Chapter 7

Re-use of digestate and recovery techniques

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ABSTRACT

Biogas plants receive inputs of different sources of carbon, nutrients, metals and other pollutants from large areas that result in a digestate that is a very complex and concentrated matrix. How to redistribute all these components without causing imbalances in the receiving environments is one of the main questions that arises regarding the reuse of digestate. The main end destinations of digestate within the EU are agriculture, landfill and incineration, in addition to open-mine land reclamation. There are European and country specific end destinations of digestate that have been recently reviewed and made publicly available in an EU commission report. In terms of agricultural application, digestate is seen as a valuable source of carbon and nutrients, but its application is conditioned by disposal limits for nitrogen, phosphorous and metals. Here, we discuss the need for redesign of the process of digestate manipulation in order to increase its value as fertiliser, through addition of compounds, different solid/liquid phases separation or additional treatments. Potential recovery techniques are also discussed. Phytoremediation, the use of plants to uptake metals from different substrates, can be used not only to remove trace metals from the digestate but also for the recovery of metals from plant biomass or their reintroduction into the biodigester. In addition, a combination of landfill with phytoremediation can be a good alternative for the recovery of degraded soils, or for the reclamation of polluted soil for landscape recovery. Another option can be the use of digestate to produce biochar to be applied in agriculture, a technique that increases carbon content in soils while decreasing trace metal bioavailability. Finally, we discuss the new opportunities that are arising for the use of digestate, including microalgae biomass production and bioenergy.

KEYWORDS: anaerobic digestion, biochar, digestate, recovery, reuse, trace metal

7.1 INTRODUCTION

Digestate is the effluent of the anaerobic digestion (AD) process after recovery of biogas. It can be used as fertiliser on land due to its excellent fertiliser qualities, based on a rich content of plant macronutrients including nitrogen (N), phosphorus (P), potassium (K), and sulphur (S), various micronutrients and also organic matter. AD leads to the reduction of biodegradable organic matter of original substrates, but does not diminish the content of nitrogen, phosphorous, potassium and other nutrients. The content of total solids decreases during AD, so digestate can contain 50–80% less total solids in comparison with the input substrate (Holm Nielsen *et al.*, 1997). One of the most common technologies for agricultural biogas plant is wet anaerobic digestion: the total solids content of digestate in general varies between 2% and 10% depending on feedstocks, operational conditions (temperature, mixing system and tank geometry) and rheological proprieties of the fluid. During the AD process, part of the organic nitrogen is mineralized into ammonium (N-NH_4^+) in a way which is dependent on the feedstock used. Digestate is the result of a microbial process and therefore has characteristics that are specific to each digester tank and is also influenced by post-treatment (solid/liquid separation, stripping, evaporation, drying, composting, biological oxidation steps, others).

7.1.1 The complexity of digestate

Biogas plants receive inputs of different sources of carbon, nutrients, metals and other pollutants from large areas that result in a digestate that is a very complex and concentrated matrix. The term ‘feedstock’ could be defined to include any substrate that can be anaerobically converted to methane; feedstocks suitable for AD are many and varied and many billions of tonnes are available in Europe. Historically AD has mainly been associated with the treatment of animal (pig, cattle, poultry) manure and sewage sludge from aerobic wastewater treatment plants. However, in the 1970s increased environmental consciousness, accompanied by a demand for new waste-management strategies and renewable energy forms, broadened the field of applications for anaerobic digestion and hence introduced additional industrial and municipal wastes (Steffen *et al.*, 1998) (Figure 7.1). Nevertheless, agriculture accounts for the largest potential feedstocks. Mono-digestion of manure and slurries as substrate for AD gives relatively low biogas yields per unit of wet weight; for this reason, frequently agricultural wastes are co-digested with other energy-rich feedstock to provide higher biogas yields (Braun & Wellinger, 2003). Commonly used co-substrates include energy crops for their high content in cellulose and hemicellulose. The use of ensiled plants cereals (maize, sorghum, triticale) for AD in agricultural digesters is a common practice. The silage can be stored over prolonged periods of time and used for biogas production during the year.

The nutrient composition of input substrates is very important to ensure stable process conditions and efficient organic matter degradation. Mainly, C/N ratio of the feedstock influences the growth of microorganisms. A high C/N ratio carries a risk of nitrogen limitation for the growth of microorganisms, buffer capacity limitation in fermentation medium and volatile fatty acids accumulation which can result in low efficiency of degradation (Igoni *et al.*, 2008), while a low C/N ratio may lead to an increase in ammonia concentration, which may inhibit the microbial communities (Rajagopal *et al.*, 2013). The C/N ratio of the organic substrate should be around 15–30:1 (Igoni *et al.*, 2008; Weiland, 2010) to obtain maximum bacterial growth in biogas reactors. However, stable process can be obtained at both lower and higher C/N ratio (Mata-Alvarez *et al.*, 2014; Moestedt *et al.*, 2015; Yan *et al.*, 2015) showing that other operational factors are also relevant.

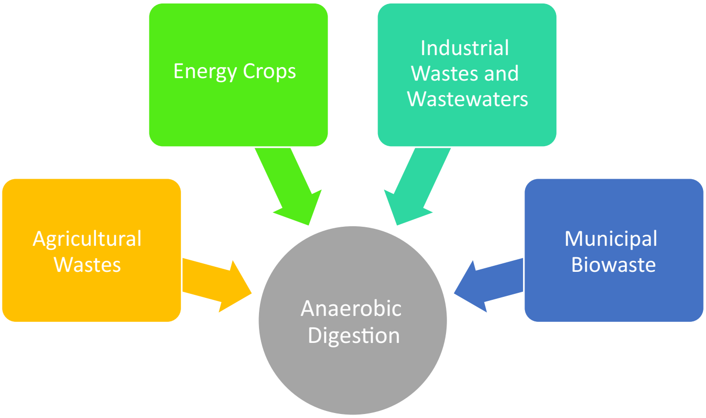

Figure 7.1 Sources of substrates for anaerobic digestion (adapted from Steffen *et al.*, 1998).

The content of carbon in the digestate is generally lower in comparison with the input substrate used as feedstock. This lower carbon concentration in digestate can be explained by the mineralization of carbon in CO_2 and by methane (CH_4) production, both originating from the partial anaerobic degradation of carbon. It is generally accepted that lignocellulosic feedstocks containing relatively large amounts of the structural plant polymer lignin have a very low degradability, while substrate containing fats, sugars and alcohols have very high digestibility. In studies comparing fresh manure with digested manure, carbon losses of up to 25–53% have been reported (Kirchmann & Witter, 1992; Möller & Stinner, 2009).

