. In view of this, composting mixture of digestate should be enriched with suitable bulking materials (e.g. straw, wood chips, etc.) in order to ensure optimum C/N ratio and aeration conditions. Despite the concentrations of nutrients during composting, N losses have also been reported [33]. Rehl and Müller [99] estimated ammonia emissions up to 20% of TAN, nitrous oxide up to 1.4% of TN and methane up to 8.12 of carbon during a 10-week composting. However, Grigatti et al. [17] concluded that composting of food waste digestate may reduce CO<sub>2</sub> emissions without affecting fertilising properties. Coupling AD with composting may prove beneficial resulting in an integrated scheme. Shorter composting times along with high quality products are ensured [113].

#### 3.3.2. Biodrying

The basic principle of biodrying is as composting. Nevertheless, in this case elimination of moisture is set as a priority while maintaining high carbon content. Biodried digestates with 45% carbon, stable and odorless could be valorized in various applications. The risk of nitrous oxide emissions is high and special care should be taken [55].

Processes for P recovery from dried digestate such as coupling of low-pressure wet oxidation and nanofiltration, wet chemical extraction and struvite formation and metallurgical P recovery are commercially available [12].

#### 3.3.3. Drying

A 98% dry matter digestate-based stream free of odour and ammonia derives after thermal drying. The high energy needs of this process in most cases is covered from the waste heat of anaerobic digestion process. Pelletisation of end-product may improve its fertilising features, reduce transportation cost and facilitate land application strategies [3,55]. Binders such as lime and starch have been tested producing pellets with improved mechanical properties [99]. Numerous applications have been proposed including agriculture, landscaping or specific cultivations (e.g. mushroom) [3]. There are hundreds of drying digestate systems on farms in Europe and the predominant systems used are: belt dryers, mechanical drum dryers and solar drying systems [3,42].

Belt dryer achieves 85% TS content in the digestate when high temperature (85 °C) air is fed. During mechanical drum drying, the influent digestate is pretreated by mechanical means and then it is sent to the rotating drum. Its energy needs in terms of heat and electricity are up to 3 GJ and 0.31 GJ/t water, respectively. Another promising alternative is solar drying. Mechanically pretreated digestate is fed in a solar green-house dryer where it is mixed and aerated. The evaporation rate may range between 0.6 and 3.5tn water/y/m<sup>2</sup>. The energy needs for mixing and aeration may rise up to 200kWh/t water resulting in a digestate with 65% dry matter while the heating needs are covered by AD excess heat [99].

#### 3.3.4. Thermochemical treatment

The application of thermal treatments is relatively restricted. Regarding incineration, the ashes produced during this process

contain up to 20–25% P<sub>2</sub>O<sub>5</sub>, as well as K, Si, Mg and Al traces and perhaps a few heavy metals (e.g. Cd, Zn, Cu). The prospect of recovering nutrients (mostly phosphorous) from ashes has been reported reaching recoveries of 78% in P [64]. The economic viability is threatened especially in small scale from the intensive flue gas cleaning and energy demands [36].

Biochar as a value-added product of pyrolysis and hydrothermal carbonization has demonstrated high nutrient capacity with improved fertilising properties. Complete retention of phosphorous has been demonstrated when manure digestate was pyrolyzed [12]. The performance of biochars regarding nutrients recovery is better compared to incineration ashes. Nevertheless, pyrolysis biooil in qualitative and quantitative terms, was inefficient [36]. Furthermore, nitrogen losses, over 90% of N, were diffused in the carrier gas [64].

Hydrothermal carbonization of digestate favors immobilization and retention of nitrogen and potassium over 50% in the liquid phase and their subsequent recovery via membrane-based processes with lower energy needs. For hydrochar, energy demands were up to 27kWh per m<sup>3</sup> solid digestate and the respective cost was estimated 157€/ton [64].

Biochars either from hydrothermal carbonization or pyrolysis could stand as promising advanced bio-based materials with high fertilising and agronomic properties improved by their absorption capacity, nutrient slow release and CO<sub>2</sub> immobilization [64]. The estimated value of phosphorous in biochar is higher (4.25€/m<sup>3</sup>) than the respective value of phosphorous in ash (<1€/m<sup>3</sup>) [36].

## 4. Integrated biorefinery

A major concern in full scale plants that treat digestate and recover bio-based products is the management of process residues. For instance, in membrane-based processes only 50% of digestate is turned to purified water, while the remaining nutrient condensate requires further management. Thus, valorisation concepts that meet simultaneously technical, economical and environmental viability should be established. In this context, residues that usually present high nutrients concentrations, should be further processed in order to meet commercial standards [3].

To this end, biorefinery concepts that include biobased materials and energy recovery are currently very popular. Based on the principles of oil refinery, biorefinery produces numerous bioproducts or chemical blocks from renewable feedstocks by applying plethora of technologies and configurations. Thus, biorefineries are very promising alternatives, since they turn waste into secondary resources in a circular, zero-waste, environmental friendly and economical viable approach [114].

Technology is out of question the core issue, given that a biorefinery is materialised through the synthesis of the best available techniques into an integrated valorisation scheme. Beyond the technological maturity of each system, close collaboration of all supply chain key actors (farmers, AD managers, scientists, engineers and decision makers) is more than necessary [114].

In line with the basic principles of biorefineries, two scenarios involving the recovery of nutrients from digestate were investigated. These scenarios were based upon the literature analysis discussed above, assuming efficient and established technological approaches suitable for digestate valorisation. Rough mass balances were estimated, taking into consideration moderate assumptions. They propose an integrated approach for closing the loop in the management of digestate for the agri-food supply chain, reducing external inputs of fossil mineral fertilisers and irrigation water required to agriculture. They also promote the establishment of new sustainable value chains of digestate nutrient recycling and valorisation leading to high quality biobased products, including liquid/solid fertilisers and soil amenders.

