



# Nitrogen and Phosphorus Recovery From Anaerobically Pretreated Agro-Food Wastes: A Review

José Luis Campos<sup>1\*</sup>, Dafne Crutchik<sup>1</sup>, Óscar Franchi<sup>1</sup>, Juan Pablo Pavissich<sup>1,2</sup>, Marisol Belmonte<sup>3</sup>, Alba Pedrouso<sup>4</sup>, Anuska Mosquera-Corral<sup>4</sup> and Ángeles Val del Río<sup>4</sup>

<sup>1</sup> Facultad de Ingeniería y Ciencias, Universidad Adolfo Ibáñez, Viña del Mar, Chile, <sup>2</sup> Center of Applied Ecology and Sustainability (CAPES-UC), Santiago, Chile, <sup>3</sup> Laboratory of Biotechnology, Environment and Engineering, Faculty of Engineering, University of Playa Ancha, Valparaíso, Chile, <sup>4</sup> Department of Chemical Engineering, School of Engineering, University of Santiago de Compostela, Santiago de Compostela, Spain

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### \*Correspondence:

José Luis Campos  
jluis.campos@uai.cl

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Anaerobic digestion (AD) is commonly used for the stabilization of agro-food wastes and recovery of energy as methane. Since AD removes organic C but not nutrients (N and P), additional processes to remove them are usually applied to meet the stringent effluent criteria. However, in the past years, there was a shift from the removal to the recovery of nutrients as a result of increasing concerns regarding limited natural resources and the importance given to the sustainable treatment technologies. Recovering N and P from anaerobically pretreated agro-food wastes as easily transportable and marketable products has gained increasing importance to meet both regulatory requirements and increase revenue. For this reason, this review paper gives a critical comparison of the available and emerging technologies for N and P recovery from AD residues.

**Keywords:** ammonia combustion, ammonia hydrolysis, bioaccumulation, CANDO process, environmental benefit, nutrient recovery, phosphorus precipitation

## INTRODUCTION

Anaerobic digestion is the most widely applied technology for the treatment of agro-food industry waste, given its proven operational reliability and the obtaining of methane as a source of renewable energy, which generally allows amortizing the initial investment costs (Ren et al., 2017). However, it has the drawback of generating an effluent (digestate) that has a high amount of solids and nutrients (N and P) that do not meet the characteristics required by the regulations to be discharged directly to water courses. During anaerobic digestion hydrolysis takes place and organic matter, ammonia, phosphate, potassium, magnesium, calcium, and sulfur are released to the bulk liquid. Organic matter is mainly converted into methane while both ammonia and phosphate are not consumed during the process (Amini et al., 2017; Ma et al., 2018; Mai et al., 2018).

Phosphate is a key compound in fertilizers and its annual demand is increasing in line with the increase in the world's population. Therefore, it is necessary to guarantee its availability in the future to maintain an adequate production of food. Since the main source of phosphorus is the phosphate rock which burn time ranges from 50 to 400 years, there is now a growing interest in the technical and economic feasibility of large scale systems for phosphorus recovery from agro/industrial digestates (Cordell et al., 2011; Bradford-Hartke et al., 2012; Reijnders, 2014). Although phosphorus recovery and reuse is of great importance to reduce phosphate rock dependency and also to avoid pollution of water resources, P recovery is barely carried out currently due to the higher production costs of recovered P compared to those of mined P (Egle et al., 2016; Peng et al., 2018). Nevertheless,

if the social and environmental benefits of P recovery are quantified, the economic balance turns in favor of P recovery (Molinos-Senante et al., 2011; Mayer et al., 2016; Corbala-Robles et al., 2018). Contrary to phosphorus, N can be considered as a renewable resource but its conversion into fertilizer by means of the Haber-Bosch process requires a high amount of energy, with its cost dependent on the price and supply of natural gas (Zarebska et al., 2015). As in the case of phosphorous, ammonia market price makes not advisable its recovery from digestates but the scenario changes if nitrogen pollution costs are taken into account (Sutton et al., 2011; Alitalo et al., 2012; Peng et al., 2018).

The most economical option to manage digestates is their direct application as fertilizer to agricultural lands which also allows conserving their nutrients and reducing the requirement of chemical fertilizers (Alburquerque et al., 2012; Möller and Müller, 2012). Nevertheless, there is a surplus of nutrients in areas with intensive agro-livestock activities and limited agricultural land as a result of excess digestate production (Hjorth et al., 2011). Therefore, transport of nutrient surplus over long distances is necessary to avoid environmental problems related to nutrient overdoses (Fuchs and Drosch, 2013; Svehla et al., 2017). Since this strategy implies high operating costs, other ways to manage digestates should be chosen (Sheets et al., 2015). The separation of digestate into a liquid fraction rich in inorganic N and a solid fraction rich in phosphorus is generally applied in order to partly solve problems related to high costs of transport (Figure 1). The solid fraction can be used to produce compost or transported longer distances as a concentrated fertilizer since this fraction suppose only the 25–35% of the original digestate but contains 60–80% of its dry matter and almost all its phosphorus. However, only 20–25% of the initial nitrogen is retained in the solid fraction (Holm-Nielsen et al., 2009; Romero-Güiza et al., 2016). Another alternative is to burn the solid fraction in order to recover the nutrients from the ashes (Amann et al., 2018; Gorazda et al., 2018). This alternative, although very attractive in terms of volume reduction of solids, implies high operating costs that makes difficult its application on an industrial scale only interesting in countries where sewage sludge incineration is mandatory (Egle et al., 2016).

