Nutrient recovery technologies for anaerobic digestion systems: An overview

Tecnologías de recuperación de nutrientes para los sistemas de digestión anaeróbica: revisión

Tecnologias de recuperação de nutrientes para os sistemas de digestão anaeróbia: revisão

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Abstract

Anaerobic digestion is a worldwide technology to treat organic waste streams, primarily due to its capacity to produce methane as renewable energy. However, there is an increasing interest on nutrient recovery (N and P), which from both environmental and economic reasons have been identified as key feature in anaerobic digestion plants. The manuscript presents a comprehensive overview on recent advances in nutrient recovery technologies applicable for anaerobic digestion systems. The review focus on N and P recovery through the use of digestates as fertilizers, struvite precipitation and biological systems such as phycoremediation (i.e. algae cultivation) and polyphosphates accumulating organisms.

Keywords: Anaerobic digestion, nutrient recovery, struvite, phycoremediation, fertilizer.

Resumen

La digestión anaeróbica es una tecnología mundialmente aplicada para el tratamiento de residuos orgánicos, principalmente debido a su capacidad de producir metano como fuente de energía renovable. Sin embargo, existe un creciente interés en la recuperación de nutrientes (N y P), el cual desde el punto de vista ambiental y económico ha sido identificado como un factor clave en las plantas de tratamiento vía digestión anaeróbica. El presente manuscrito presenta una visión global de los recientes avances en las tecnologías de recuperación de nutrientes aplicables a sistemas de digestión anaeróbica. La revisión está enfocada en la recuperación de N y P mediante el uso del digestado como fertilizante, la precipitación de estruvita y sistemas biológicos como la ficoremediación (ej. cultivos de algas) y organismos acumuladores de polifosfatos.

Palabras clave: Digestión anaeróbica, recuperación de nutrientes, estruvita, ficoremediación, fertilizante orgánico.

Resumo

A digestão anaeróbia é uma tecnologia mundialmente conhecida para o tratamento de resíduos orgânicos, principalmente devido a sua capacidade de produzir metano como energia renovável. No entanto, há um interesse crescente sobre a recuperação de nutrientes (N e P), que a partir de razões ambientais e econômicas têm sido identificados como elemento-chave em plantas de digestão anaeróbia. O presente manuscrito apresenta uma visão abrangente sobre os recentes avanços em tecnologias de recuperação de nutrientes aplicáveis para sistemas de digestão anaeróbia. O foco da revisão é a recuperação do N e P através do uso de fertilizantes, como digestates precipitação estruvite e sistemas biológicos, tais como phycoremediation (por ex, cultivo de algas) e organismos acumuladores de polifosfatos.

Palabras-chave: digestão anaeróbia, recuperação de nutrientes, estruvite, fitorremediação, adubo orgânico.

Introducción

Anaerobic digestion (AD) stands as an important technology in the emerging green energy economy [1]. Advantages of AD over other technologies are: (i) cost-effective organic wastes treatment for wastewater and solid waste streams, and (ii) energy/economy alternative in rural sector through the digestion of agro-wastes and/or energy crops [2,3]. AD plants are usually of large scale, with digester capacities ranging from few hundred m^3 up to several thousand m^3 [4]. In urban areas AD plants mostly treat sewage sludge and organic fraction of municipal solid wastes (OFMSW) [5,6]; while, rural biogas plants, centralized and on-farm, co-treat animal manure and other suitable organic residues [3]. Centralized plants commonly develops in high density of livestock areas linked to insufficient accessible arable land (i.e. Europe) [7,8]; while on-farm plants are becoming for interest on extensive regions with biogas incentives (i.e. United States and Australia) [9]. However, the uses of house digester have started to rise in the developing countries as energy/biogas source. On biogas plants the biogas can, after cleaning, produce heat in a quality adapted burner, or electricity and heat in a combined heat and power unit [8]. However, biogas can also be transformed into green gas by upgrading which has the same quality as natural gas and can be supplied to the natural-gas grid or used as transport fuel [10].

Besides renewable energy, AD of organic wastes produces a digestate which is a mixture of partially degraded organic matter, anaerobic biomass and inorganic matter (including nutrients) [11]. The AD process facilitates the mobilization of nutrients (N and P) from the organic matter to the liquid phase. N is converted into ammonium and organic P is hydrolyzed to soluble P [12,13]. Digestate quality and mobilization extent depend on the three main components of the anaerobic digestion system: (i) the feedstock, (ii) the digester design and operational conditions, and (iii) digestate post-treatment [14]. As an example, Figure 1 illustrates the most common organic fraction municipal solid waste (OFMSW) AD plant configurations.

Today, most AD plants are energy focused with low attention on nutrient recovery. Nevertheless, the continuous increase in fertilizer prices (mainly formed of N, P and K) has raised interest on nutrient recovery from digestate. Batstone and Virdis [15] clearly stated that new wastewater treatment plants have to: (i) achieve existing public health and environmental goals, (ii) recover maximal energy from wastewater, and (iii) preserve and recover nutrients for reuse. Moreover, the economic success of investment in AD plants is strictly related to incentive polices adopted in the countries. Actually, a high proportion of AD operators seldom sell digestates above cost recovery prices, despite its high agronomic value [9]. Therefore it has been provide interest and incentives to nutrient recovery from AD effluents. For instance, biogas Italy subsidies provide a plus an added bonus (15-30€/MWh) if nitrogen is removed to produce a fertilizer [16,17].