Digestate application on soils promotes the improving soil structure through input of inert organic matter and fibres (primarily lignocellulose), which contributes to the formation of humus in the medium to long term. Digestate spreading on soil can increase the organic matter content of the soil, which is very important for maintaining soil fertility (Masciandaro & Ceccanti, 1999).

7.1.2 End destination

EU-wide biogas plants receive inputs of different sources of carbon, nutrients, metals and other pollutants from physically large areas, hence the resulting organic mass for transformation to biogas derives from a wide area. As a result of this approach of constant concentration, the digestate is a very complex and concentrated organic-inorganic matrix subjected to microbial analysis. How to redistribute all these components without causing imbalances in the receiving environments is one of the main questions that arises with regard to the reuse of the digestate. The main end destinations of digestate within EU are agriculture (e.g., Spain 30%), landfill and incineration, in addition to open-mine land reclamation.

In fact, digestate could be considered as a resource from which several nutrients could be recycled or recovered, mostly nitrogen, phosphorous and potassium, which are used as fertilisers. The feedstock and the operation process are decisive for the composition and quality of the digestate. So, the feedstock used in the AD process is key to selection of the end destination of the digestate. The separated waste streams such as agriculture biomass or households waste provide clear potential criteria for the end destination. However, industrial waste streams such as sewage sludge or co-digestion of a mixed waste might pose problems for the selection of end destination due to the composition of the digestate. While the richness in nutrients makes the digestate a potential source for the agriculture or horticulture, the presence of heavy metals, pharmaceuticals, nano-particles, pathogens and other micro-organic pollutants might limit this potential end destination. In the European Union, the most extended end destination is agriculture and land application, mainly as a result of the main advantages of closing the nutrients cycle and contribution for carbon sequestration and the associated reduction in atmospheric carbon dioxide levels. According to Dahlin *et al.* (2015), 95% of the digestate produced in the European Union has agriculture as the end destination.

Despite the main end destination for the digestate being fertiliser for agriculture, digestate producers must diversify end destinations according to the digestate properties and operation processes. Other end destinations usually include incineration, landfill and open-mine land reclamation. In addition, other sectors which could be potential end destinations are horticulture, landscaping, cattle raising, fuel materials or alternative building materials.

7.1.2.1 Agriculture

7.1.2.1.1 Valuable source of carbon and nutrients

In terms of agriculture application, digestate is seen as a valuable source of carbon and nutrients, but its application is conditioned by disposal limits for nitrogen, phosphorous and metals. Therefore, it is very important to understand how to get rid of the potentially undesirable or over concentrated compounds so that the valuable part of the digestate can be introduced into agricultural soils. In AD of various biologically degradable substrates, proper handling of digestate is a necessity. Many studies so far have been made in applying digestate to crop fields, determining additional values of fertilising with macronutrients (N, P, K) (Insam *et al.*, 2015), their availability (Teglia *et al.*, 2011) and influence on different soil types by using different frequency of application and composition of digestate to improve the properties of the soil. However, long term applications of biogas digestate on human health and the environment still remain insufficiently explored area (Nkoa, 2014). Most of the biogas plants in the past primarily focused on improving biogas production, neglecting digestate properties. Now, safe and quality digestate is an important factor in fertilisation of crops, otherwise problems with inefficiently anaerobically degraded substrates, inappropriate storage of digestate, problems with odor, toxic compounds, pathogen microorganisms and phytotoxicity may cause negative impacts on soil ecosystems and fertility (Alburquerque *et al.*, 2012).

7.1.2.1.2 Limiting factors for disposal of N, P and trace metals

When combining mineral fertilisers and intensive agriculture, many major threats to soil functions have been recognized (Riding *et al.*, 2015): (i) loss of organic matter; (ii) loss of biodiversity; iii) compaction; (iv) erosion; (v) acidification; and (vi) loss of nutrients through leaching. All this can lead to upsetting or even failing of the ecosystem in arable land. Despite many studies having shown that anaerobic liquid and solid digestate can be as effective as mineral fertilisers (Nkoa, 2014), and in some cases even better than raw manure (Chantigny *et al.*, 2007), there are several environmental risks associated with land application of anaerobic digestate (Nkoa, 2014). These risks include atmospheric pollution (e.g., ammonia and nitrous oxide emission), nutrient pollution and soil contamination, both chemical (phytotoxic compounds and metals) and biological.

Publicly available specification (PAS) BSI PAS 110:2014 specifies upper limits for Cd, Cr, Cu, Pb, Hg, Ni and Zn in digestate, while other trace-element upper safe limits are not determined. Several studies have shown that digestate contains lower levels of heavy metals than laid out in German, British and Spanish standards (Nkoa, 2014), however the long-term application of heavy metals and its accumulation in soil over repeated applications is not known and needs to be investigated in the future. Toxicity, availability for plant uptake and downward mobility are determined by solubility and speciation of trace elements in soils. However, not all trace elements in soils interact with plants, and interaction is further dependent on physical, chemical, microbial and plant factors compounded by stochastic environmental events and cyclic seasonal fluctuations. Higher concentrations of Zn and Se are toxic to plants and animals, excessive dosing or inhomogeneous application to soils may cause soil infertility (Robinson *et al.*, 2009). Contamination of soil by micronutrients can be seen in mobility and higher heavy metal uptake by plant tissues in sandy soils than in clay soils (Liu, 2016), where pH and organic carbon have influence on transfer of heavy metals from digestate to soils. Furthermore, different parts of plants uptake different amounts of heavy metals.

7.1.2.1.3 Effects of long-term use of digestate and other digestate-related products on soil

The versatility and complex composition of digestate and the many different components that interact with the soil upon its application affect a wide range of physical, chemical and biological properties of the soil (e.g., Makádi *et al.*, 2012). Some of the general physical changes include reducing soil bulk density, increasing hydraulic conductivity and moisture-retention stability and aggregate stability (Diacono & Montemurro, 2010; Hargreaves *et al.*, 2008; Möller, 2015). Hereafter are listed the major long-term effects of the digestate on the chemical and physical properties of soil covering: pH, sodicity, nitrogen, macroelements (P, K and Ca), organic matter, trace elements and microbial activity.

Soil pH: Digestates have an alkaline nature with typical pH values of 7.5–9 (e.g., Gómez *et al.*, 2007; Kataki *et al.*, 2017, Möller & Müller, 2012; Pognani *et al.*, 2009), thus an increase in the soil pH should be expected for natural and acidic soils. However, digestate often includes various acidic compounds (Makádi *et al.*, 2012). Polycondensation, connection to organic and inorganic colloids and transformation of these acids can also have an effect on soil chemical properties through impacting soil colloid content that can decrease of soil pH (Tombácz *et al.*, 1998, 1999).