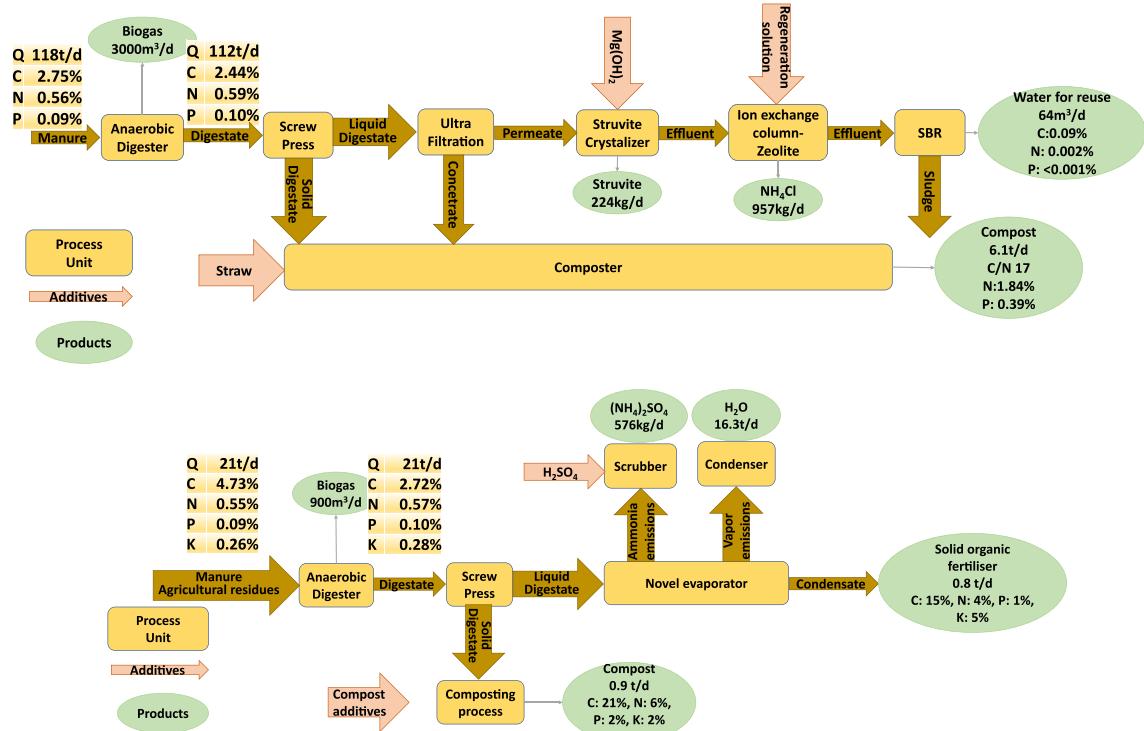
In the first scenario proposed, the treatment train refers to larger scale anaerobic digestion plants, whereas the second one could be easily adopted even on a single farm.

In the first scenario, the digestate valorisation from an anaerobic digester that treats manure (125 t/d), producing 1000 m<sup>3</sup>/d biogas is

proposed. A two-stage solid/liquid separation process including a screw-press and an ultrafiltration (UF) membrane unit is used for the separation of the whole digestate. The efficiency of screw-press, in terms of mass removal of digestate solids, typically exceeds 20% and reaches up to 45%. Regarding nutrients, they are divided into solid and liquid fractions in different ratios (Fig. 2). In the end, around 70% of nitrogen and 40% of phosphorous content of the digestate will be treated in the following stages of the liquid line and the remaining fraction present in the sludge will be sent to composting. The liquid effluent will then be treated in a UF configuration with frame and plate membranes. The UF process will operate with a recovery of 75% and the permeate will be free of TS. The UF concentrate will have a TS concentration of approximately 12% and will be mixed with the other solid fractions and thus sent for composting. A Struvite crystallization reactor (SCR) will be incorporated in the treatment train for phosphate recovery. Reactors that include in the same vessel chemicals addition and precipitation of the struvite white crystals are proposed. The settler (for the solid-liquid separation) will be located in the bottom of the reactor with a conical shape in order to collect the larger crystals produced. Appropriate number of parallel struvite crystallization units should be designed for the liquid fraction of digestate, with a maximum phosphate concentration of 1000 mgP/L. As it can be seen in Fig. 4a, up to 2 kg of struvite could be produced per t of animal waste treated, meaning that 80% of P entering the unit is recovered. Furthermore, ammonium ions will be recovered by an Ion Exchange Unit using natural zeolite. The ion exchange column design should take into consideration aspects, such as the volume of absorbent, its surface area, the height of column, the number of columns and the pressure drop. Ammonium loaded zeolite (2.9 t/d) could stand as a promising end-product, given its slow release fertilizing properties. Alternatively, ammonium ions will be recovered (957 kg/d) during the regeneration process. A Sequencing Batch reactor (SBR) is also included as a polishing step in order to obtain clean water for reuse. The quantity of liquid fed to the SBR shall be around 71 m<sup>3</sup>/d. The sludge produced from SBR could be included in the feedstocks of the

composting unit. As presented in the Figure above, almost 80% of carbon entering the SBR is expected to be removed from the liquid phase. Finally, a composting reactor is proposed for the treatment of the solid by-products (i.e. solids from screw-press and the UF units and sludge from the SBR) mixed with appropriate bulking agents (e.g. straw). The by-products to be composted have an elevated moisture content (85%) and very low C/N ratio (6.6). Therefore, a suitable additive should be added to optimise the C/N ratio around 20:1–40:1 and to reduce the moisture level below 70% (50–70%). This shall produce a total wet weight of almost 50 t/d that needs to be composted. The main objective of this stage is the maturation of the solid fraction resulting from the previous stages of the system in order to obtain high-quality compost. According to Fig. 4a, 8.2t compost with 45% moisture can be produced daily.