Although the liquid fraction from separated digestate has a low nutrient concentration that cannot be economically transported for use as a fertilizer, its concentration levels precludes the direct discharge. Therefore, in order to avoid that transport costs penalize the *ex-situ* use of nutrients, it is necessary to carry out their further separation, which can be achieved by concentrating the liquid stream itself or by converting the nutrients into solid compounds and making a subsequent solid-liquid separation. In this way, liquid streams generated containing high nitrogen and phosphorous concentrations could be easily transported and could be sold and make a profit (Meixner et al., 2015). An alternative to these traditional systems of direct nutrients recovery is their valorization through the generation of energy by means of their *in-situ* combustion using the own infrastructure for burning the biogas. This can be applied for the case of  $\text{NH}_4^+$  by its transfer to the gaseous phase in the form of  $\text{NH}_3$  or its conversion to  $\text{N}_2\text{O}$  (Gao et al., 2014) (Figure 2).

## NUTRIENT ACCUMULATION

The economic feasibility of using the nutrients, contained in the liquid fraction of the digestates, as a fertilizer is conditioned by transportation costs. Therefore, it is important to apply to the digestate technologies that allow the concentration of nutrients in order to reduce transport costs. There are different technologies based on chemical, physical and biological processes to carry out this concentration (Sengupta et al., 2015) (Table 1). Most of them were already applied to the anaerobic sludge digester supernatant of municipal WWTPs or to effluents of anaerobic digesters treating industrial wastewater but few applications related to agro-industrial effluents are reported (Desmidt et al., 2015). According to data show in Table 1, fertilizers sale would not cover their production which would indicate nutrient recovery is not economically feasible. Moreover, most of times the products obtained have only a local market due to administrative restrictions and their sale prices are lower than those of commercial fertilizers (Xu et al., 2018). However, the economical balance should also take into account costs related the environmental impact caused by nutrients disposal. For example, nitrogen pollution costs the European Union between 70 and 100 billion euros/year (Sutton et al., 2011). Besides, the implementation of P-recovery systems in WWTPs could avoid the scaling problem caused by struvite. This is the case of the Amsterdam West WWTP whose operating costs were reduced by €500,000 euros/year after the installation of a struvite crystallizer (Waternet, 2017). In any case, nutrient recovery driver is more related to the legislation of each country than to the economic feasibility of the process.

Full scale applications of physical technologies such as evaporation, membranes or air stripping showed this kind of technologies are highly expensive (5.4–7.0 Euros/m<sup>3</sup> digestate; Bolzonella et al., 2018) due to the high energy and material input requirements which also entails a negative environmental balance (Bradford-Hartke et al., 2015). Therefore, in order to improve economy of the recovery processes and decrease their environmental impact, the use of biological methods alone, such as bioaccumulation, or combined with chemical precipitation is preferable (Barbera et al., 2018; Xu et al., 2018).

### Bioaccumulation

The application of heterotrophic microorganisms, such polyphosphate-accumulating organisms, to carry out the bioaccumulation of nutrients is not viable due the low ratio COD/nutrients of digestates. Therefore, the use of autotrophic organisms such as microalgae seems to be a more suitable option. These organisms are able to remove both nitrogen and phosphorus via assimilation for biomass growth without oxygen consumption (Equation 1) (Park and Craggs, 2011; Rusten and Sahu, 2011; Chen et al., 2013; Posadas et al., 2015). Application of microalgae for wastewater treatment is generally carried out in open raceway ponds due to their low capital costs compared to photobioreactors (Shoener et al., 2014). These microalgae ponds have large footprint and, then, their possible implementation is conditioned by the availability of land. Another disadvantage of the microalgae application relies on their poor settling properties,