Digestate direct land application

Today, using digestate as organic fertilizer or soil conditioner seem to be the best option for its recycling [3,13,18]. The use of digestate as fertilizer allow to recycle nutrients and reduce the use of chemical fertilizers [19]. Nonetheless, the quality of the digestate must be carefully evaluated prior usage [18].
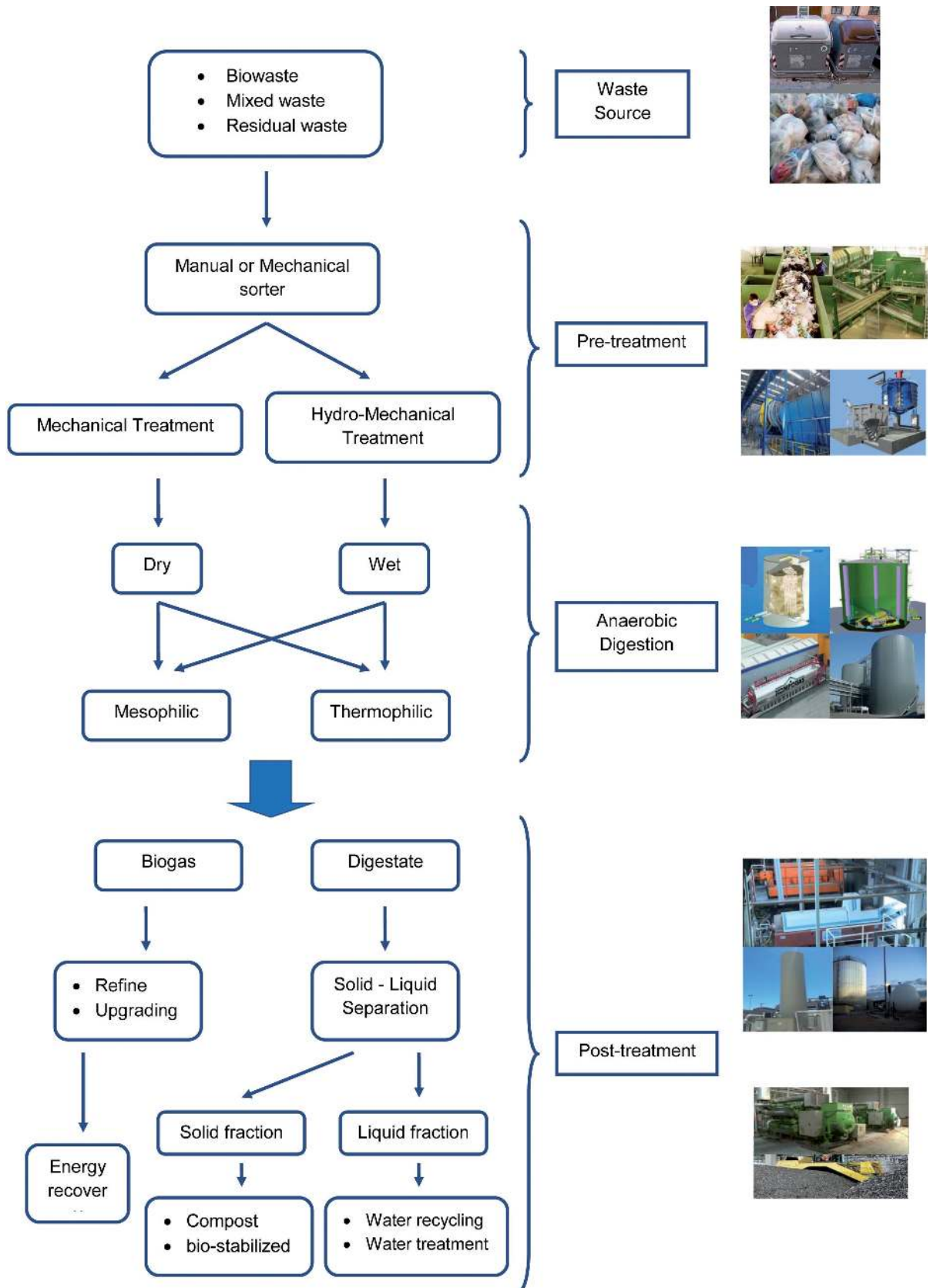
Figure 1. Current OFMSW AD plant schemes.

High quality digestate fit for use as fertilizer is defined by essential features such as declared content of nutrients, pH, dry matter and organic dry matter content, homogeneity, purity (free of inorganic impurities such as plastic, stones, glass, etc), content of biological (pathogenic) material and of chemical pollutants (organic and inorganic) [20]. From an agricultural point of view, the main parameters to take into consideration are pH, salinity, nutrients, pathogens and heavy metals [3,13,21], while environmental concerns are inappropriate digestate handling, storage and application, which may led to ammonia emissions, nitrate leaching and phosphorous overdoses [22]. Table 1 shows the heavy metals, micro- and macro-nutrients composition of different AD digestate, which have been grouped in five categories [3,23]: (i) sewage sludge (SS); (ii) animal manures; (iii) food industry wastes; (iv) energy crops and harvesting residues; and (v) OFMSW. It can observe that element concentrations are highly variable and substrate type dependent. For instance, sewage sludge digestate present a relatively high P concentration while slaughterhouse waste digestate present high N concentration. Digestate are also evaluated in terms of salinity, remaining biodegradable organic matter, phytotoxicity and pathogens abundance [24,25]. Such facts determine the need for applying additional specific treatment to increase digestate quality until acceptable levels [26].

The risk of inappropriate use of digestate is related with the salinity (i.e. Na^+ and Al^{3+}) and digestate stability. High doses or continued application of high salinity digestate can lead to an excessive salt and heavy metals accumulation in soil, which might inhibit plant growth [3,26,27]; while application of unstable digestate (i.e. digestate with large amounts of non-degraded organic matter) may exert negative impact on organic matter mineralization and nutrient turn-over in the plant-soil system [13,27,28]. Unstable digestate can be obtained from badly operated digesters or digesters operated at intense conditions such as short hydraulic retention times, high organic loading rates and co-substrate addition based on random or heuristic decisions [3]. Enlarging digestion time can decrease the amount of labile compounds in digestates; however it may reduce the specific volumetric biogas production of digesters as well as require a higher investment (larger vessel). Aerobic post-treatment can be used to decrease digestates phytotoxic impact without affecting AD feasibility as well as improve pathogens destruction.