In the second scenario, the digestate treatment train is suggested for a smaller scale AD plant treating a mixture of manure with agricultural residues (70:30) producing 900 m<sup>3</sup>/d biogas. An integrated digestate valorisation scheme is proposed, producing compost, solid organic fertiliser, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and process water as presented in Fig. 4b according to rough estimations of mass balances. Specifically, a conventional mechanical separation technique as screw press is included taking into consideration its low cost (CAPEX and OPEX) and energy needs. The liquid fraction rich in ammoniacal nitrogen will be further processed by an evaporating system, which separates digestate liquid fraction into (a) nutrient rich condensate in a solid form (2 t/d) and (b) water (37 m<sup>3</sup>/d) that can be used as process water in the AD and/or composting process as well as water supply for irrigation purposes after conformity to the relevant quality assurance assessment. An ammonia scrubbing system is also incorporated in the evaporator's gas emission stream, producing an inorganic nitrogen high quality fertiliser (576 kg/d (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). The solid fraction of the digestate is composted towards the delivery of nitrogen, phosphorous and potassium rich solid organic fertiliser (0.9 t/d). By use of additives (e.g. zeolite, perlite, biochar) and bulking agents (agrowaste, sawdust etc) in appropriate ratios that would control C/N



**Fig. 4.** a. Flow diagram and end-products analysis of the first scenario proposed from an anaerobic digestion plant producing 112 t/d digestate from manure. All percentages are in wet basis (w.b.). Flow diagram and end-products analysis of the second scenario proposed from an anaerobic digestion plant producing 21 t/d digestate from manure. All percentages are in wet basis (w.b.).

ratio, an advanced biobased fertiliser with enhanced agronomic properties will derive. This plant is characterised as a zero liquid discharge system, since digestate water is recovered as process water and partly as moisture content of the products.

The proposed scenarios showcase the feasibility of treatment technologies for digestate's valorisation, in order to recover nutrients primarily nitrogen, phosphorous and potassium and process water. Both scenarios materialize the circular economy concept of digestate with direct benefits in the whole agro-food value chain by turning a problem into a solution through innovative or already available technologies in a new context.

## 5. Future perspectives of nutrients recovery from digestate

This paper aspires to practically demonstrate a spectrum of circular-nature based technologies for the valorisation of biogas digestate, via sustainable pathways, that will be, by design and intention, restorative aiming at recovering process water and nutrients in new biobased fertilisers and at minimizing risks induced by storing, managing and direct land use of digestate. Nevertheless, prior to the commercialization of the fertilising end-products, some key issues have to be dealt with.

First of all, the recovered products from the demonstration of the proposed processes need to be fully characterised, evaluated and validated in terms of physico-chemical and biological quality in order to ensure that all possible health risks are alleviated. According to the findings of the aforementioned assessment, the output products should be adequately tested in field trials in order to examine the agronomic properties, the effect on the environment and the food safety of biogas digestate products. The end-products should be thoroughly assessed in terms of quality in order to establish a concrete view for their suitability for direct use on arable land or in combination with other fertilisers/additives. To this end, high quality fertilisers which meet field trial requirements in terms of crops cultivation, climate and soil conditions in conformity to EU and national policy and regulations shall be produced.

The production of high efficiency fertilisers from digestate does not guarantee their commercial success and if market conditions are not favourable, it is unlikely that a profit will be made from their sale. Waste-derived fertilisers usually face the scepticism of end-users. In addition, the adoption of new innovative solutions often comes with the need for change of the deep-rooted agricultural practices and this may stand as a bottleneck to the full commercialization of a scheme. Economic incentives, the new EU legislation (Regulation (EU) 2019/1009) as well as consumers awareness may aid to overcome these aforementioned barriers.

Thus, as a next step, it is necessary to define and setup business models, marketing concepts and a suitable market entry strategy for the technological solutions that have been successfully demonstrated and their end-products. To this end, new business models in rural areas should be developed, that are synergised with existing ones creating further value from digestate. It is also important to unveil and enhance technologies and end-product market potential through targeted support actions, and to foster networking and create synergies between commercialized outputs and potential customers/end-users, advancing further market uptake. By considering those dimensions, a credible path to deliver the innovations to the market, maximizing economic, environmental and societal impacts and generating added value to the companies involved shall emerge.

## 6. Conclusions

Conclusively, this review outlines the inherent potential of digestate in terms of nutrients recovery in a sustainable context. In addition, this paper traces the basic constituents of digestate which may be valorized. Various technologies such as solid-liquid separation, ammonia stripping, membrane-based separation, struvite formation, composting, as well as thermal treatments used for digestate valorisation have been presented

in this study. Hence, it is undeniable that digestate could be considered as an appropriate feedstock for bio-base products promoting in turn circular economy.

Through the in-depth knowledge on technological schemes on nutrients recovery from digestate, the prospect of classifying digestate as a secondary resource for biobased fertilisers has been established. Taking into account the state-of-the-art, two integrated biorefineries, customised for AD plants were developed. Hitherto, apart from the technical challenges, economical and environmental feasibility should also be assessed. Policy and decision-makers should promote these "green" technological approaches and the respective products, so as to ensure social acceptance.

To sum up, it is indisputable that digestate could stand as a secondary nutrient resource. Although many technological alternatives are available, many challenges have to be overcome for full scale sustainable implementation.

## Credit author statement

Elli Maria Barampouti: Conceptualization; Investigation; Methodology; Validation; Visualization; Roles/Writing - original draft; Writing - review & editing. Sofia Mai: Conceptualization; Investigation; Methodology; Validation; Visualization; Roles/Writing - original draft; Writing - review & editing. Dimitris Malamis: Conceptualization Kostantinos Moustakas: Conceptualization Maria Loizidou: Supervision