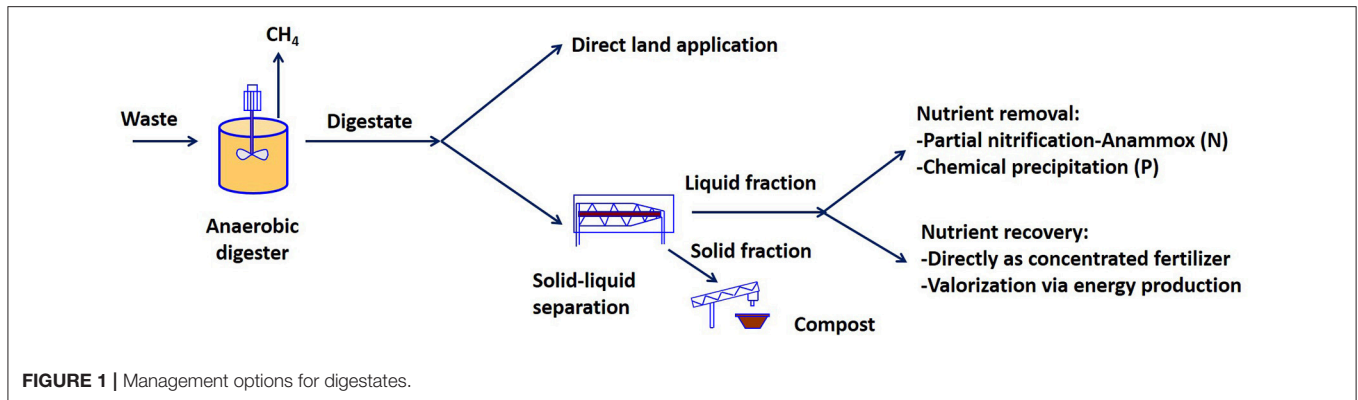


FIGURE 1 | Management options for digestates.

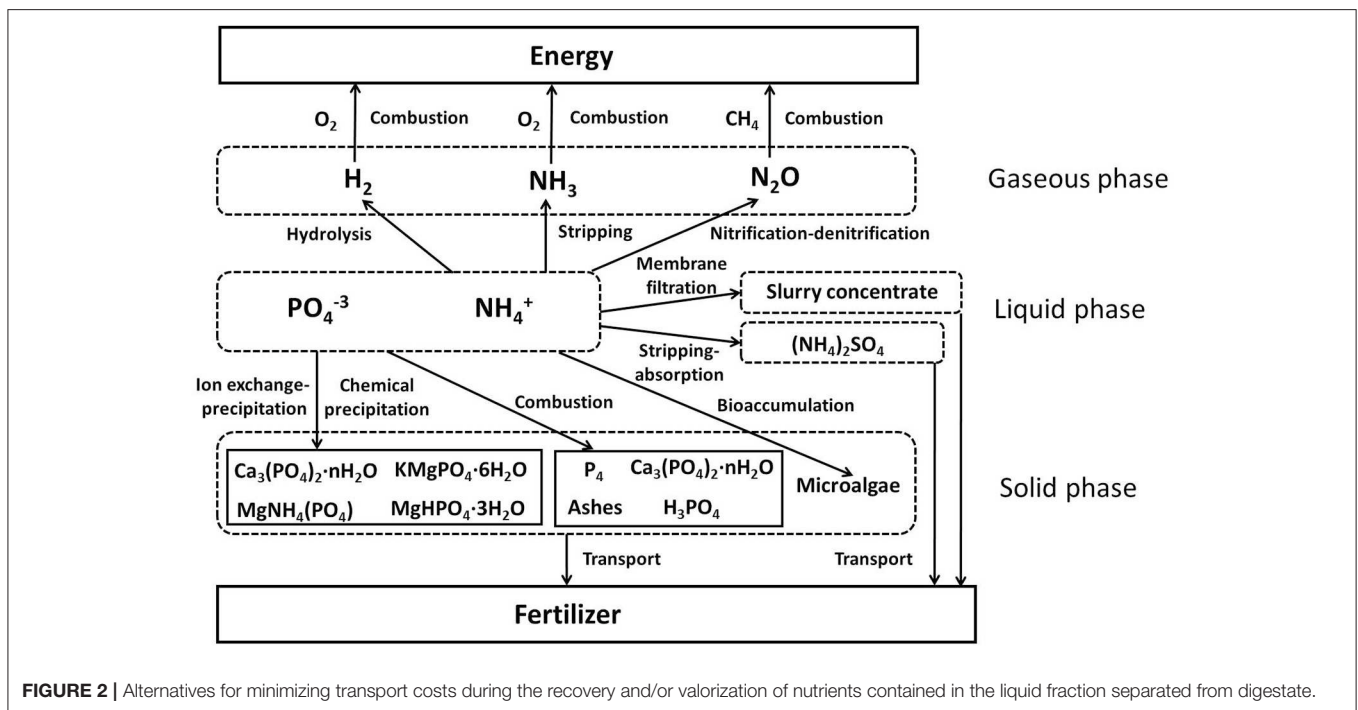
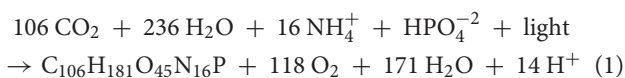


FIGURE 2 | Alternatives for minimizing transport costs during the recovery and/or valorization of nutrients contained in the liquid fraction separated from digestate.