Soil sodicity: In a recent publication, Pawlett and Tibbett (2015) observed a significant increase in soil sodicity (manifested as increase in both available Na^+ and sodium adsorption ratio (SAR)), with an increased digestate application rate in two field experiments on grassland sites in UK. The increased salinity was attributed to the presence of high sodium concentration in food residue which in turn may jeopardize soil structural stability and plant growth if soil continuously receives digestate application. Reported sodium concentrations in digestates are variable and often range between ~500 mg/Kg^{-1} (Alburquerque *et al.*, 2012) and 3100 mg/Kg^{-1} (Vaneeckhaute *et al.*, 2013). In a different study, Kataki *et al.* (2017) used electrical conductivity (EC) values and their increase compared with a control to demonstrate higher salinity that originates from a continuous application of digestate. In this case too, the authors note that the source of digestate has a strong impact on the applied concentration of salts and consequently on the long-term salinization process.

Soil nitrogen: Generally, the digestate application does not cause any significant changes in the total nitrogen. Many publications (e.g., Alburquerque *et al.* 2012) reported that most nitrogen in digestates occurs as inorganic forms, representing mostly $NH_4^+ - N$. This form of N can be easily lost by ammonia volatilization during storage and land spreading due to the alkaline pH of the digestates (Sommer & Husted, 1995). In addition, NH_4^+–N may be nitrified rapidly in soil, this form being highly available to crops but also subjected to leaching through the soil profile, which may result in groundwater pollution. Therefore, storage and land-spreading operations with digestates must be carefully controlled to avoid negative environmental impacts.

Other macroelements (P, K and Ca): Digestate has higher phosphorus (P) and potassium (K) concentration than that of composts (Tambone *et al.*, 2009), therefore it is more suitable for supplementing these missing macronutrients in soils. However, while no significant change in soil available P content is often reported (e.g., Makádi *et al.*, 2012; Möller & Müller, 2012), the K content of soil is reported to increase with digestate application. Moreover, Möller & Müller (2012) note that the shift in pH has a strong impact on the solubility of P and micronutrients. Raising the pH moves the chemical equilibrium toward the formation of phosphate and subsequent precipitation as calcium or magnesium phosphates.

Soil organic matter: Generally, the amounts of organic dry matter and carbon content of the digestate are decreased by the decomposition of easily degradable carbon compounds in the digestors and leads to the increase of more recalcitrant molecules like lignin, cutin, humic acids, steroids and complex proteins (Pognani *et al.*, 2009; Stinner *et al.*, 2008; Tambone *et al.*, 2009). It is further noted that the digestate like many other organic amendments to soil contain surplus of alkali cations (e.g. K^+, Ca^{2+}, Mg^{2+}, Na^+, NH_4^+) over anions ($H_2PO_4^-$, SO_4^2, Cl^-) which are compensated by bicarbonate, carbonate and organic acids which in turn lead to decreased soil acidity (Yan *et al.*, 1996).

Trace elements: Trace metal content of the feedstock usually originates from anthropogenic source and is not degraded during AD. The main origins of the heavy metals are animal-feed additives, food-processing industry, flotation sludge, fat residues and domestic sewage. One example of a report on trace metals originating from digestate application on soil is a study by Makádi *et al.* (2012) that found that Cd, Co, Cu, Ni and Sr content of soil solutions did not change following digestate application, while Zn content decreased significantly, and the amount of manganese (Mn) increased by almost 40%.

Four to seven years studies on applying digested sludge to soils showed that the concentrations of trace metals (Cu, Pb, Zn) in the top layer of soil was increasing, which calls for close monitoring of trace-metal concentrations in soils and plants, or for a change in a policy of application to an on-off strategy in order to retain trace metal concentration below set limits. Furthermore, other pollution risks such as groundwater contamination by trace metals must be also considered, especially when dealing with sandy soils (Liu, 2016). For example, biogas residues mean values of four-year application rates of heavy metals such as Cu, Zn, Cd, Ni and Pb in the study of Odlare *et al.* (2008) were 57–110, 0.1–0.2, 3–6, 3–5, and 7–13 g ha^{-1} $year^{-1}$, respectively.

Soil microbial activity: When applying digestate to crops, an 11% increase in soil substrate-induced respiration was achieved, indicating an increase in microbial mineralization potential of organic matter. Microbial activity is important as it liberates nutrients from complex organic materials and makes them available to plants and other members of microbial community. Investigators also found increase an in dormant microbial biomass. The use of biogas digestate gave the largest crop yield and higher levels of active microorganisms compared with undigested fertilisers and mineral fertilisers. Digestate increased the substrate-induced respiration, nitrogen mineralization, potential ammonia oxidation and increased the number of active microorganisms (Odlare *et al.*, 2008), showing that application of biogas digestate alleviated much of the limiting factors present in agricultural soils due to long-term exploitation.

7.1.2.2 Incineration and co-incineration

Anaerobic degradation and transformation of organic matter thermodynamically affects the process under which fermentation is favorable only to a limited extent. This in turn leaves a large mass of organic matter that is locked and inaccessible for further anaerobic degradation and can only be processed in the presence of oxygen, either via microbiological pathways or incineration. Incineration results in a large reduction in the volume of the waste. Depending on the possibilities of re-using ashes, the decrease in the amount of material to be landfilled will be of variable importance. Even though investment costs are more intensive than the cost of the other sludge treatment options, units of significant size can balance investment costs, making incineration a technically and economically viable treatment process in highly dense population areas. The combination of different waste streams, municipal solid waste and waste sludges, also enables optimization of incinerator operations. For incineration, the economic value is limited to close proximity of biogas plants to incineration plants and hence is not universally feasible, nor publicly acceptable, despite the fact that ashes can be seen as a valuable byproduct for subsequent extraction of various inorganic compounds in downstream processing units.

After pre-drying, sludges can also be incinerated in cement kilns because they have a high calorific value. Pollutants are stabilised in the clinker which is an interesting way of treating polluted sludges. From an economic point of view these methods of treatment are mainly justified for sludges not permitted for use in agriculture or incineration in municipal solid waste incinerators. The economics of incineration depend to a great extent on auxiliary fuel requirements and, therefore, temperature, dry matter, volatile solids and calorific value are all important parameters to ensure autogeneous combustion. Rheological properties are important as far as the feeding system is concerned. The toxicity of emissions (gaseous, liquid, solid) depends on the presence of heavy metals and organic micropollutants at origin and/or when improper operating conditions occur. When the sludge is digested, the dry solid content (DS) will be reduced by approximately 20%, due to transformation of organics into biogas. However, in order to use digestate for incineration the DS is normally raised to 40–50%. To make a storable product for multipurpose use, for instance as fertiliser, soil conditioner, fuel etc., the DS is raised to 90–95% and granulated, which is most often a cost-ineffective strategy. Consequently, it is no surprise that today incineration is considered as the last method used in the treatment of digestates, either alone or in combination with other wastes. In saying that, treatment by incineration has represented up to 15% of the total mass of sludges treated in Europe (EEA reports) for the past two decades. Trace metals can be recovered from the resulting ashes and returned to anaerobic digestion in the form of specially formulated chemical additives.