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## References

- [1] Association EB. EBA statistical report 2018. 2018. Brussels, Belgium.
- [2] Burns C, Turley D, Hopwood L, Maio D Di. Assessment of digestate drying as an eligible heat use. 2016.
- [3] Drosig B, Fuchs W, Al Seadi T, Madsen M, Linke B. Nutrient recovery by biogas digestate processing. 2015.
- [4] EUROSTAT. eurostat.pdf. 2018. [https://ec.europa.eu/eurostat/statistics\\_explained/index.php/Farm\\_structure\\_statistics](https://ec.europa.eu/eurostat/statistics_explained/index.php/Farm_structure_statistics).
- [5] Calabi-Floody M, Medina J, Rumpel C, Condon LM, Hernandez M, Dumont M, et al. Smart fertilizers as a strategy for sustainable agriculture. first ed., vol. 147. Elsevier Inc.; 2018. <https://doi.org/10.1016/bs.agron.2017.10.003>.
- [6] GIZ (Deutsche Gesellschaft für Internationale Zusammenarbeit) GmbH. German biogas association. Digestate as Fertilizer 2018.
- [7] Dahlin J, Herbes C, Nelles M. Biogas digestate marketing: qualitative insights into the supply side. Resour Conserv Recycl 2015;104:152–61. <https://doi.org/10.1016/j.resconrec.2015.08.013>.
- [8] Risberg K. Quality and function of anaerobic digestion residues. 2015.
- [9] Debosz K, Petersen SO, Kure LK, Ambus P. Evaluating effects of sewage sludge and household compost on soil physical, chemical and microbiological properties. Appl Soil Ecol 2002;19:237–48. [https://doi.org/10.1016/S0929-1393\(01\)00191-3](https://doi.org/10.1016/S0929-1393(01)00191-3).
- [10] Nkao R. Agricultural benefits and environmental risks of soil fertilization with anaerobic digestates: a review. Agron Sustain Dev 2014;34:473–92. <https://doi.org/10.1007/s13593-013-0196-z>.
- [11] Sheets JP, Yang L, Ge X, Wang Z, Li Y. Beyond land application: emerging technologies for the treatment and reuse of anaerobically digested agricultural and food waste. Waste Manag 2015;44:94–115. <https://doi.org/10.1016/j.wasman.2015.07.037>.
- [12] Ivb AI, Ivb I, Community F. <Report-2013-Inventory Techniques for nutrient recovery from digestate.pdf> n.d.
- [13] Loosvelt Lien, Vanhecke B, Verdonckt P, Vervisch B, De Dobbelaere A, Annicaert B, et al. Case study report: nutrient recovery from digestate. Arbor. 2015.
- [14] Lukehurst C, Wrap Defra. IEA task 37 – biogas UK country report – status of the UK industry. 2013.
- [15] Hjorth M, Christensen KV, Christensen ML, Sommer SG. Soli-liquid separation of animal slurry in theory and practice. A review. Agron Sustain Dev 2010;30: 153–80.
- [16] Peng W, Pivato A. Sustainable management of digestate from the organic fraction of municipal solid waste and food waste under the concepts of back to earth alternatives and circular economy. Waste and Biomass Valorization 2019;10: 465–81. <https://doi.org/10.1007/s12649-017-0071-2>.

[17] Grigatti M, Barbanti L, Hassan MU, Ciavatta C. Fertilizing potential and CO<sub>2</sub> emissions following the utilization of fresh and composted food-waste anaerobic digestates. *Sci Total Environ* 2020;698:134198. <https://doi.org/10.1016/j.scitotenv.2019.134198>.

[18] Fouda S, Von Tucher S, Lichti F, Schmidhalter U. Nitrogen availability of various biogas residues applied to ryegrass. *J Plant Nutr Soil Sci* 2013;176:572–84. <https://doi.org/10.1002/jpln.201100233>.

[19] Tiwary A, Williams ID, Pant DC, Kishore VVN. Emerging perspectives on environmental burden minimisation initiatives from anaerobic digestion technologies for community scale biomass valorisation. *Renew Sustain Energy Rev* 2015;42:883–901. <https://doi.org/10.1016/j.rser.2014.10.052>.

[20] Menardo S, Gioelli F, Balsari P. The methane yield of digestate: effect of organic loading rate, hydraulic retention time, and plant feeding. *Bioresour Technol* 2011;102:2348–51. <https://doi.org/10.1016/j.biortech.2010.10.094>.

[21] Holm-Nielsen JB, Al Seadi T, Oleskowicz-Popiel P. The future of anaerobic digestion and biogas utilization. *Bioresour Technol* 2009;100:5478–84. <https://doi.org/10.1016/j.biortech.2008.12.046>.

[22] Fricke K, Santen H, Wallmann R, Hüttner A, Dichtl N. Operating problems in anaerobic digestion plants resulting from nitrogen in MSW. *Waste Manag* 2007;27:30–43. <https://doi.org/10.1016/j.wasman.2006.03.003>.

[23] Sahlström L. A review of survival of pathogenic bacteria in organic waste used in biogas plants. *Bioresour Technol* 2003;87:161–6. [https://doi.org/10.1016/S0960-8524\(02\)00168-2](https://doi.org/10.1016/S0960-8524(02)00168-2).

[24] Angelidakis I, Ellegaard L. Codigestion of manure and organic wastes in centralized biogas plants: status and future trends. *Appl Biochem Biotechnol Part A Enzyme Eng Biotechnol* 2003;109:95–105. <https://doi.org/10.1385/ABAB:109:1:3:95>.

[25] Limoli A, Langone M, Andreottola G. Ammonia removal from raw manure digestate by means of a turbulent mixing stripping process. *J Environ Manag* 2016;176:1–10. <https://doi.org/10.1016/j.jenvman.2016.03.007>.

[26] Romero Güiza MS, Mata Alvarez J, Chimenos Rivera JM, Astals Garcia S. Nutrient recovery technologies for anaerobic digestion systems: an overview. *Rev Investig Optim y Nuevos Procesos En Ing* 2016;29:7–26. <https://doi.org/10.18273/review.v29n1-2016001>.

[27] Fanguero D, Snauwaert E, Provolo G, Hidalgo D, Adani F, Kabbe C, et al. Mini-paper – available technologies for nutrients recovery from animal manure and digestates. 2011. p. 1–20.

[28] Mehta CM, Khunjar WO, Nguyen V, Tait S, Batstone DJ. Technologies to recover nutrients from waste streams: a critical review. *Crit Rev Environ Sci Technol* 2015;45:385–427. <https://doi.org/10.1080/10643389.2013.866621>.

[29] Campos JL, Crutchik D, Ó Franchi, Pavissich JP, Belmonte M, Pedrouso A, et al. Nitrogen and phosphorus recovery from anaerobically pretreated agro-food wastes: a review. *Front Sustain Food Syst* 2019;2:1–11. <https://doi.org/10.3389/fsufs.2018.00091>.