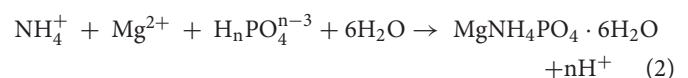
which increase the operating costs related to their harvesting and dewatering (Fasaei et al., 2018). Despite these disadvantages, operating costs are still lower than those of other technologies (Xu et al., 2018). Moreover, microalgae can be used to upgrade the quality of biogas generated during the anaerobic process (Meier et al., 2015) or sold as high-protein animal feed (Shilton et al., 2012).



## Chemical Precipitation

One of the most widely studied P recovery technologies is struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) precipitation, which is a simple method for the simultaneous removal of ammonium and phosphate from aqueous waste streams (Kataki et al., 2016a,b; Li et al., 2019). Struvite can precipitate in a wide range of pH values but, its

optimum pH range is from 7.5 to 9.0 (Miles and Ellis, 2001; Nelson et al., 2003; Rahman et al., 2014) while pH values of anaerobic digestates streams have generally values between 7.0 and 8.2 (Wu et al., 2001; Marti et al., 2010; Lahav et al., 2013). In the range of the optimal pH value for struvite formation the phosphorous specie present in the liquid media is  $\text{HPO}_4^{2-}$  and not  $\text{PO}_4^{3-}$ . This supposition is also supported by the decrease of the pH value observed during the precipitation process (Equation 2):



Struvite formation requires equimolar amounts of  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$ . Generally,  $\text{Mg}^{2+}$  content in anaerobic digestates is lesser than phosphate and ammonium concentration (Kataki et al., 2016b). Then, if the final objective of the process is

**TABLE 1 |** Processes for nitrogen and phosphorous recovery.

Process	Products	Production costs (Euro/Ton)	Market price* (Euro/Ton)	Transport feasibility** (km)	Recovery efficiency (%)	Bottlenecks
P-precipitation from liquid phase	Struvite (MgNH <sub>4</sub> PO <sub>4</sub> )	270–410 <sup>[1]</sup> 270 <sup>[2]</sup> 760–1,270 <sup>[3]</sup> 280–1,110 <sup>[4]</sup> 560–2,060 <sup>[5]</sup> 780 <sup>[6]</sup>	480	1,090	85–99 <sup>[7]</sup>	High consumption of reagents to fit pH
	Calcium phosphate (Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·nH <sub>2</sub> O)		170–290***	390–660	95–98 <sup>[8]</sup>	
	K-struvite (KMgPO <sub>4</sub> ·6H <sub>2</sub> O)		420	950	80–90 <sup>[9]</sup>	
	Newberite (MgHPO <sub>4</sub> ·3H <sub>2</sub> O)		590	1,340	≈100 <sup>[10]</sup>	
	Calcium phosphate (Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·nH <sub>2</sub> O)		170–290***	390–660	70–100 <sup>[3]</sup>	High consumption of reagents to extract P from ashes High energy consumption (if sludge incineration is not mandatory)
Membrane: filtration	Phosphoric acid (H <sub>3</sub> PO <sub>4</sub> )	1,420 <sup>[3]</sup>	600	1,360		
	White Phosphorus (P <sub>4</sub> )	3,000 <sup>[3]</sup>	1,900	4,320		
	Slurry concentrate	34.8–41.8 <sup>[11]</sup> 77.6 <sup>[12]</sup> ****	6.1 <sup>[9]</sup>	14	N: 47–65 <sup>[11]</sup> P: 43–75 <sup>[11]</sup> N: ≈70 <sup>[12]</sup> P: ≈55 <sup>[12]</sup> P: 80–100 <sup>[13]</sup> 90 <sup>[14]</sup>	Membrane excessive operational costs Membrane clogging and fouling
Ion exchange/precipitation	Struvite (MgNH <sub>4</sub> PO <sub>4</sub> )	3,670 <sup>[3]</sup>	480	1,090		Need of pretreatment to remove suspended solids in order to avoid clogging of the exchange column
Stripping/Absorption	Ammonium sulfate ((NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> )	280–660 <sup>[2]</sup> 400–780 <sup>[9]</sup>	230	160****	70 <sup>[2]</sup> 80–90 <sup>[9]</sup>	High energy requirements High consumption of reagents Scaling and fouling of packing material
	Bioaccumulation: algal biomass (C <sub>106</sub> H <sub>181</sub> O <sub>45</sub> N <sub>16</sub> P)	500–1,200 <sup>[15]</sup> 1,300–5,000 <sup>[16]</sup> 12,600 <sup>[17]</sup>	120	60****	P: 70–100 <sup>[18]</sup>	High requirement of implantation area Dilution often required