7.1.2.3 Landfill and other land reclamation techniques

Landfill disposal of digestate is most limited in EU and hence not a viable large-scale strategy for the massive disposal of digestate in the future. This also holds for parks, land restoration and landscaping, and open-mine reclamation approaches. However, it is still very important to know whether the sludge is consistent enough to be landfilled. Waste-water sludge can contain all the pollutants contained in raw (inflow) waste water, and the content of organic material varies depending on the proportion of the industrial waste water, but usually falls to the range of 60–70%. From this, it follows that dry matter and volatile solids are the most important parameters in sludge characterisation involved in all the application/disposal methods. These can be modified through stabilisation and solid-liquid separation processes, which are operations almost always present in a waste-water treatment system. Additionally, rheological properties are essential in relation to sludge-bearing capacity. The amount of volatile solids has an impact on the development of malodours and process evolution, including biogas production. Trace metals can negatively affect the evolution of biological processes and the quality of the leachate. Therefore, in the process of siting landfills it has always been taken into account that, even in case of the most careful setting and proper operation, some degree of subsurface pollution may occur. This is the reason why geologically vulnerable sites are avoided (karstic areas and gravel terraces forming subsurface aquifer layers) when locating landfill sites and is very similar to the agricultural use of digestates. In this particular mode of digestate disposal, the reuse of trace metals is not possible, however one must bear in mind that the ongoing microbial processes coupled to newly created soil-like environments will continue to actively degrade organic matter and produce a stream of trace-metal and nutrient-contaminated waters under a variety of conditions.

7.1.3 Regulations for digestate disposal

In the previous section, the potential end destinations for the digestate have been shown. The use in agriculture as fertiliser or the land application as soil conditioner have important advantages, such as reducing dependence on chemical fertilisers and peat, and closes the cycle of nutrients and carbon. Good management in the end destination of digestate will reduce the climate change impact of the waste. However, some health and environmental concerns over the amount and composition of digestate to the selected end destination have been identified.

Health, safety and environmental protection must be ensured to avoid the risks described. The European Union is responsible for marking the guidelines to member states in this challenge. The definition of what is considered waste and what is considered non-waste is *a priori* a key aspect of this challenge. Each state must adjust the protection measures necessary to face these risks in its own waste-management scenarios. The feedstock used in digestate production, waste collection, weather, soil composition and hydrology are some of the parameters to take into account to optimize the digestate end destination in each state.

7.1.3.1 European

The European Union has developed use criteria for waste that becomes a product. The use of digestate on the land can be summarized in three strategies: digestate is a product which is used, digestate is a waste which can be used or the use of which is restricted, and digestate cannot be used. The European Union has considered the following legislative framework to provide optimal guidelines in the selection of the end destination for the digestate.

Directive 2008/98/EC (CEU, 2008) on waste introduces the basis of waste management, the definition of waste, reuse and recovery. The communication from the EU Commission on future steps in bio-waste management in the European Union in 2010 analysed the stage implementation of Directive 2008/98/EC on waste and Directive 1999/31/EC (CEU, 1999) on the landfill of waste. The main conclusions of this communication were: improvement of the separate bio-waste collection, prevention of bio-waste production, revision of the Urban Waste Water Treatment Directive 91/271/EEC (CEU, 1991a) to protect EU soils, chase zero landfilling and the optimization of energy recovery to achieve the renewable energy target for 2020 under the Renewable Energy Directive (proposal). In 2012 the Guidance on the interpretation of key provisions of Directive 2008/98/EC on waste showed the advantages of separate collection bio-waste to produce a high-quality digestate.

Directive on nitrates (91/676/EEC) (CEU, 1991b) protects ground and surface water from nitrate pollution which could be associated with digestate end destination. Fertilisers Regulation (EC/2003/2003) (EC, 2003) ensures nutrient content, safety, and environmental acceptability. The Animal By-products Regulation (EC/1069/2009) (EC, 2009) set the instructions for the collection, use, and removal of animal by-products. Regulation EC/834/2007 (EC, 2007) on organic production and labelling of organic products evaluates which digestates are allowed in organic farming production. Directive 2000/76/EC (CEU, 2000) on the incineration of waste limits negative impact from the co-incineration of waste. This directive restricts the operational conditions for waste co-incineration. Incineration as an end destination for digestate, even with energy recovery, could be influenced by this directive.

7.1.3.2 State specific

There are different approaches to determine the status of digestate as a waste or product according to the individual member state legislation.

When the digestate can be used as fertiliser, the regulation of this end destination has three approaches. One describes the requirements for waste to become a product according to a waste law or environmental regulation. This is the situation of member states such as Germany, France, Denmark, and Austria, which regulate a quality or standardization criteria. Another approach is based on the evaluation of digestate and end destination taking account of the characteristics of the soil and application rate, among other parameters, according to recognized protocols and standards. This is the case for the United Kingdom where the Environment Agency for England and Wales defines the end destination for each situation. Finally, the use in agriculture requires previous registration as a fertiliser according to fertiliser regulations. The Czech Republic, Finland, Greece, Hungary, Italy, Latvia, Netherlands, Poland, Portugal, Spain, and Slovenia show this approach.