In this regard, Abdullahi et al. [28] found that the seed germination increased with dilution and incubation time, suggesting that lower application rates and longer lag periods between application of aerobically treated digestate and planting can reduce the occurrence of phytotoxicity. Abubaker *et al.* [29], who studied bacterial community structure and microbial activity in different soils amended with digestate and untreated cattle slurry, observed that differences in microbial community structure induced by the digestate appeared to be smaller than those induced by cattle slurry, and those changes did not translate into altered microbial functioning.

Digestate Solid-Liquid separation
Although digestate direct land application is widely applied, the large amount of digestate produced in intensive livestock regions can led to nutrient surplus problems [40–42]. Additionally, the large amount of water (>80%) in digestates will increase transport expenses and difficult its utilization.

To avoid negative impacts on the environment, complementary treatment of digestate are needed in context of nutrient surplus removal and/or recovery [43,44]. One of the simplest digestate post-treatment methods is the separation of the solid and the liquid fraction (known as digestate dewatering) [45,46].

The solid-liquid separation provides two materials fractions that can be handling independently [47]. The solid fraction can be transported longer distances because of the reduction in the water content, or undergo further processing to produce value-add products (e.g. compost and organic fertilizer by bio-stabilization) [47]. The liquid fraction can be returned to the process, treated to meet lands requirements (nutrient removal), or treated to recover valuable nutrients (P and N) [48–53]. The aims of solid and liquid separation are: (i) increase the possibilities of digestate management as by-product; (ii) avoid uncontrolled decomposition process; and (iii) reduce transport cost (solid fraction) [54]. The common solid and liquid separation technologies are decanting, centrifuge, brusch-roller, vibrating screen, screw press, belt press and run-down screen [55]. The kind of technology used in the solid-liquid separation of the digestate will determine the composition of the fractions. Moreover, the separation efficiency is determined by the flows, solid content, use of additives and digestate degradation [45,53,54,56].

For instance, in manure centrifuged digestate, the dry matter content of the solid fraction is typically 25-35%, containing 60-80% of the digestate dry matter and almost the totally of phosphorus from the original slurry, but only 20 – 25% on the nitrogen and 10-15% of the potassium [14]. Another factor to consider in the solid-liquid separation is the economic efficiency which is mainly determined by the organic matter and nutrient (N, P and K) retention in the solid fraction [53].

Therefore, some processes integrate two sequential separation technologies to increase separation efficiency and provide different: (i) operation conditions (flows), (ii) performances (N and P recovery) and (iii) expenses (investment and operation cost) [57].

For instance, Parera et al. [58] evaluated the economic viability of two solid and liquid separation systems, run down screen-screw press and screw press–centrifuge; concluding that operational conditions regulation and calibration (i.e. flows and mesh pore diameter) determinate the separation efficiency. The run down screen-screw press system allowed high flow (20m^3/h) with N and P recovery of 15 and 20%, respectively, while screw press–centrifuge systems worked at low flow (4.5m^3/h) with N and P recovery of 45-80%, respectively. However, the economic balance showed that run-down screen-screw press system presented lower operation cost (1.03€/m^3; 1.96€/kg N and 4.96€/kg P) than the screw press–centrifuge systems (3.68€/m^3; 2.34€/kg N and 4.43€/kg P) [58].

Digestate solid fraction treatment
From the solid-liquid separation, the solid fraction can subsequently be applied directly as fertilizer in agriculture, composted or dried for intermediate storage and enhanced transportability. The solid fraction can be also be sold as a phosphorous rich fertilizer, without any further treatment [20]. Nest et al. [59] showed that the use of solid fraction of separated digestate may replace mineral fertilizer and leads to enhanced the availability of P. Digestate composting and stockpiling are widely used, since these technologies are the simplest techniques and the material can be considered hygienically safe [60].

On the other hand, pelletized technology is rapidly expanding. Pelletized technology consists of digestate dried (e.i. fluidized bed dryer) following by mixing with a $(NH_4)_2SO_4$ solution and pellets formation [43,61]. It has been shown that when digestate is converted to dry pelletized bagged products, digestate can reach a far greater price up €250/ton [60]. Other options for digestate solid fraction is the use for industrial purposes, this involves production of composite materials, biorefinery processes or incineration for energy production [20]. Santi et al. [62] showed that digestate solid fraction produced by commercial corn-silage AD contains a notable quantity of cell wall polymers that could potentially be used in biorefinery processes for ethanol and xylo-oligosaccharide production.

Digestate liquid fraction treatment
From the solid-liquid separation the liquid fraction generates greater interest, since it contains most nitrogen and potassium. Digestate liquid fraction can be used to dilute high solid feedstock and re-fed to the digester and/or applied as irrigation water [48,63]. However, the accumulation of nitrogen due to liquid recirculation can lead to anaerobic biomass inhibition [64–66] and restricts land application directives limiting N spreading on lands [67,68]. Therefore, AD plants are currently focusing their efforts on providing adequate technologies to process digestate liquid fraction, giving strategic importance to reduce nitrogen content by either removal or recovery technologies (Figure 2) [14]. Removal consist in reduce the nitrogen concentration on digestate, converting the ammonium into nitrogen gas, enhancing the nitrogen concentrations to directive limits or land requirements; while recovery consist in ammonium fixation and concentration on liquid or solid medium that are potentially reusable as agricultural fertilizer or chemical reagent [15]. Today, nitrogen treatment technologies are mainly focus on its elimination rather than on its recovery. However, conventional nitrogen removal methods are being recognised as wasteful [15,63]. For instance, the conventional nitrification-denitrification process, where nitrogen is converted to elemental nitrogen gas requires both electrical and chemical energy [15]. In this regard, new technologies such as Anammox, absorption and membrane have been presented as alternative nitrogen treatment options. A brief description of the main technologies is discussed below.