<sup>[1]</sup>Desmidt et al. (2012); <sup>[2]</sup>De Vrieze et al. (2016); <sup>[3]</sup>Eggle et al. (2016); <sup>[4]</sup>Sikosana et al. (2017); <sup>[5]</sup>Sarvajayakesavalu et al. (2018); <sup>[6]</sup>Vanotti et al. (2017); <sup>[7]</sup>Vanotti et al. (2018); <sup>[8]</sup>Vanotti et al. (2018); <sup>[9]</sup>Peng et al. (2018); <sup>[10]</sup>Acien et al. (2012); <sup>[11]</sup>Xu et al. (2018). \*Price of the different fertilizers were calculated based on the price of their individual components (Dockhorn, 2009); \*\*Transport feasibility was calculated as the ratio price of product (euro/ton)/Transport cost (euro/ton-km), assuming a transport cost of 0.44 euro/ton-km (Adapted from Spielmann et al., 2007); \*\*\*Market price of calcium phosphate was calculated taking into a P content of 9–15% (Xu et al., 2018); \*\*\*\*A concentration factor of 5 was supposed according to Bozonella et al. (2018); \*\*\*\*\*Value calculated considering a product concentration of 30% (Vaneckhaute et al., 2017); \*\*\*\*Value calculated considering a product concentration of 22% (Fassal et al., 2019).



to obtain a maximum efficiency of phosphorus recovery,  $Mg^{2+}$  should be added to the effluent of the anaerobic digester (Sheets et al., 2015). Besides, the reaction of struvite precipitation causes a release of protons, as shown in Equation (2), which could cause a pH drop. Consequently, an alkali source must be added to maintain the pH in a suitable range for struvite precipitation.

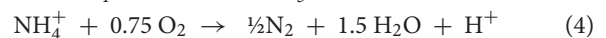
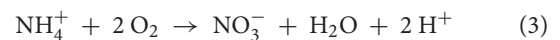
The costs of struvite precipitation are strongly dependent on the magnesium and alkali sources used. These costs may contribute to up to 75% of overall production costs (Dockhorn, 2009). In the literature, the use of high grade magnesium sources, such as  $MgCl_2$ ,  $MgSO_4$ ,  $MgO$ , or  $Mg(OH)_2$  has been reported (Kataki et al., 2016b). Nevertheless, the utilization of these high grade and expensive magnesium sources can lead to high operating costs compromising the viability of the process. In this sense, the use of low cost magnesium sources, such as industrial grade  $MgO$  or  $Mg(OH)_2$ , seawater or bittern can significantly reduce the cost of struvite precipitation. In this regard, the cost of phosphorus precipitation by conventional processes, adding aluminum, or iron salts, is between 2,000 and 3,000 Euros/t-P precipitated (Dockhorn, 2009). In struvite precipitation, the cost of the addition of an external magnesium source has been estimated between 700 and 4,000 Euros/t-P precipitated. Indeed, the struvite precipitation cost by adding  $MgCl_2$  and  $NaOH$  is around of 4,000 Euros/t-P precipitated (Carballa et al., 2009); whilst that the cost for struvite precipitation by using  $MgSO_4$  is estimated around 2,000 Euros/t-P precipitated (Etter et al., 2011; Sakthivel et al., 2012). Similar struvite operating cost has been determined by using magnesium dosing by electro-dissolution (Hug and Udert, 2013). On the other hand, Señoráns et al. (2011) reported that the operating cost of struvite precipitation at industrial scale was around to 2,900 Euros/t-P precipitated. These authors have used seawater as magnesium source, in fact, the chemical cost was mainly due to the alkali requirements. Meanwhile, Crutchik et al. (2017) estimated that the chemical costs associated with the use of an industrial  $Mg(OH)_2$  as magnesium and alkali sources for struvite precipitation at industrial scale was around to 1,000 Euros/t-P precipitated.

Moreover, the presence of other ions in solution such as calcium or carbonate can interfere with struvite precipitation by competing for magnesium and/or phosphate to form other precipitates species such as calcium phosphates or calcium/magnesium carbonate species. These ions can negatively affect the precipitation of struvite, decreasing the availability of the ions involved in struvite precipitation, and also affecting the purity of the produced struvite (Le Corre et al., 2005; Hosni et al., 2007; Song et al., 2007; Huchzermeier and Tao, 2012; Desmidt et al., 2013). In general, the formation of calcium and/or magnesium phosphates depends mainly on operational pH and wastewater characteristics (Jaffer et al., 2002; Le Corre et al., 2005; Pastor et al., 2008; Moerman et al., 2009). In this regard, struvite precipitation is more affected by the presence of calcium at low phosphate concentrations ( $<40$  mg  $PO_4^{3-}$ -P/L) than at high phosphate concentrations ( $>60$  mg  $PO_4^{3-}$ -P/L) (Desmidt et al., 2013).