The animal by-products regulation also applies as a guideline to the digestate production and end destination because these are potential feedstocks and influence digestate composition. Therefore, the end destination of the digestate from mixed bio-waste should be regulated. United Kingdom adopts the AD quality protocol which classifies quality feedstocks from separated bio-waste. Germany includes legal requirements in the waste and fertilisers legislation which identify bio-waste available for use on soil in the Ordinance on the Utilization of Bio-wastes on Land used for Agricultural, Silvicultural and Horticultural Purposes. The Netherlands defines one quality criteria to the end destination of digestate from different bio-waste in its fertiliser legislation. Three different bio-waste streams are identified, compost, sewage sludge, and other bio-waste from industrial processes. Spain does not specifically regulates the end destination of digestate, but legislation on sewage sludge, digested source-separated bio-waste and digestate organic matter from mixed municipal waste define the end destination. The digestate from co-digestion of bio-waste can be used in agriculture, but digestate from mixed municipal waste cannot. In Estonia, the end destination is regulated by waste, fertiliser, and water legislation on to the use of sewage sludge in agriculture is heavily regulated. Slovenia presents a Decree on the treatment of biodegradable waste which regulates the mandatory controls on the feedstock in the digestate production. This regulation identifies a list of suitable bio-waste to be taken into account in the selection of end destination. Austria has a Guideline on the use of digestate on agricultural land according to a positive list of feedstocks which are based on waste-separated collection and uses clean organic sources. The Italian regulation introduces a section dedicated to the agronomic use of digestate from agricultural biogas plants depending on the characteristic of the feedstock used (quality standards of digestate are defined in the regulation).

7.2 REDESIGN OF THE DIGESTATE PROCESS TO INCREASE DIGESTATE VALUE AS FERTILISERS

Characteristics of the digestate are strictly related to feedstock properties and are specific to each digester tank or, even, within the same batch of digestate (Lukehurst *et al.*, 2010). During AD, the carbon content in the digestate is significantly reduced since the organic dry matter is transformed into methane and carbon dioxide. Also, a part of organically bound nitrogen is mineralized and the amount of ammonium in the digestate is higher than in the other organic fertilisers (Roschke & Plöchl, 2006).

During the storage of the digestate a certain amount of ammonia is released into the atmosphere. Also, storage can cause a decrease in the total solids, chemical oxygen demand and alkalinity of the digestate (Laureni *et al.*, 2013). An excess of nutrients present in the digestate can cause environmental problems. So, the digestate needs to be processed in order to manage nutrient content. Removal of particulate nitrogen can be performed by solid-liquid separation, while ammonia removal can be achieved through the use of chemical/physical and biological processes (Silvestri *et al.*, 2013).

Quality of the digestate for use as a fertiliser is defined by nutrient content, pH, dry matter and organic dry matter content, homogeneity, purity (free of inorganic impurities such as plastic, stones, glass, etc.), sanitization and safety for living organisms and the environment with respect to its biological content (pathogenic) material and chemical pollutants (organic and inorganic) (Al Seadi & Lukehurst, 2012). The use of digestate must meet a range of legislative requirements both for agricultural best practice and environmental protection. To increase a digestate value as fertiliser, without adverse impact on methane yield, the following different techniques can be applied before and after the digestion process.

7.2.1 Pre-digestion techniques – Feedstock pre-treatment

Due to its ability to degrade many of unwanted compounds and pollutants within the feedstock, a stable AD process has a positive effect on digestate quality for use as fertiliser. If a digestate is used as fertiliser or for other agricultural purposes, a feedstock must not be used in biogas plants if efficient pollutant removal cannot be guaranteed either by pre-treatment or through the AD process (Al Seadi & Lukehurst, 2012). In order to remove, decompose or inactivate unwanted impurities, the feedstock can be pre-treated by mechanical, chemical and/or thermal techniques. The unwanted impurities or contaminants that influence the quality and safety of digestate used as fertiliser are grouped as: physical impurities (indigestible materials), chemical impurities (trace metals and organic pollutants), and pathogens and other unwanted biological matter (animal and plant pathogens, weed seed).

Despite the fact that the most common pathogens and common viruses are killed during mesophilic and thermophilic digestion, a pre-sanitation step (mostly by batch pasteurization) can be applied for some specific feedstock types, prior to being added to the digester and mixed with the rest of the material. Others pre-treatments for enhancing digestibility of the material include maceration, thermal and chemical hydrolysis, ultra-sound treatments etc., and they are usually applied to materials that contain significant portions of lignocelluloses and hemicelluloses.

7.2.2 Post-digestion techniques

After removal from the digester, digestate can be used as fertiliser without any further treatment. Since storage, transport and application of the digestate are expensive due to low dry matter content, digestate processing is a necessary option for volume reduction and quality enhancement. Digestate processing can be partial (solid-liquid separation, volume reduction), or it can be complete, separating the digestate into solid fibres, fertiliser concentrates and pure water (Al Seadi & Lukehurst, 2012). The aim is to produce a standardized solid or liquid biofertiliser with improved quality (higher concentrations of plant nutrients than unprocessed digestate, separate nutrients in mineral form) and marketability.

7.2.2.1 Solid-liquid separation

The first step in digestate processing is to separate the solid phase from the liquid phase. Digestate separation techniques have been divided into categories based on the type of process employed, that is, mechanical, thermal (evaporation) or biological (bio-drying), or a combination of these. Efficiency of separation essentially depends upon the nature of the digestate and the characteristics of particles. Different methods can be used for mechanical liquid separation (Lukehurst *et al.*, 2010; Pöschl *et al.*, 2010) including: belt press, screw press, sieve drum, sieve centrifuge, decanter centrifuge. Bauer *et al.* (2009) indicated that a screw separator is more suitable for separation comparing with a rotary screen separator. In the same research, the dry matter content in the liquid fraction was 4.5% and in the solid fraction 19.3%. After filtering through the pore size under 0.5 mm a significant enrichment of nutrients in the solid phase can be expected (Møller *et al.*, 2000). Depending on the method efficiency, the separation of dry matter, phosphorus, nitrogen and potassium can vary (Lukehurst *et al.*, 2010). The dispersion of the nutrients between the liquid and solid fraction is different, so the liquid fraction has more nitrogen and potassium, while the solid fraction contains volatile solids, carbon, raw ash and phosphorus (Bauer *et al.*, 2009; Liedl *et al.*, 2006). For digestate evaporation, the heat is sourced from the gas engine surplus heat in order to make the process financially sustainable. Bio-drying refers to the removing of water by the composting process, i.e using aerobic bacteria to heat the digestate and remove the water (Al Seadi & Lukehurst, 2012).

Solid-liquid separation has several advantages (Lukehurst *et al.*, 2010; Wu *et al.*, 2016): (i) the volume of the required storage tank is reduced; (ii) digestate is separated into a stackable dry fraction and a pumpable liquid fraction; (iii) nitrogen uptake is more efficient from the liquid fraction; (iv) liquid fraction can be recirculated into the digestor; and (iv) there is little need for mixing of the liquid phase before the spreading.

The drawback of the use of liquid phase is in uneconomical transportation due to the high content of water and low efficiency compared to chemical fertilisers (Möller & Müller, 2012). The solid fraction can be used directly after separation, or can be dried or composted (Pöschl *et al.*, 2010). Since the solid fraction of digestate is considered as a waste in order to be marketed and used it can be composted (Tambone *et al.*, 2015). The aim of the composting is to obtain a stable and mature compost that can be easily stored and handled (Himanen & Hänninen, 2011), but some results (Tambone *et al.*, 2015) showed that the process does not significantly improve the characteristics of the solid fraction of the digestate.