Table. 1. AD digestates composition (adapted and expanded from Zirkler *et al.* [30])

Feed	Reactor size	pH	TS	TOC	N	P	K	S	Ca	Mg	Fe	Mn	Zn	Cu	Pb	Cd	Ni	Mo	Se	Ref.
							(gkg⁻¹)*								(mgkg⁻¹)*					
Animal manure and energy crops																				
CM	F	8.6	52	274	22	1	17		20	6	2.0	164	137	44						[31]
CM	L	8.5		500	42	9	13	3.6	20	18										[32]
CM	L	7.7	92	355	43	7	47													[33]
PM	L	7.3		551	43	20	18	4.6	34	12	1.0	245	1304	121						[32]
Poultry manure	L			452	67	24	24	5.3	92	6	1.8	663	578	105						[32]
Horse manure	L												43	14	3.2	0.3	3.8			[34]
Maize	L	7.8											34	29	1.3	0.05	5			[34]
AcoD using manure as principal substrate																				
CM + 4% glycerol	L	5.6	38	465	49	13	47	4.6	40	7	3.0	358	473	282						[26]
CM + 6% glycerol	L	7.4	73	587	32	5	22	3.6	24	5	2.3	235	388	178						[26]
CM + 5% orange peel residues	L	7.9	24	385	59	8	45	4.6	41	11	1.2	246	316	115						[26]
PM + 0.6% SHW + 6.5%biodiesel wastewater	L	8.0	21	276	138	24	105	10	38	15	2.4	543	4019	681						[26]
PM + 1% SHW + 6.5% biodiesel wastewater	F	8.2	20	303	205	10	103	35	11	3	1.1	149	1779	206						[26]
CM + 4.3% CM + 11.6% maize oat silage	F	7.5	90	374	44	9	34	5	45	8	3.3	305	307	120						[26]
PM + 1% SHW + 6.5% biodiesel wastewater	F	8.3	19	247	200	6	52		26	10	1	158	1158	211	2	0.5	0.5			[35]
PM + 24% milk serum + 14% CM +10% maize silage + 4% rice residues	F		40	483	93	11	13.5													[36]
PM + 20% blood industry residues + 15% maize silage	F		60	488	88	12	28													[36]
Rabbit manure and SS + 17% fat + 8% duck SHW	F		200	365	25	14														[37]
CM + 7% manure + 3% garden wastes + 17% fruits and vegetables	F		240	330	20	8														[37]
25 different mixtures of PM and/or CM , maize and/or grass silage	F							4.4			2.6						6.2	3	0.5	[26]
OFMSW																				
Source-selected OFMSW	F		440	274	14	6						<0.7								[38]
OFMSW	L	8						7	50	10										[39]
Source-separated OFMSW	F		15		152	16	78						77	25	5	0	50			[39]
OFMSW + 20% PM	F		40	481	144	5.4	23						79	13						[38]
Sewage sludge																				
SS	F		19		2.8	0.43	0.1		0.04	0.03			0.1	0.15		0.12	0.16			[40]
SS	F		200	291	42	32														[37]

L = Lab-scale reactor ; F = Full-scale reactor; PM = Pig manure; CM = Cattle manure; SHW = Slaughterhouse waste; SS = Sewage sludge; OFMSW: Organic fraction municipal solid waste; *Data expressed on dry basis
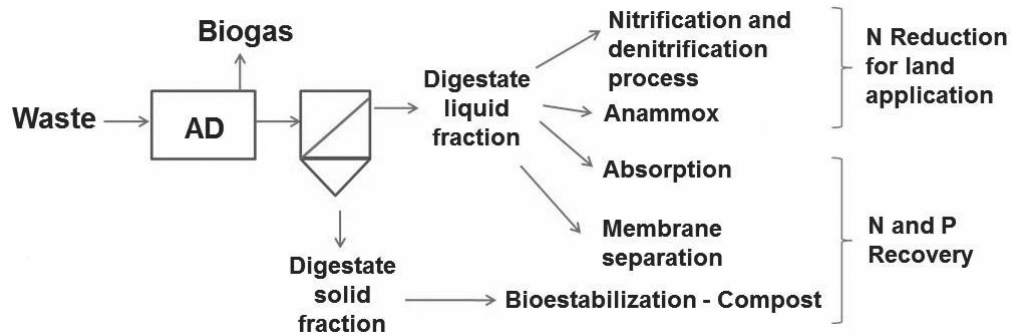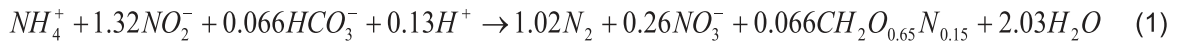
Figure 2. General scheme treatment of nitrogen rich digestates.

Anammox

Anaerobic ammonium oxidation (Anammox) is growing on importance as an alternative technology for biological nitrogen removal from wastewater due to its lower energy, oxygen and carbon requirements [69]. The Anammox process consist of ammonia oxidation in the absence of oxygen but in the presence of nitrite (Equation 1) [70,71]. Therefore, a pre-requisite of the Anammox process is a partial nitrification unit where about 50% of the ammonium is converted to nitrite concentration appropriate to the stoichiometry for the Anammox reaction as shown in Equation1 [72]. Figure 3 shows the general scheme of Anammox process. The optimal operational conditions for Anammox have been reported at pH=7-8.5; C/N ration 0.6:1; hydraulic retention time of 1 day and temperature 30-37ºC [73]. However, Anammox reactors have already been operated at psychrophilic temperatures [74,75].

$$NH_4^+ + 1.32NO_2^- + 0.066HCO_3^- + 0.13H^+ \rightarrow 1.02N_2 + 0.26NO_3^- + 0.066CH_2O_{0.65}N_{0.15} + 2.03H_2O \quad (1)$$