[30] Delzeit R, Kellner U. The impact of plant size and location on profitability of biogas plants in Germany under consideration of processing digestates. *Biomass Bioenergy* 2013;52:43–53. <https://doi.org/10.1016/j.biombioe.2013.02.029>.

[31] Akhbar A. Characterization of liquid fraction of digestates after solid-liquid separation from anaerobic co-digestion plants Afifi Akhbar to cite this version. HAL Id : tel-01684830 Délivré par Université de Montpellier 2018. 207–18.

[32] Magrì A. Research trends on nutrient management from digestates assessed using a bibliometric approach. *Front Sustain Food Syst* 2018;2. <https://doi.org/10.3389/fsufs.2018.00040>.

[33] Möller K, Müller T. Effects of anaerobic digestion on digestate nutrient availability and crop growth: a review. *Eng Life Sci* 2012;12:242–57. <https://doi.org/10.1002/elsc.201100085>.

[34] Tambone F, Orzi V, D'Imporzano G, Adani F. Solid and liquid fractionation of digestate: mass balance, chemical characterization, and agronomic and environmental value. *Bioresour Technol* 2017;243:1251–6. <https://doi.org/10.1016/j.biortech.2017.07.130>.

[35] Ledda C, Schiavano A, Salati S, Adani F. Nitrogen and water recovery from animal slurries by new integrated ultrafiltration, reverse osmosis and cold stripping process: a case study. *Water Res* 2013;47:6157–66. <https://doi.org/10.1016/j.watres.2013.07.037>.

[36] Vaneechoutte C, Lebuf V, Michels E, Belia E, Vanrolleghem PA, Tack FMG, et al. Nutrient recovery from digestate: systematic technology review and product classification. *Waste and Biomass Valorization* 2017;8:21–40. <https://doi.org/10.1007/s12649-016-9642-x>.

[37] Guilain F, Jimenez J, Rouez M, Crest M, Patureau D. Digestate mechanical separation: efficiency profiles based on anaerobic digestion feedstock and equipment choice. *Bioresour Technol* 2019;274:180–9. <https://doi.org/10.1016/j.biortech.2018.11.090>.

[38] Bachmann S, Uptmoor R, Eichler-Löbermann B. Phosphorus distribution and availability in untreated and mechanically separated biogas digestates. *Sci Agric* 2016;73:9–17. <https://doi.org/10.1590/0103-9016-2015-0069>.

[39] Bolzonella D, Fatone F, Gottardo M, Frison N. Nutrients recovery from anaerobic digestate of agro-waste: techno-economic assessment of full scale applications. *J Environ Manag* 2018;216:111–9. <https://doi.org/10.1016/j.jenvman.2017.08.026>.

[40] Fuchs W, Drosig B. Assessment of the state of the art of technologies for the processing of digestate residue from anaerobic digesters. *Water Sci Technol* 2013;67. <https://doi.org/10.2166/wst.2013.075>. 1984–93.

[41] Teglia C, Tremier A, Martel JL. Characterization of solid digestates: Part 1, review of existing indicators to assess solid digestates agricultural use. *Waste and Biomass Valorization* 2011;2:43–58. <https://doi.org/10.1007/s12649-010-9051-5>.

[42] Hallbar Consulting. Evaluation of nutrient recovery technologies for dairy manure and digestate n.d.:27.

[43] Buckwell A, Uhre AN, Williams A, Poláková J, Blum WEH, Schiefer J, et al. Sustainable intensification of European agriculture 2014.

[44] Zarebska A, Romero Nieto D, Christensen KV, Fjærbaek Søtoft L, Nordahl B. Ammonium fertilizers production from manure: a critical review. *Crit Rev Environ Sci Technol* 2015;45:1469–521. <https://doi.org/10.1080/10643389.2014.955630>.

[45] Meixner K, Fuchs W, Vaikova T, Svardal K, Loderer C, Neureiter M, et al. Effect of precipitating agents on centrifugation and ultrafiltration performance of thin stillage digestate. *Separ Purif Technol* 2015;145:154–60. <https://doi.org/10.1016/j.seppur.2015.03.003>.

[46] Mahmoud A, Olivier J, Vaxelaire J, Hoadley AFA. Advances in mechanical dewatering of wastewater sludge treatment. In: Sharma SK, Sanghi R, editors. *Wastewater reuse manag*. New York: Springer US; 2013. p. 253–303.

[47] David G, Negrelli C, Vachoud L, Ruiz E, Delalonde M, Wisniewski C. An environmental application of functionalized chitosan: enhancement of the separation of the solid and liquid fractions of digestate from anaerobic digestion. *Pure Appl Chem* 2016;88:1155–66. <https://doi.org/10.1515/pac-2016-0705>.

[48] Garcia MC, Szogi AA, Vanotti MB, Chastain JP, Millner PD. Enhanced solid-liquid separation of dairy manure with natural flocculants. *Bioresour Technol* 2009;100:5417–23. <https://doi.org/10.1016/j.biortech.2008.11.012>.

[49] Burton CH. The potential contribution of separation technologies to the management of livestock manure. *Livest Sci* 2007;112:208–16. <https://doi.org/10.1016/j.livsci.2007.09.004>.

[50] Xia M, Tao W, Shayya W, Lu Z. Passive solid-liquid separation of anaerobically digested dairy manure using two-stage filtration. *Biosyst Eng* 2012;111:392–7. <https://doi.org/10.1016/j.biosystemseng.2012.01.006>.

[51] Tao W, Fattah KP, Huchzermeier MP. Struvite recovery from anaerobically digested dairy manure: a review of application potential and hindrances. *J Environ Manag* 2016;169:46–57. <https://doi.org/10.1016/j.jenvman.2015.12.006>.

[52] Hidalgo D, Corona F, Martín-Marroquín JM, del Álamo J, Aguado A. Resource recovery from anaerobic digestate: struvite crystallisation versus ammonia stripping. *Desalin Water Treat* 2016;57:2626–32. <https://doi.org/10.1080/19443994.2014.1001794>.