Some authors found that the presence of calcium could not affect the precipitation of struvite under certain conditions (Wang et al., 2006; Moerman et al., 2009; Huchzermeier

and Tao, 2012). Most of these studies concluded that the molar ratio of  $Ca^{2+}:PO_4^{3-}$  is a determinative parameter to promote struvite precipitation rather than calcium phosphates formation,  $Ca^{2+}:PO_4^{3-}$  molar ratio should be  $<0.5$  to obtain an efficient precipitation in terms of phosphorus recovery and struvite purity. However, most of the aforementioned results are restricted to the experimental conditions in which they were specifically determined. Moreover, Stratful et al. (2001) and Crutchik and Garrido (2011) indicated that a high ammonium concentration could be highly beneficial to the reaction of struvite precipitation, so to obtain a relatively pure solid phase in terms of struvite purity. In this regard, it could be possible to obtain a high purity in terms of struvite, instead of precipitates of calcium phosphates in high ammonium wastewater.

The main drawback to carry out struvite precipitation for recovering ammonia and phosphate is the high costs of chemical compounds needed to obtain an adequate pH of struvite precipitation, and consequently to obtain an efficient nutrients recovery (Çelen et al., 2009; Ryu and Lee, 2010). This fact is due to the high buffer capacity of the anaerobic digester effluent caused by  $NH_3/NH_4^+$  and  $H_2CO_3/HCO_3^-/CO_3^{2-}$  equilibria. In this sense, the use of biological processes, which involve reactions with  $HCO_3^-$  and/or ammonium consumption or pH changes, could be considered an attractive pretreatment to reduce the consumption of reagents during phosphorus recovery (Mañas et al., 2011; Johansson et al., 2017; Simoes et al., 2018). For example, the previous application of nitrification (Equation 3) or partial nitrification-anammox processes (Equation 4) would decrease the amount of  $NaOH$  required up to 50 and 89%, respectively, and, in the last case, struvite recovery would be economically profitable (Campos et al., 2017). It should be taken into account that the liquid fraction of digestate has a temperature around  $30^\circ C$  and a low amount of organic matter which are propitious conditions to carry out these autotrophic processes.



Another strategy to reduce alkali requirements during phosphorus recovery is the application of low-rate aeration to promote  $CO_2$  stripping (Desmidt et al., 2012; Vanotti and Szogi, 2015). Due to the consequent pH rise, a fraction of ammonia ion is converted into  $NH_3$  which can be directly recovery from liquid bulk by means of gas-permeable membranes. Complete ammonia removal causes phosphates precipitate mainly as newberyte ( $MgHPO_4 \cdot 3H_2O$ ) instead of struvite (Vanotti et al., 2017).

## NITROGEN VALORIZATION AS ENERGY SOURCE

As it happens with organic compounds, the potential energy available in chemical bonds of the ammonia molecule exceeds significantly the electricity requirements of the applied treatments (Garrido et al., 2013). Therefore, in the same way that organic matter is removed from agroindustrial effluents

by means of anaerobic digestion in order to obtain energy in form of CH<sub>4</sub>, ammonia could be hydrolyzed to generate H<sub>2</sub>, or oxidized, directly or via N<sub>2</sub>O, into N<sub>2</sub>, obtaining renewable energy. This could be an attractive option compared to removal alternatives such as nitrification-denitrification and partial nitrification-anammox processes that always implies the supply of energy to convert NH<sub>3</sub> into N<sub>2</sub> (Flotats et al., 2009; Morales et al., 2015).

## Ammonia Hydrolysis

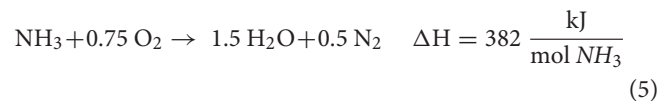
Ammonia present in the effluents of the anaerobic sludge digesters can be also considered as a source of hydrogen. NH<sub>3</sub> can be converted into N<sub>2</sub> and H<sub>2</sub> by a catalytic reaction in gas phase after its stripping from the liquid phase (Babson et al., 2013) or its electrolysis directly in liquid phase (Bonnin et al., 2008; Gwak et al., 2016; Zhang et al., 2017). Electrolysis seems a more viable way to obtain hydrogen since it can be carried out at ambient temperature in contrast to the catalytic reaction that needs temperatures around 800–900°C. Theoretically, the electrolysis of ammonia consumes 1.55 W h/g H<sub>2</sub> (Table 2) (Boggs and Botte, 2009). However, the present energy consumption for different ammonia electrolysis systems, which depends on the used catalyst, support material, and electrolytic cell configuration, is around 15 W·h/g H<sub>2</sub>, that is, 1.34 kW·h/Nm<sup>3</sup> H<sub>2</sub>generated (Bonnin et al., 2008; Botte and Feickert, 2012).