Separation can be improved by the use of chemicals for coagulation or flocculation of liquid before the centrifugation (Lukehurst *et al.*, 2010). After the separation of digestate, complete conditioning of digestate can be performed in order to get three final products: water, concentrated mineral nutrients and organic fibres. Conditioning of digestate can be performed by the use of membrane separation and evaporation (Lukehurst *et al.*, 2010). Other techniques that can be used are microfiltration, ultrafiltration and reverse osmosis (Ledda *et al.*, 2013; Silvestri *et al.*, 2013). As a result of the separation by ultrafiltration and reverse osmosis, a nutrient-concentrated fertiliser rich in organic compounds and decontaminated water can be obtained. If the process is effective, the water quality can be similar to potable water (Silvestri *et al.*, 2013). Despite being the most expensive technology, membrane purification is among the most frequently applied approaches in more complex digestate processing facilities in Germany, Switzerland, and Austria (Drosg *et al.*, 2015).

Changes in pH value can shift the ammonium ion/ammonia equilibrium. Acidification of the digestate can cause the capture of nitrogen in the form of ammonium salts and reduce nitrogen loss after the application of digestate to the land. Increasing the pH value neutralizes odours and reduces the levels of pathogenic microorganisms. Alkaline stabilization is usually achieved by the addition of lime (WRAP, 2012; Silvestri *et al.*, 2013).

7.2.2.2 Digestate recirculation

Digestate recirculation in the AD plant is an interesting possibility which can produce more biogas and reduce unwelcome greenhouse gases emissions (methane and carbon dioxide) into the atmosphere. The residual biomethane potentials of digestate are not only dependent on feedstock, but also upon the hydraulic retention time in the digester. The results of the several studies (reviewed in Monlau *et al.*, 2015) have shown a very high range of values of residual potentials of digestate.

Post-treatment of the entire digestate (mechanical, thermal, thermochemical or enzymatic) or solid digestate prior to recirculation is necessary in order to enhance the methane production of digestate and to improve economic effects. The aim is to enhance the biodegradability of hard-to-digest compounds present in solid digestate.

Two major economic benefits presented by post-treatment of digestate are enhanced process efficiency (an increase of methane yield) and lower cost of post-treating digestates compard with pre-treating feedstock (Monlau *et al.*, 2015). Moreover, reactor perfomance can be improved by enhancing microbial population, since washed-out microorganisms are reintroduced into the process.

7.3 POTENTIAL RECOVERY TECHNIQUES

Biogas digestates have been predominantly used for agricultural soils application. However, the significant increase of digestate production generates problems related to transport costs, greenhouse gas emissions during storage as well as high nitrogen concentrations that restrict its use to land application only (Monlau *et al.*, 2015). Accordingly, different options of biogas digestate reuse are currently under development, such as the use of solid digestate for energy production through biological (e.g., anaerobic digestion) and thermal processes (i.e., combustion, hydrothermal carbonization (HTC) and pyrolysis) (i.e., combining biological and thermochemical processes to obtain higher bioenergy recovery) (Feng & Lin, 2017; Lü *et al.*, 2018; Monlau *et al.*, 2015, 2016) and the conversion of solid digestate into added-value products (e.g., biochar) through thermochemical processes as discussed in the next section.

7.3.1 Biochar digestates

According to the definition given by the International Biochar Initiative, biochar is ‘a solid material obtained from thermochemical conversion of biomass in an oxygen-limited environment’ (Lehmann & Joseph, 2015). Biochar may be produced from forest or agricultural residues. Biochar production from biogas digestates has emerged as a new valorisation approach over the last decade. Dry feedstock, for example, with moisture content below 50 w%, is generally converted by slow pyrolysis (350–600°C) and wet feedstock by HTC (180–250°C in water above saturated pressure). Biochar properties are affected by the original feedstock physicochemical characteristics and thermal treatment conditions (Hung *et al.*, 2017; Mumme *et al.*, 2011; Stefaniuk & Oleszczuk, 2015). Generally, biochar is rich in stable aromatic carbon and nutrients, making it an eco-friendly material in several ways for soil improvement, mitigation of climate change, nutrient/contaminant pollution, waste management, and energy production (Lehmann & Joseph, 2015; Monlau *et al.*, 2015; Mumme *et al.*, 2011). The use of biochar as an adsorbent for soil and water treatment of organic and metal pollutants has rapidly emerged as a low-cost option (Ahmad *et al.*, 2014; Inyang

& Dickenson, 2015; Laird, 2008; Mohan *et al.*, 2014). More recently another end-use is biochar admixing (as an additive) during anaerobic digestion which has been shown to improve process stability and biogas production (Fagbohungbe *et al.*, 2017; Mumme *et al.*, 2014; Wambugu *et al.*, 2019).

When considering the type of organic waste streams processed, increasing attention has been given recently to finding alternative options in handling biogas digestates, as it is an important aspect for the sustainable development of biogas projects while improving the economic profitability of anaerobic digestion plants. Biochar production from biogas digestate has been reported by several authors (e.g., Hung *et al.*, 2017, Luz *et al.*, 2018; Wongrod *et al.*, 2018a, and many others). For instance, thermochemical conversion of biogas digestate to biochar and its subsequent application to soil as a mechanism to enhance water and nutrient retention is becoming a widely accepted practice (Kataki *et al.*, 2017; Monlau *et al.*, 2016; Mumme *et al.*, 2011; Nansubuga *et al.*, 2015). Monlau *et al.* (2016) reported that solid-digestate and biochar digestate showed good soil amendments properties but with complementary effects. Biochar digestates may act as a source/sorbent of nutrients in soils. Such features have been studied for nitrogen compounds (Takaya *et al.*, 2016; Zheng *et al.*, 2018) as well as phosphorus compounds (Bekiaris *et al.*, 2016; Bruun *et al.*, 2017; Takaya *et al.*, 2016). Biochar digestate may be used for organic and inorganic contaminant immobilization encountered in contaminated soils and water streams. Several authors investigated the performance of biochar digestates in sorbing inorganic pollutants such as Pb and As (Wongrod *et al.*, 2018a, b; Wongrod *et al.*, 2019), Cu and As (Jiang *et al.*, 2018), Cu, Pb and Zn immobilization in industrial soil (Gusiatin *et al.*, 2016) and organic pollutants such as antibiotics (e.g., tetracycline) (Fu *et al.*, 2017; Jiang *et al.*, 2018) and herbicides (e.g., isoproturon) (Eibisch *et al.*, 2015). Biochar digestate application on agricultural land may also contribute to mitigation of climate change. For instance, Schouten *et al.* (2012) reported that biochar produced from cattle manure digestate contributes to decreased CO_2 emission and stabilized N_2O gas emissions when compared with raw cattle manure and anaerobically treated cattle manure digestate when spread onto soils.