[53] Sengupta S, Nawaz T, Beaudry J. Nitrogen and phosphorus recovery from wastewater. *Curr Pollut Reports* 2015;1:155–66. <https://doi.org/10.1007/s40726-015-0013-1>.

[54] Szymański M, Szara E, Sosulski T, Waś A, Van Praussen GWP, Cornelissen RL, et al. A Bio-Refinery concept for n and p recovery - a chance for biogas plant development. *Energy* 2019;12. <https://doi.org/10.3390/en12010155>.

[55] Monfet E, Aubry G, Ramirez AA. Nutrient removal and recovery from digestate: a review of the technology. *Biofuels* 2018;9:247–62. <https://doi.org/10.1080/17597269.2017.1336348>.

[56] Morales N, Boehler MA, Buettnert S, Liebi C, Siegrist H. Recovery of N and P from urine by struvite precipitation followed by combined stripping with digester sludge liquid at full scale. *Water (Switzerland)* 2013;5:1262–78. <https://doi.org/10.3390/w5031262>.

[57] Nordahl B, Horn VG, Larsson M, du Preez JH, Christensen K. A membrane contactor for ammonia stripping, pilot scale experience and modeling. *Desalination* 2006;199:172–4. <https://doi.org/10.1016/j.desal.2006.03.037>.

[58] Jiang A, Zhang T, Zhao QB, Li X, Chen S, Frear CS. Evaluation of an integrated ammonia stripping, recovery, and biogas scrubbing system for use with anaerobically digested dairy manure. *Biosyst Eng* 2014;119:117–26. <https://doi.org/10.1016/j.biosystemseng.2013.10.008>.

[59] Bonmatí A, Flotats X. Air stripping of ammonia from pig slurry: characterisation and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion. *Waste Manag* 2003;23:261–72. [https://doi.org/10.1016/S0956-053X\(02\)00144-7](https://doi.org/10.1016/S0956-053X(02)00144-7).

[60] Değermenci N, Ata ON, Yıldız E. Ammonia removal by air stripping in a semi-batch jet loop reactor. *J Ind Eng Chem* 2012;18:399–404. <https://doi.org/10.1016/j.jiec.2011.11.009>.

[61] Ukwuani AT, Tao W. Developing a vacuum thermal stripping – acid absorption process for ammonia recovery from anaerobic digester effluent. *Water Res* 2016;106:108–15. <https://doi.org/10.1016/j.watres.2016.09.054>.

[62] LGL Ammonia Stripper n.d.

[63] Törnwall E, Pettersson H, Thorin E, Schwede S. Post-treatment of biogas digestate-An evaluation of ammonium recovery, energy use and sanitation. *Energy Procedia* 2017;142:957–63. <https://doi.org/10.1016/j.egypro.2017.12.153>.

[64] Shi L, Simplicio WS, Wu G, Hu Z, Hu H, Zhan X. Nutrient recovery from digestate of anaerobic digestion of livestock manure: a review. *Curr Pollut Reports* 2018;4:74–83. <https://doi.org/10.1007/s40726-018-0082-z>.

[65] Guo JS, Abbas AA, Chen YP, Liu ZP, Fang F, Chen P. Treatment of landfill leachate using a combined stripping, Fenton, SBR, and coagulation process. *J Hazard Mater* 2010;178:699–705. <https://doi.org/10.1016/j.jhazmat.2010.01.144>.

[66] Quan X, Wang F, Zhao Q, Zhao T, Xiang J. Air stripping of ammonia in a water-sparged aerocyclone reactor. *J Hazard Mater* 2009;170:983–8. <https://doi.org/10.1016/j.jhazmat.2009.05.083>.

[67] Emerson K, Russo RC, Lund RE, Thurston RV. Aqueous ammonia equilibrium calculations: effect of pH and temperature. *J Fish Res Board Can* 1975;32:2379–83. <https://doi.org/10.1139/f75-274>.

[68] Laureni M, Palatsi J, Llovera M, Bonmatí A. Influence of pig slurry characteristics on ammonia stripping efficiencies and quality of the recovered ammonium-

sulfate solution. *J Chem Technol Biotechnol* 2013;88:1654–62. <https://doi.org/10.1002/jctb.4016>.

[69] Gustin S, Marinsek-Logar R. Effect of pH, temperature and air flow rate on the continuous ammonia stripping of the anaerobic digestion effluent. *Process Saf Environ Protect* 2011;89:61–6. <https://doi.org/10.1016/j.psep.2010.11.001>.

[70] Macura B, Johannsdottir SL, Piniewski M, Haddaway NR, Kvarnström E. Effectiveness of ecotechnologies for recovery of nitrogen and phosphorus from anaerobic digestate and effectiveness of the recovery products as fertilisers: a systematic review protocol. *Environ Evid* 2019;8:1–9. <https://doi.org/10.1186/s13750-019-0173-3>.

[71] Vaneechoutte C, Meers E, Michels E, Buysse J, Tack FMG. Ecological and economic benefits of the application of bio-based mineral fertilizers in modern agriculture. *Biomass Bioenergy* 2013;49:239–48. <https://doi.org/10.1016/j.biombioe.2012.12.036>.

[72] Vaneechoutte C, Meers E, Michels E, Ghekiere G, Accoe F, Tack FMG. Closing the nutrient cycle by using bio-digestion waste derivatives as synthetic fertilizer substitutes: a field experiment. *Biomass Bioenergy* 2013;55:175–89. <https://doi.org/10.1016/j.biombioe.2013.01.032>.

[73] Serna-Maza A, Heaven S, Banks CJ. Biogas stripping of ammonia from fresh digestate from a food waste digester. *Bioresour Technol* 2015;190:66–75. <https://doi.org/10.1016/j.biortech.2015.04.041>.

[74] Melse RW, Ogink NWM. A *Ir S* scrubbing *T* echniques for a mmonia and. *Society 2005*;48:2303–13.