The electrolysis process requires that ammonia is present at its unionized form (NH<sub>3</sub>). This implies that the pH value of the effluent should be increased up to 12.0. Taking into account the stoichiometry of the overall ammonia electrolysis reaction and considering that HCO<sub>3</sub><sup>-</sup> is the counter anion of NH<sub>4</sub><sup>+</sup>, a consumption of 59.5 mol NaOH/Nm<sup>3</sup> H<sub>2</sub>generated can be calculated. Then, operating costs due to NaOH and energy required make that the production of 1 Nm<sup>3</sup> of H<sub>2</sub> costs 1.12 Euros which is more expensive than 0.26–0.35 Euros reported for other technologies as steam reformed of natural gas, electrolysis with conventional electricity or steam reforming of biomethane (Bonnin et al., 2008). Since most part of these operating costs are related to pH fitting, the electrolysis process could be also carry out with NH<sub>4</sub><sup>+</sup>. However, the metal of the anode is oxidized and combined with the counter anion of NH<sub>4</sub><sup>+</sup>, causing the electrode corrosion on the anode (Goshome et al., 2016).

## Ammonia Combustion

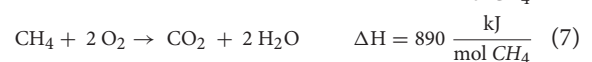
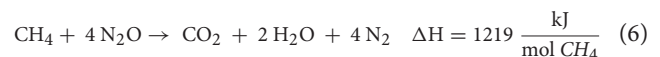
NH<sub>3</sub> oxidation into nitrogen gas and water is an exothermic reaction (Equation 5) that could be used to generate energy without CO<sub>2</sub> emissions (Degnan, 2018). NH<sub>3</sub> can be directly oxidized in the bulk liquid by means of electrochemical fuel cells (Rees and Compton, 2011) or burned together to methane to

generate power (Valera-Medina et al., 2017). This last option would have two drawbacks: (1) the increase of NO<sub>x</sub> during combustion which can be avoid by using suitable burners designs (Okafor et al., 2018) or catalyzers (Hinokuma et al., 2018); (2) the energy required for gas stripping which is generally higher than that energy recovered (van Eekert et al., 2012). Moreover, costs associated to pH fitting made no economically viable these processes to valorize ammonia from the liquid fraction of digestates.



## N<sub>2</sub>O Combustion

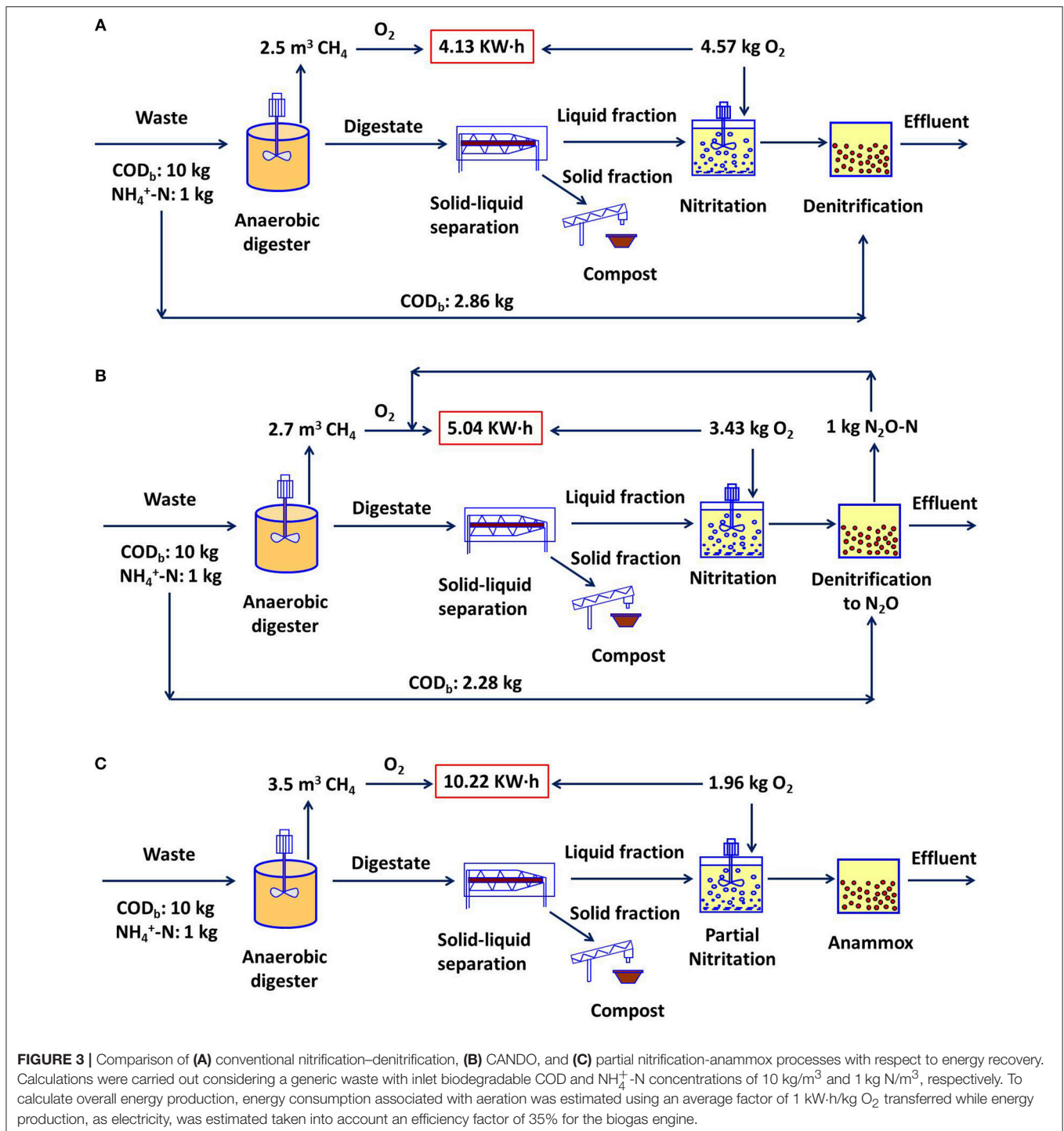
Recently, Scherson et al. (2013) introduced a new N removal process called CANDO (Coupled Aerobic-anoxic Nitrous Decomposition Operation) which involves three steps: (1) biological conversion of NH<sub>4</sub><sup>+</sup> to NO<sub>2</sub><sup>-</sup>; (2) biological or chemical partial anoxic reduction of NO<sub>2</sub><sup>-</sup> to N<sub>2</sub>O; and (3) N<sub>2</sub>O conversion to N<sub>2</sub> with energy recovery. Then, from steps 1 and 2 ammonia is converted to N<sub>2</sub>O, which is used in step 3 as a co-oxidant for CH<sub>4</sub> combustion or decomposed over a metal oxide catalyst to recover energy. Compared to the conventional nitrification-denitrification processes commonly used to remove ammonia, the CANDO process allows reducing the requirements of organic matter consumed during denitrification and utilizing N<sub>2</sub>O as a renewable energy source. Combustion of CH<sub>4</sub> with N<sub>2</sub>O releases roughly 30% more heat than using O<sub>2</sub> (equations 6 and 7), and, mitigates the release of N<sub>2</sub>O to the atmosphere. However, an overall energy balance shows this process is less efficient than the partial nitrification-anammox process (Figure 3). This is due to the fact that this last process is totally autotrophic and only requires the oxidation of 50% ammonia into nitrite, which supposes more available organic matter to produce methane and a low oxygen requirement during ammonia oxidation.