Biochar digestates may be used as additives in anaerobic digesters. Anaerobic digestion is performed using microbial consortia that harbour acid producers, which convert substrate to desired acetic acid, CO_2, and H_2, and undesired volatile fatty acids (VFA). The desired products are converted to biogas by the methane producers (Gerardi, 2003). Anaerobic digestion may suffer from low process stability as microbes are sensitive to inhibition. During substrate-induced inhibition, microbes are either inhibited: (1) directly, by toxic substrate fractions (e.g., lipids, metals, pesticides); or (2) indirectly, by toxic degradation products, for example, VFAs, which lower pH as they accumulate, eventually inhibiting the methane producers (Fagbohungbe *et al.*, 2017).

When admixed in anaerobic digestion, biochar can: (1) adsorb direct and indirect toxic compounds; (2) buffer against the increasing VFA since biochar is often alkaline; and (3) provide a surface to immobilize microbes by forming a biofilm (Fagbohungbe *et al.*, 2017). Positive synergistic effects were firstly reported from admixing activated carbon with trace elements (Capson-Tojo *et al.*, 2018, 2019; Zhang *et al.*, 2018). Thus, system integration of biogas and biochar looks promising to take advantage of several profitable synergies (Fagbohungbe *et al.*, 2017; Luz *et al.*, 2018).

7.3.2 Reclamation (landscape recovery)

Reclamation is focused on areas disturbed by human activities, with the intention of returning these areas to optimal conditions of sustainable natural or human-influenced environment. The key priority of reclamation is not oriented to achieve the maximum amount of crop production on the reclaimed areas, but to achieve ecological landscape stability through colonization by microorganisms, plants and animals.

Unique methodology developed for reclamation includes the addition of reclamation compost or similar well stabilized organic or organic-mineral substrate (including aerobically stabilized separated digestate) into the soil production (Ust'ak *et al.*, 2010). This addition, in large quantities, typically from 800 to 1200 t/ha occurs only once at biological recultivation, for reasons of rapid topsoil recovery. Thereafter in the coming years, the soil is treated by conventional methods according to the current applicable regulations in the field of organic fertiliser use (including digestates) during agricultural production (Ust'ak *et al.*, 2010).

Reclamation focused on agricultural activity is based on the cultivation of so-called 'fertilising plants' in a modified crop rotation, leading to the enhancement of soil organic matter provisions and to optimize soil structure. For example, reclamation of areas devastated by mining activities can be achieved by using appropriate agrotechnical methods and crop rotations for agricultural reclamation (Čermák *et al.*, 2002).

7.3.3 Phytoremediation

Clean-up of metal-contaminated soils is truly indispensable due to the metals possible toxic effects. Different physical, chemical and biological methodologies have been employed for this clean up. In general, physical and chemical methodologies have some limitations such as high cost, intensive work, modifications in soil properties, and some of them are irreversible, and can have negative effects on native soil microflora (Ali *et al.*, 2013).

An alternative to physical and chemical methodologies is the use of phytoremediation. This biological methodology has been a promising approach to cleaning up metal-contaminated soils, namely through extraction (phytoextraction), stabilization (phytostabilization), and/or transformation (phytovolatilization) processes (Ma *et al.*, 2016).

Phytoremediation basically refers to the use of plants (and microorganisms associated to plants rhizosphere) to reduce/eliminate contaminants from different environmental compartments (Ali *et al.*, 2013). In fact, the term ''phytoremediation'' combines two words, the Greek word *phyto* meaning 'plant' and Latin word *remedium* meaning 'to correct or remove an evil'.

This methodology takes advantage of a variety of plant biological processes to support in-site remediation (Pivetz, 2001). It is an innovative, cost-effective, environmental friendly methodology that can be applied in situ, being a solar-driven remediation strategy. It can be applied at very large field sites where other remediation methods are not cost effective or feasible. In general, phytoremediation methodologies have lower installation and maintenance costs than other remediation techniques. In fact, it has been indicated that phytoremediation can cost as little as 5% of alternative remediation methods (Ali *et al.*, 2013, and reference therein). Moreover, vegetated areas are more resistant to erosion and, in the case of metal-contaminated soils, vegetation can also prevent metal leaching. Phytoremediation also has great acceptability for the general public as a ''green clean'' alternative to chemical facilities and bulldozers (Ali *et al.*, 2013, and references therein).

Among the different phytoremediation techniques, phytoextraction is the most suitable to be used in the removal of metals from contaminated soil and water. Phytoextraction implies the accumulation of metals in harvestable plant biomass that is, aboveground plant shoots (Ali *et al.*, 2013). Phytoextraction includes contaminant uptake by plant roots followed by metal translocation to the aboveground portion of plants and, generally, followed by harvesting and disposal of plant biomass (Pivetz, 2001).

The efficiency of phytoextraction depends on many factors, like bioavailability of the metals in soils. For instance, strong binding of metals to soil particles or metal precipitation can significantly reduce metal availability and therefore significantly reduce metal uptake by plants (Ali *et al.*, 2013, and references therein). However, plants have developed certain mechanisms for increasing metals bioavailability in soil. Plant roots can exude metal-mobilizing compounds in the rhizosphere, for instance phytosiderophores or low molecular weight organic acids (Rocha *et al.*, 2014, 2016). Moreover, microorganisms present in the plant rhizosphere (mainly bacteria and mycorrhizal fungi) may significantly increase the bioavailability of metals in soil (Ma *et al.*, 2016, and references therein). One should be aware that rhizosphere microbial communities also have a key role in phytoremediation. In fact, microorganisms can enhance the phytoremediation potential of a plant in different manners: by promoting plant biomass, increasing (phytoextraction) or decreasing (phytostabilization) metal availability in soil, as well as facilitating metal translocation from soil to root (bioaccumulation) or from root-to-shoot tissues (translocation) (Ma *et al.*, 2016; Oliveira *et al.*, 2014; Rajkumar *et al.*, 2012; Silva *et al.*, 2014).

Plant-root morphology and length are plant characteristics that are also important for phytoremediation. For instance, a fibrous root system with numerous fine roots spread throughout the soil will provide higher contact with the soil due to the higher surface area of the roots. In general, plants have root zones limited to the top layer of soil, which may restrict the use of phytoextraction to shallow soils (Pivetz, 2001).