[75] Rahman MM, Salleh MAM, Rashid U, Ahsan A, Hossain MM, Ra CS. Production of slow release crystal fertilizer from wastewaters through struvite crystallization - a review. *Arab J Chem* 2014;7:139–55. <https://doi.org/10.1016/j.arabjc.2013.10.007>.

[76] Marti N, Bouzas A, Seco A, Ferrer J. Struvite precipitation assessment in anaerobic digestion processes. *Chem Eng J* 2008;141:67–74. <https://doi.org/10.1016/j.cej.2007.10.023>.

[77] Parsons SA, Doyle JD. Struvite formation, control and recovery. *Water Res* 2002;36:3925–40.

[78] Le Corre KS, Valsami-Jones E, Hobbs P, Jefferson B, Parsons SA. Struvite crystallisation and recovery using a stainless steel structure as a seed material. *Water Res* 2007;41:2449–56. <https://doi.org/10.1016/j.watres.2007.03.002>.

[79] Pastor L, Mangin D, Ferrer J, Seco A. Struvite formation from the supernatants of an anaerobic digestion pilot plant. *Bioresour Technol* 2010;101:118–25. <https://doi.org/10.1016/j.biortech.2009.08.002>.

[80] Aryianto E, Ang HM, Sen TK. Impact of various physico-chemical parameters on spontaneous nucleation of struvite ( $MgNH_4PO_4 \cdot 6H_2O$ ) formation in a wastewater treatment plant: kinetic and nucleation mechanism. *Desalin Water Treat* 2014;52:6620–31. <https://doi.org/10.1080/19443994.2013.821042>.

[81] Castro LDP, Vecino-Gutierrez KP, Díaz-Moyano LJ, Jaimes-Estévez J, Escalante-Hernández H. Lighting the anaerobic digestion process in rural areas: obtainment of struvite from bovine manure digestate. *Rev Colomb Biotecnol* 2018;20:78–88. <https://doi.org/10.15446/rev.colomb.biote.v20n2.71184>.

[82] Cordell D, Rosemarin A, Schröder JJ, Smit AL. Towards global phosphorus security: a systems framework for phosphorus recovery and reuse options. *Chemosphere* 2011;88:747–58. <https://doi.org/10.1016/j.chemosphere.2011.02.032>.

[83] Kataki S, West H, Clarke M, Baruah DC. Phosphorus recovery as struvite: recent concerns for use of seed, alternative Mg source, nitrogen conservation and fertilizer potential. *Resour Conserv Recycl* 2016;107:142–56. <https://doi.org/10.1016/j.resconrec.2015.12.009>.

[84] Battistoni P, De Angelis A, Prisciandaro M, Boccadoro R, Bolzonella D. P removal from anaerobic supernatants by struvite crystallization: long term validation and process modelling. *Water Res* 2002;36. [https://doi.org/10.1016/S0043-1354\(01\)00401-8](https://doi.org/10.1016/S0043-1354(01)00401-8). 1927–38.

[85] Lee SI, Weon SY, Lee CW, Koopman B. Removal of nitrogen and phosphate from wastewater by addition of bittern. *Chemosphere* 2003;51:265–71. [https://doi.org/10.1016/S0045-6535\(02\)00807-X](https://doi.org/10.1016/S0045-6535(02)00807-X).

[86] Yu R, Geng J, Ren H, Wang Y, Xu K. Combination of struvite pyrolylate recycling with mixed-base technology for removing ammonium from fertilizer wastewater. *Bioresour Technol* 2012;124:292–8. <https://doi.org/10.1016/j.biortech.2012.08.015>.

[87] Huang H, Xu C, Zhang W. Removal of nutrients from piggy wastewater using struvite precipitation and pyrolysis technology. *Bioresour Technol* 2011;102:2523–8. <https://doi.org/10.1016/j.biortech.2010.11.054>.

[88] Quintana M, Sánchez E, Colmenarejo MF, Barrera J, García G, Borja R. Kinetics of phosphorus removal and struvite formation by the utilization of by-product of magnesium oxide production. *Chem Eng J* 2005;111:45–52. <https://doi.org/10.1016/j.cej.2005.05.005>.

[89] Desmidt E, Ghyselbrecht K, Monballiu A, Rabaey K, Verstraete W, Meesschaert BD. Factors influencing urease driven struvite precipitation. *Separ Purif Technol* 2013;110:150–7. <https://doi.org/10.1016/j.seppur.2013.03.010>.

[90] Zhang H, Lo VK, Thompson JR, Koch FA, Liao PH, Lobanov S, et al. Recovery of phosphorus from dairy manure: a pilot-scale study. *Environ Technol* 2015;36:1398–404. <https://doi.org/10.1080/09593330.2014.991354>.

[91] Moerman W, Carballa M, Vandekerckhove A, Derycke D, Verstraete W. Phosphate removal in agro-industry: pilot- and full-scale operational considerations of struvite crystallization. *Water Res* 2009;43:1887–92. <https://doi.org/10.1016/j.watres.2009.02.007>.

[92] Huchzermeyer MP, Tao W. Overcoming challenges to struvite recovery from anaerobically digested dairy manure. *Water Environ Res* 2012;84:34–41. <https://doi.org/10.2175/106143011x13183708018887>.

[93] Uludag-Demirer S, Demirer GN, Frear C, Chen S. Anaerobic digestion of dairy manure with enhanced ammonia removal. *J Environ Manag* 2008;86:193–200. <https://doi.org/10.1016/j.jenvman.2006.12.002>.

[94] Zeng L, Li X. Nutrient removal from anaerobically digested cattle manure by struvite precipitation. *J Environ Eng Sci* 2006;5:285–94. <https://doi.org/10.1139/S05-027>.

[95] Gaterell MR, Gay R, Wilson R, Gochin RJ, Lester JN. An economic and environmental evaluation of the opportunities for substituting phosphorus recovered from wastewater treatment works in existing UK fertiliser markets. *Environ Technol* 2000;21:1067–84. <https://doi.org/10.1080/0959332108618050>.

[96] Schoumans OF, Rulkens WH, Oenema O, Ehler P a I. Phosphorus recovery from animal manure. *Alterra Rep* 2010;2158.