The feasibility of the process has been demonstrated in laboratory and full scale wastewater treatment [76] and full-scale experiences in the treatment of digestates by Anammox are now become known [77,78]. Anammox is a promising alternative since it has several advantages compared to conventional wastewater treatment bio-systems for N removal [79]. Anammox present ~60% reduction in the oxygen required for nitrification, elimination of organic carbon requirement for denitrification, reduction in the production of biosolids, higher rates of N removal and good coupling with biogas production [80]. The main challenges for implementing Anammox are: (i) the low growth rate of Anammox organisms, causing long start-up periods and the need to ensure bacterial cells retention inside the reactor [81]; (ii) high concentrations of N inside Anammox reactor should be a risk of biomass inhibition, therefore, digestate may be diluted before being supplied to the Anammox reactor, increasing both operational and capital costs; and (iii) digestate sulphide and phosphorus content may interfere in the Anammox process [79].
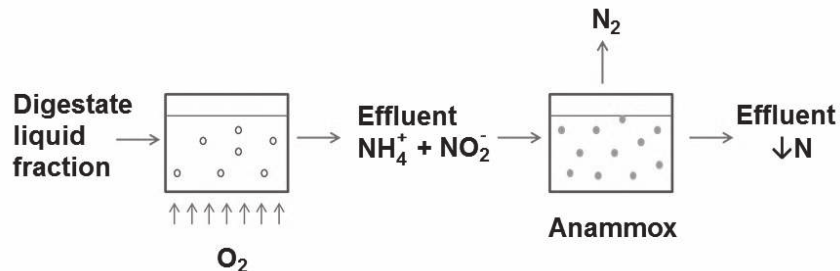

Figure 3. General scheme of Anammox process.

Absorption

Inorganic nitrogen existing in digestates is an equilibrium between free ammonia (NH_3) and ammonium (NH_4^+). Ammonia recovery from digestates has been investigated with methods such as coupled gas stripping and liquid/solid absorption [82]. Ammonia stripping is carried out by displacing the equilibrium to free ammonia by increase of digestate pH and/or temperature. Ammonia stripping has been trialled using a range of approaches, including with and without solid/liquid separation and using air, nitrogen, steam or biogas as the stripping agent [83]. The ammonia absorption can be done by ion exchange materials or acid solution, of which acid absorption is the widely used since high purity ammonium sulphate crystals can be produced when sulphuric acid solutions are used. Ammonium sulphate crystals isolated from the absorption process is a useful fertilizer with high commercial value [84,85].

Ammonium plays a vital role as a buffer agent in the AD process [86]. However, high ammonium concentrations are inhibitory for anaerobic biomass, especially aceticlastics methanogens [87].

Consequently, several research efforts have been made to reduce the ammonium concentration in the digester medium [24,64,87]. Chemical absorptions use new reactors configuration to capture the ammonium in a solid or liquid medium. Serna-Maza et al. [88] proposed a side-stream ammonium stripping using thermal alkaline treatment (Figure 4a). In this method, reactor content and biogas are treated in the stripping column and the biogas leaving the stripping column is passed through acid (0.25N H_2SO_4) traps to remove ammonia, while the biogas and reactor content return to the reactor. Sun et al. [89] reduced ammonia during thermophilic anaerobic digestion of protein rich stillage at a higher organic loading rate ($7gL^{-1}d^{-1}$) by biogas recirculation on water-washed biogas system (Figure 4b). Wirthensohn et al. [90] tested acidic gel cation exchange resin column (to remove ammonium by ion exchange) after filtration and reverse osmosis at a full-scale AD plant. Resin shows 99% of ammonium removal (27.6g NH_4^+-N L^{-1} resin) and present also a regeneration with 3 bed volumes of 2M HCl, recovering 91.7% of the original cation exchange capacity [90].
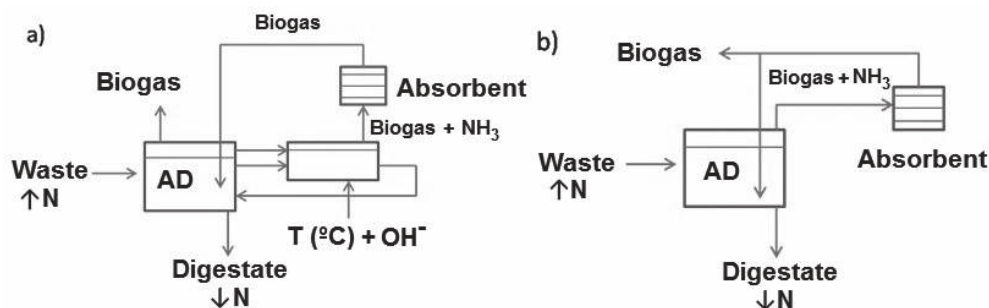

Figure 4. Nitrogen reduction form anaerobic digester by a) ammonium stripping and b) NH_3 absorption by biogas recirculation ($\uparrow$N = relative high N concentration; $\downarrow$N = relative low N concentration).

Phycoremediation

Microalgae biomass has been presented an intense interest application in environmental biotechnology since it can be used for bioremediation of wastewaters [91]. Hence, combining microalgae biomass production with organic wastewater treatment can mitigate: (i) water consume; (ii) substitute for fertilizer requirements of algal cultures by wastewater rich in nitrogen and phosphorus and (iii) algal biomass produced may be further valorized in the bio-fuel production [92–94]. Nitrogen and phosphorus are considered as essential nutrients for algal cultivation. Nitrogen is directly associated with the primary metabolism of algae as it is the main constituent of nucleic acid

and proteins [95]. Phosphorus needs to be supplied as phosphates because phosphorus in other forms may combine with metal ions and get precipitated, thus becoming unavailable to the microalgae [95]. Association of microalgae culture and AD seems a promising technology for sustainable algal biomass and biogas production. The use of digestate liquid fraction for sustaining the growth of microalgae reduces the cost and the environmental impacts associated with the algal nutrient requirements [96]. However, the growth of the microalgal resulting biomass will be driven by light, carbon source, nutrients loads (N and P), trace amount of micronutrients such as metals and vitamins [97]. In the specific use of digestates to

microalgae production, the high concentration of ammonium, as well as turbidity, salinity, toxins, etc; present harmful effects on microalgae growth and therefore digestates has to be diluted before used for microalgal cultivation, being the dilution a key element on the economic and operation feasibility [92,93]. Table 2 shows different nutrient removal experiences using microalgae from digestate liquid fraction. In addition to nitrogen and phosphorous, algae also require trace amount of micro-nutrients such as metals (Na, Mg, Ca, Mn, Zn, Cu, Fe and Mo) and vitamins for effective growth [98]. Algae can also be used as bio-sorbent to remove heavy metal ions (e.g. Cu, Pb, Cr, and Sr) [99]. Bio-sortion applied on digestates using algae has several advantages over conventional methods (e.g. chemical reduction, ion exchange, precipitation and membrane separation): (i) low operating cost;

(ii) high efficiency in detoxifying heavy metals in low concentration streams; and (iii) no nutrient requirements [100].