Steps 1 and 3 of the CANDO process have been already applied at full scale while step 2 (anoxic reduction of NO<sub>2</sub><sup>-</sup> to N<sub>2</sub>O) is still under study (Scherson et al., 2013, 2014; Myung et al., 2015). In these research works, two ways of producing nitrous oxide from nitrite are proposed: (1) abiotic reduction by Fe (II) with conversions over 90% and; (2) partial heterotrophic denitrification with 62–70% NO<sub>2</sub><sup>-</sup>-N converted to N<sub>2</sub>O-N when COD/N fed ratios of 3–4 are applied in the anoxic stage (Weißbach et al., 2018a,c). Later, N<sub>2</sub>O obtained can be recovered (3,700 ppmv) by a micro porous hollow fiber membrane contactor with efficiencies around 77 % (Weißbach et al., 2018b).

**TABLE 2** | Electrochemical reactions for the ammonia electrolysis process.

Reaction	Stoichiometry	E°
Anode	2 NH <sub>3</sub> + 6 OH <sup>-</sup> → N <sub>2</sub> + 6 H <sub>2</sub> O + 6 e <sup>-</sup>	-0.770 V
Cathode	2 H <sub>2</sub> O + 2 e <sup>-</sup> → H <sub>2</sub> + 2 OH <sup>-</sup>	-0.829 V
Overall	2 NH <sub>3</sub> → N <sub>2</sub> + 3 H <sub>2</sub>	-0.059 V



## CONCLUSIONS

If the importance of the recovery of nutrients from the digestates is evaluated only in terms of the current economic value of nitrogen and phosphorus in the market, it is not attractive and, in many cases, nutrients removal is more profitable than their recovery. However, this perspective will change in the future

if the economic damages of the environmental impacts due to pollution caused by the inappropriate use of the digestates and the increase in prices that the production of chemical fertilizers will suffer are included.

Many of the technologies used to carry out nutrient recovery involve high reagent and/or energy requirements, which can lead to a negative net environmental impact. In this regard, biological

technologies should be applied alone or combined with chemical technologies in order to generate synergistic effects that reduce the energy and reagent needs.

## AUTHOR CONTRIBUTIONS

JC, AM-C, and ÁV wrote the manuscript with input from all authors. ÓF, JP, and MB searched for the most recent references on the topic and provided critical feedback. DC and AP performed the calculations.

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**Conflict of Interest Statement:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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