[97] Daumer ML, Picard S, Saint-Cast P, Dabert P. Technical and economical assessment of formic acid to recycle phosphorus from pig slurry by a combined acidification-precipitation process. *J Hazard Mater* 2010;180:361–5. <https://doi.org/10.1016/j.jhazmat.2010.04.039>.

[98] Graeser S, Postl W, Bojar HP, Berlepsch P, Armbuster T, Raber T, et al. Struvite-(K),  $KMgPO_4 \cdot 6H_2O$ , the potassium equivalent of struvite - a new mineral. *Eur J Mineral* 2008;20:629–33. <https://doi.org/10.1127/0935-1221/2008/0020-1810>.

[99] Rehl T, Müller J. Life cycle assessment of biogas digestate processing technologies. *Resour Conserv Recycl* 2011;56:92–104. <https://doi.org/10.1016/j.resconrec.2011.08.007>.

[100] Ganrot Z. Use of zeolites for improved nutrient recovery from decentralized domestic wastewater. In: Inglezakis VJ, Zorbas AA, editors. *Handb. Nat. zeolites*. Beijing: Bentham Science Publishers; 2012.

[101] Guo X, Zeng L, Li X, Park HS. Removal of ammonium from RO permeate of anaerobically digested wastewater by natural zeolite. *Separ Sci Technol* 2007;42:3169–85. <https://doi.org/10.1080/01496390701514949>.

[102] Kizito S, Wu S, Kipkemot Kirui W, Lei M, Lu Q, Bah H, et al. Evaluation of slow pyrolyzed wood and rice husks biochar for adsorption of ammonium nitrogen from piggy manure anaerobic digestate slurry. *Sci Total Environ* 2015;505:102–12. <https://doi.org/10.1016/j.scitotenv.2014.09.096>.

[103] Wirthensohn T, Waeger F, Jelinek L, Fuchs W. Ammonium removal from anaerobic digester effluent by ion exchange. *Water Sci Technol* 2009;60:201–10. <https://doi.org/10.2166/wst.2009.317>.

[104] Minardi ER, Chakraborty S, Calabro V, Curcio S, Drioli E. Membrane applications for biogas production and purification processes: an overview on a smart alternative for process intensification. *RSC Adv* 2015;5:14156–86. <https://doi.org/10.1039/c4ra11819g>.

[105] Gerardo ML, Aljohani NHM, Oatley-Radcliffe DL, Lovitt RW. Moving towards sustainable resources: recovery and fractionation of nutrients from dairy manure digestate using membranes. *Water Res* 2015;80:80–9. <https://doi.org/10.1016/j.watres.2015.05.016>.

[106] Masse L, Massé DI, Pellerin Y. The use of membranes for the treatment of manure: a critical literature review. *Biosyst Eng* 2007;98:371–80. <https://doi.org/10.1016/j.biosystemseng.2007.09.003>.

[107] Bilstad T, Madland M, Espedal E, Hanssen PH. Membrane separation of raw and anaerobically digested pig manure. *Water Sci Technol* 1992;25:19–26.

[108] Fugère R, Mameri N, Gallot JE, Comeau Y. Treatment of pig farm effluents by ultrafiltration. *J Membr Sci* 2005;255:225–31. <https://doi.org/10.1016/j.memsci.2005.01.036>.

[109] Zhang K, Farahbakhsh K. Removal of native coliphages and coliform bacteria from municipal wastewater by various wastewater treatment processes: implications to water reuse. *Water Res* 2007;41:2816–24. <https://doi.org/10.1016/j.watres.2007.03.010>.

[110] Kim S, Lee DW, Cho J. Application of direct contact membrane distillation process to treat anaerobic digestate. *J Membr Sci* 2016;511:20–8. <https://doi.org/10.1016/j.memsci.2016.03.038>.

[111] Holloway RW, Childress AE, Dennett KE, Cath TY. Forward osmosis for concentration of anaerobic digester centrate 2007;41:4005–14. <https://doi.org/10.1016/j.watres.2007.05.054>.

[112] Chiumenti A, da Borsig F, Chiumenti R, Teri F, Segantini P. Treatment of digestate from a co-digestion biogas plant by means of vacuum evaporation: tests for process optimization and environmental sustainability. *Waste Manag* 2013;33:1339–44. <https://doi.org/10.1016/j.wasman.2013.02.023>.

[113] Manyi-Loh CE, Mamphweli SN, Meyer EL, Okoh AI. Microbial anaerobic digestion: process dynamics and implications from the renewable energy, environmental and agronomy perspectives. *Int J Environ Sci Technol* 2019;16:3913–34. <https://doi.org/10.1007/s13762-019-02380-w>.

[114] Barampouti EM, Mai S, Malamis D, Moustakas K, Loizidou M. Liquid biofuels from the organic fraction of municipal solid waste: a review. *Renew Sustain Energy Rev* 2019;110. <https://doi.org/10.1016/j.rser.2019.04.005>.

[115] Zhang T, He X, Deng Y, Tsang DCW, Jiang R, Becker GC, et al. Phosphorus recovered from digestate by hydrothermal processes with struvite crystallization and its potential as a fertilizer. *Sci Total Environ* 2020;698:134240. <https://doi.org/10.1016/j.scitotenv.2019.134240>.

[116] Huttunen S, Manninen K, Leskinen P. Combining biogas LCA reviews with stakeholder interviews to analyse life cycle impacts at a practical level. *J Clean Prod* 2014;80:5–16. <https://doi.org/10.1016/j.jclepro.2014.05.081>.

[117] Monlau F, Sambusiti C, Ficara E, Aboulkas A, Barakat A, Carrère H. New opportunities for agricultural digestate valorization: current situation and perspectives. *Energy Environ Sci* 2015;8:2600–21. <https://doi.org/10.1039/c5ee01633a>.

[118] Yasar A, Rasheed R, Tabinda AB, Tahir A, Sarwar F. Life cycle assessment of a medium commercial scale biogas plant and nutritional assessment of effluent slurry. *Renew Sustain Energy Rev* 2017;67:364–71. <https://doi.org/10.1016/j.rser.2016.09.026>.