Algae growth also becomes attractive for AD systems by the capacity of remove CO_2 from biogas. AD produces biogas at CH_4 and CO_2 concentration between 50-80% and 50-20%, respectively [101]. There are several methods available for the removal of CO_2 from biogas (i.e. liquid and solid absorption, pressure swing adsorption, membrane filtration and cryogenic separation) [10]. These processes require considerable amount of energy and their operation may be complex [102]. Microalgae biomass production and biogas upgrading can be also integrated with digestate liquid fraction treatment [103]. Figure 5 shows the microalgae biomass production and biogas upgrading integration.
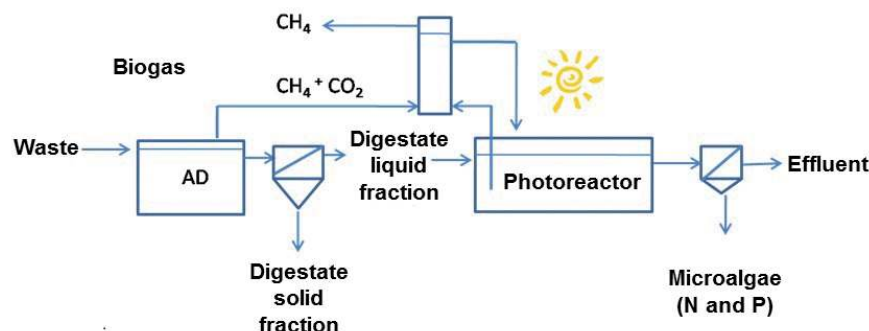

Figure 5. Microalgae biomass production with digestates nutrient recovery.

Table 2. Comparison of major nutrient removal rates by microalgae cultivation in various anaerobic digestion wastewater conditions (adapted and expanded from Ji *et al*. [92])

Anaerobic digestion wastewater	Gas source	Microalgae species	Cultivation period (d)	Initial nutrient (mgL^{-1})	Nutrient removal (mgL^{-1}d^{-1})	Dry cell weight (gL^{-1}d^{-1})	References
Digested dairy manure (20x dilution)	CO_2	*Chlorella* sp.	21	NH$_4$-N = 89.1 TNK= 172.8 TP= 12.5	4.28 6.24 0.20	0.0814	[102]
Digested dairy manure (50x dilution)	2-3% CO_2	*Neochloris oleoabundans*	16	NH$_4$-N = 42	6.48	0.0883	[103]
Digested pig manure (10x dilution)		*Scenedesmus accuminatus*	10	NH$_4$-N = 120	5.20	0.0458	[104]
Anaerobic Digestete (6x dilution)	Biogas	*Chlorella* sp.	6	NH$_4$-N = 59.6 TP= 6.21	8.33 0.83	0.1026	[105]
Digested cattle manure (20x dilution)	CO_2	*Chlorella vulgaris*	21	NH$_4$-N = 81.7 PO$_4^{3-}$-P= 3.65	5.2 0.19	0.25	[106]
Anaerobic Digestate	3% air	*Synechocystis* sp.	10	TN = 80 NH$_4$-N = 6.8 TP= 1.143	0.15	0.1509	[107]

Membrane separation

Membrane technology has acquired significant relevance in many industry sectors. Membranes can be designed to allow gas transfer between two liquid phases. To accomplish this mass transfer, a microporous hydrophobic membrane separates the two liquid phases, which are an NH_3 rich feed and an acidic absorption solution (Figure 6a). The gas filled pores of the membrane are the transfer area. The difference in the NH_3 partial pressure between the two liquid phases is the driving force for the mass transfer. Hollow fiber membrane contactors have been used to remove NH_3 from anaerobic digestate [109] and also directly from an operating AD reactor [110].

Other uses of membranes in nutrient recovery of anaerobic digestion system are bio-electrochemical systems (BES). The representative system includes microbial fuel cells (MFCs) (Figure 6b), microbial electrolysis cells (MECs) (figure 6c) and microbial desalination cells (MDCs) [111]. The foundation for realizing ammonia recovery in a BES is the fact that ammonium ions can move across ion exchange membrane via either current-driven migration or diffusion [111]. It was found that an MFC could achieve 100% ammonia recovery in efficiency and reduce ammonia inhibition on anaerobic digestion [111,112]. The theoretical analysis of energy consumption and production suggested that ammonia recovery in an MFC had significant energy advantage (with a positive energy balance) [111,113]. One of the key factors in ammonia recovery is the high pH of cathode, which can drive ammonium to ammonia gas [114]
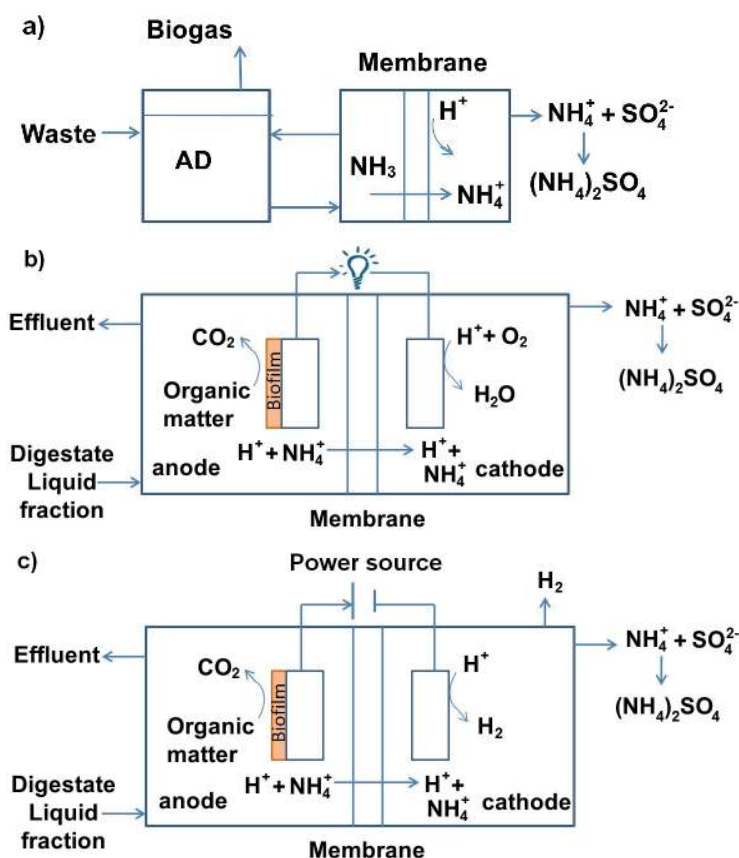

Figure 6. N recovery from digestates with membrane technologies as a) fibre membrane, b) MFC and c) MEC.

Struvite

Struvite precipitation has been attracting an increased interest as a technique to recover N and/or P, since struvite has a high nutrient value per unit weight (low transport cost) and is highly effective as a slow-release fertilizer [115,116]. Struvite is a crystalline solid phase consisting of magnesium, ammonium and phosphorus in equal molar concentrations and its precipitation naturally occurs, as for Equation 2, when the combined concentration exceeds the solubility product [117,118].

$$Mg^{2+} + NH_4^+ + HPO_4^{2-} + 7H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O + H_3O^+ \qquad (2)$$

The struvite crystal development occurs in two chemical phases: nucleation (crystal birth) and crystal growth [115]. Several physicochemical parameters influence these mechanisms such as pH [119], super-saturation [120], mixing energy [121], temperature and presence of foreign ions [122]. Taking account of these factors, several struvite crystalliser reactors have been development, mostly continuous flow reactors [115,122–124].

The precipitation of struvite from AD digestates (Figure 7a) normally requires the addition of Mg^{2+} since their concentration is very low with relation to NH_4^+ and PO_4^{3-} concentration [125]. Nevertheless, although the use of struvite for recovering NH_4^+ and PO_4^{3-} from wastewaters is technically feasible, it is not widely adopted because of the high costs of chemical compounds [117,126]. Several authors have evaluated the utilisation of alternative magnesium sources such as bittern [127], sea water and brine [128], magnesite [129], magnesite pyrolysate [130], struvite pyrolysate recycling [131] and electrochemical magnesium dosage [132]. Table 3 summarises the removal of NH_4^+ and PO_4^{3-}

by struvite precipitation from different wastewater and digestates using different magnesium source. Rich-magnesium by-products from the calcination of magnesite have shown good results in struvite precipitation and some advantages in comparison with other Mg^{2+} sources [117,133,134]. In this topic, Quintana *et al*. (2008) observed that the origin and the pre-treatment of the by-products have a considerable influence over the reaction time as well as on the quantity and quality of the struvite obtained.

Coupling anaerobic digestion and struvite precipitation in the same reactor have been presented as an alternative approach to further reduce treatment cost (Figure 7b) and, additionally, mitigate ammonium inhibition on anaerobic digestion systems. This approach have been trialed by some researchers on continuous reactors without any negative impact on AD performance and high nutrient recovery (N <50%; P<90%) [136–138]. However, continued dosing of Mg^{2+} can led to inhibitory phenomena by extreme pH or cation toxicity as well as high operation costs associated with Mg^{2+} reagents purchasing [117].
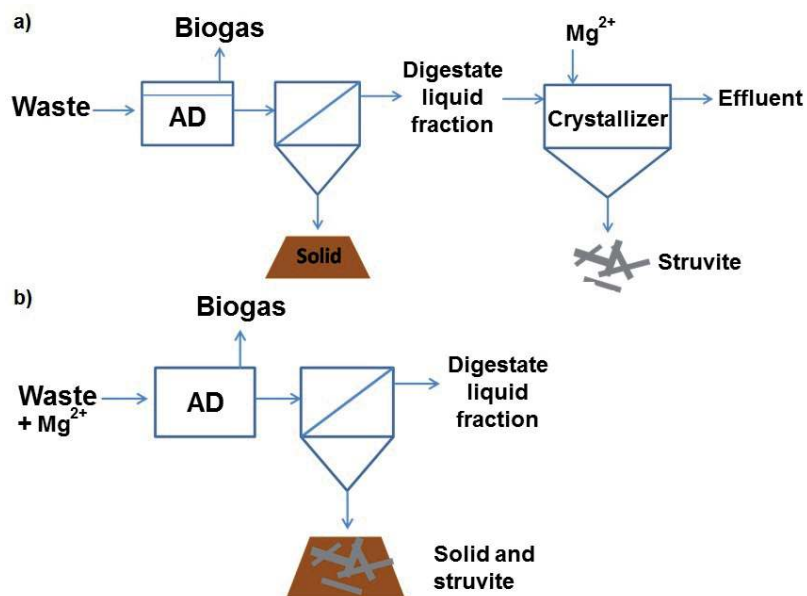

Figure 7. Struvite precipitation from a) digestate liquid fraction and b) coupling AD.

Table 3. Removal of NH4+ and PO43- by struvite precipitation from different wastewaters and digestates using different magnesium source (expanded and expanded from Uludag-Demirer *et al.*, [136])

Waste water	Chemicals added		Mg:N:P	Initial concentrations (mgL^{-1})		Removal (%)		Optimum pH	Ref.
	Mg^{2+}	PO$_4^{3-}$		N-NH$_4^+$	P-PO$_4^{3-}$	N-NH$_4^+$	P-PO$_4^{3-}$		
Activated sludge	MgCl$_2$·H$_2$O		1.4:1.1:1	60	120	53	75	9.1 - 10.2	[126]
	Seawater					54	81	10	
	bittern					39	76	9.6	
Landfill leachate	MgCl$_2$	H$_3$PO$_4$	1:1:1	2700	43	97		8.6-9.4	[128]
	MgCO$_3$					91			
Pigglery wastewaters	Struvite pyrolysate		2.5:1:1	985	161	80	96	8.6	[129]
Urine	Mg (Electrochemical)		Mg:P (1.5:1)	2540	197		100	8.9	[131]
Cochineal insects processing	LG-MgO		3.7:1.5:1	2320	3490		100	8.5-9	[116]
Sewage	LGMgO		Mg:P (1.6:1)	322	64		80	8.4-8.5	[133]
	LGMgO Pretreated [(1)]						70		
	LGMgO Pretreated [(2)]						90		
Municipal wasatewater	MgO		Mg:P (1.5:1)	630	54	82	92	8.8	[134]
	LG-MgO		Mg:P (3.6:1)			89	96	8.7	
Calf manure digestate	Bittern	bone meal	1.3:1:1.3	1060	450	91	99	9	[144]
source-sepatated urine	wood ash		(Mg+Ca):P (1.5:1)	2720	187		99	8.5-8.7	[145]
Molasses	Struvite Mg^{2+} and PO$_4^{3-}$ recycled [(3)]		1.2:1:1.2	1400	24	92		8.5	[146]
Leachate municipal landfill	MgO	H$_3$PO$_4$	1:1:1	2600	27	67		9	[63]
			2:1:1			95			

(1) Pretreated correspond to suspension at a concentration of 3g of LGMgO L^{-1} of tap water
(2) Pretreated correspond to supernatant after settling for 4h after 28h aeration
(3) Distillation with NaOH
LG-MgO = Low grade magnesium oxide

Romero-Güiza *et al.* [139] found that the use of stabilizing agent (mainly formed of newberyite (MgPO$_4$·3H$_2$O)) formulated with low-grade magnesium oxide by-product, can reduce the ammonium concentration up to 70% and increase the specific biogas production by 40% with a long-term stability.

Struvite has been successfully used as fertilizer on different crops. In fact, struvite is the preferable fertilizer for crops that needs magnesium, like sugar beet [140]. Other favorable aspects of struvite are its low leaching rate (release nutrients slowly during the plant growing season) and that it does not burn the roots like traditional ammonium-phosphate fertilizer [115]. However, in some cases struvite obtained from anaerobic digestates may contain some heavy metals [116], which are incorporated into the struvite crystalline network not only by nucleation, but also during the crystal growth process [129,141–

143]. However, it is unlikely that the heavy metals will exceed limit concentrations for land application [144].

Enhanced phosphorous recovery

Phosphorus is typically present in wastewaters, industrial streams, and anaerobic digestates at low concentrations (10-100mgPL^{-1}). Recovery of phosphates through precipitation with aluminium, iron, calcium and magnesium is technically possible; however aluminium and iron sources are expensive and makes phosphorus unavailable to plants [148]. Calcium phosphates are a poorer fertilizer (particularly in alkaline soils) [149,150], while recovery as struvite requires a higher P concentration in the solution [151]. To solve this problem enhanced biological phosphorus removal (EBPR) is suggested as technology to concentrate phosphorus in order to make phosphorus recovery and reuse feasible. EBPR sludge contains 5-7% phosphorus in contrast with normal activated sludge, ranging 1 and 2% (dry weight) [152]. EBPR relies on polyphosphates accumulating organisms (PAOs) to take up phosphorus from wastewater streams and thus concentrating P in the biomass previous anaerobic digestion [153,154], which digestate can be either directly applied to land or treated to recover P as struvite [155]. Recent advances on EBPR suggest that the main factors involving the technology are: (i) biochemical transformations performed by PAOs, (ii) process design and operation, and (iii) phosphorus recovery from EBRP sludge [152,156]. The EBPR system requires alternating anaerobic and aerobic conditions. In continuous systems this is achieved by spatially dividing the bioreactor into anaerobic and aerobic zones [157–160], while sequencing batch reactors provide anaerobic and aerobic periods in a single vessel [161,162].

Conclusions

Using anaerobic digestates as organic fertilizer or soil conditioner seem to be the best option for its nutrient recycling. However, most digestates are not suitable to be directly applied on land as their properties might cause environmental problems such as ammonia emissions, nitrate leaching and nutrient overdoses. Separation of the solid and liquid fraction is, due to its simplicity, the most widespread digestate treatment method. However, adequate treatments are still required for their correct management. The solid fraction is usually easier to treat, while the liquid fraction requires severe and expensive processes.

Nutrient recovery on anaerobic digestion systems is mainly focus on nitrogen. Nitrogen recovery has been achieved by striping, membrane, electrochemical systems and precipitation technologies. Removing nitrogen from the digester medium rather than from the effluent is an interesting approach since it also allows reducing biomass ammonia inhibition. However, phosphorous recovery has been identified as key a feature in full-scale treatment plants due to phosphorous scarcity and commercial value. In this matter, most research efforts have been made in concentrating phosphorous in polyphosphates accumulating organism's previous anaerobic digestion and subsequent recovery by precipitation. Struvite precipitation is a useful process for both N and P recovery, where research is done to investigate the feasibility of using magnesium by-products as cost-effective Mg^{2+} source. Finally, the integration of anaerobic supernatant treatment and algae cultivation has been identified as a potential ways to reduce the risk of nitrogen and phosphorus pollution from anaerobic digestion and as a biogas upgrading technology; however further research is required to overcome limiting factors.

Main limitation identified on nutrient recovery from anaerobic digestion systems is the electric and/or chemical requirements, which result in economic unviable processes. Moreover, some of the processes presented are still under development. Another limitation on using anaerobic digestates as organic fertilizer is their marketing. The negative perception by consumers and the competition with conventional fertilizers raise the need to increase digestates marketability and governmental incentives.

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