Phytoextraction initially focused on hyperaccumulator plants, plants that accumulate a particular metal from metal contaminated soil to a very high degree (such as 100-fold or 1000-fold) when compared with other plants in that soil. These plants may reach some unusually high concentrations of metal in some of its tissues. These plants are relatively rare and found only in restricted areas around the world, with less than four hundred identified species for eight metals (Pivetz, 2001). But metals can be taken up by other plants that do not accumulate as high metal concentrations as hyperaccumulator plants, for example, corn (*Zea may*), sorghum (*Sorghum bicolor*), alfalfa (*Medicago sativa L.*) and willow trees (*Salix spp.*) (Pivetz, 2001) or sunflowers (Rizwan *et al.* 2016), namely plants that produce high amounts of biomass. The larger biomass of these plants could result in a higher amount of metals being removed from the soil even though metal concentrations within the plants might be lower than in hyperaccumulator plants (Pivetz, 2001).

An important question that arises after using plants for phytoextraction of metals from contaminated soils is: what will be the fate of the plant biomass? In fact, in recent years, the disposal of plants biomass used in phytoremediation has gained a lot of attention. Direct dumping, a stack of decay heat, burning, high-temperature decomposition and chemical extraction have all been suggested (Cao *et al.*, 2015, and references therein). In addition, some economic opportunities exist for plant biomass after being used in phytoextraction. For instance, plant biomass can be treated for recovery of precious and semiprecious metals, so-called phytomining (Cao *et al.*, 2015, and references therein). Furthermore, fast-growing and high-biomass producing plants, such as willow and poplar, could be used for both phytoremediation and bioenergy production (Abhilash *et al.*, 2012). Plant biomass can be used for different energy-recovery techniques, such as anaerobic digestion, incineration, gasification and production of biodiesel (Tian & Zhang, 2016, and reference therein). Some economic balances have showed that this strategy can produce some economic gains (Tian & Zhang, 2016, and reference there in). However, some questions concerning the production of bioenergy from phytoremediation residues are still unclear (Tian & Zhang, 2016). For instance, harvested metal-contaminated shoots can be introduced in the anaerobic digestor as biomass source. But it is important to be sure that the metal burden, namely of toxic metals such as Cd, in plant biomass will not affect biogas production (Tian & Zhang 2016). So, it is essential to assess these effects of metals concentrations on digestion systems and the design of anaerobic digestion processes (Cao *et al.*, 2015, and reference therein). Moreover, selecting suitable plants is essential, as species accumulating high concentrations of pollution may be difficult to digest (Tian & Zhang 2016).

To conclude, despite the fact that re-use of biomass used for metals phytoextraction is still not universally accepted, several advantages on the integration of phytoremediation technology with bioenergy production are already known. And other avenues also need to be explored. For instance, this type of plant biomass could be used to supplement the metals needed in an anaerobic digestor, contributing to the implementation of circular economic strategies and closing the loop. So, more research on this topic is required to promote an efficient application of phytoremediation.

7.4 OPPORTUNITIES FOR NEW USES OF DIGESTATE

Anaerobic digester (AD) developers are continuously faced with falling rates for renewable energy, the loss of the state investment credit grants and increasing costs of maintaining and operating the facilities. So, the financial models have to be changed and non-energy revenue streams for AD facilities are urgent in order to help protect feasibility and enhance the technology's already substantial environmental benefits. Since the power rate is flat, additional income streams have to be found to cover increased costs, especially in the regions where electricity and natural gas prices are low (e.g., North America). Digestate has already been classified as a product of lower value which generates minimal income, but demand for organic fertilisers and nutrient management can be a starter in development of the techniques and technology for digestate valorisation (WRAP, 2012) in order to: (i) increase the value of the digestate; (ii) create new markets for digestate products; (iii) reduce the dependence on land application; (iv) ensure more secure and sustainable outlets for digestate products; and (v) potentially reduce the operating cost of the facility.

Apart from the traditional land applications, digestate can be validated by: (i) the use of the digestate liquor for replacing freshwater and nutrients in algae cultivation; (ii) the use of solid digestate for energy production through biological (i.e., AD, bioethanol) or thermal processes (i.e., combustion, hydrothermal carbonization and pyrolysis); or (iii) the conversion of solid digestate into added-value products (char or activated carbons) through a pyrolysis process (Monlau *et al.*, 2015).

7.4.1 Land application

Traditionally, the solid fraction of digestate is often used as a soil fertiliser, or dried for the use in animal bedding, while the liquid fraction is usually spread on the fields. The focus remains on the products that will enhance soil properties as fertiliser and soil conditioner on farms, grass courts and home gardens. The nutrients (large parts nitrogen and potassium in liquid portion, phosphorous in the solid fraction; Liedl *et al.*, 2006) are separated and concentrated to create organic fertilisers in liquid or dry format. The digestate originating from manure or cellulosic wastes is loaded with absorbent fibres and mainly used in products that improve the soil's ability to control moisture and nutrient release (Gorrie, 2014).

Separation and concentration of the nutrients to create organic fertilisers in liquid or dry format can be a way of converting valuable digestate ingredients (nutrients and fibres) into co-products that will generate revenue. Recovered nutrients from digestates are applied either as a fertiliser or as a base feedstock for fertiliser production. Ammonium and phosphorus can be extracted from the digestate by precipitation in the form of magnesium ammonium phosphate (struvite) for use as an inorganic fertiliser or a feedstock for fertiliser production. By using a number of different commercially available techniques, ammonia, in the form of ammonium sulphate and ammonium nitrate, can also be recovered from the digestate. (WRAP, 2012.)

The digestate can either be composted on its own or co-composted with a range of standard composting feedstock, such as wood chip and green waste (Zeng *et al.*, 2016). Co-composting is beneficial for both waste streams because digestate provides a source of nitrogen, phosphorus, magnesium and iron, as well as moisture; and the standard composting feedstock provides a bulking agent, improving the carbon/nitrogen ratio and consistency of the final product (Evans, 2008).

Another possibility to give new value to the manure fibres is making a blend of nutrient-rich digested manure and other recycled natural materials for use in organic production, as a peat moss alternative. Peat moss is used in the burgeoning business of home gardening, but significant greenhouse gas emissions (both carbon and methane) are associated with the harvesting (for every acre harvested, 2400 tons of methane are released). An example for successful market utilisation of digested dairy manure fibres and improved long-term success of facilities is a bagged potting soil product (named 'Magic Dirt') by Cenergy, SA which has the ability to hold more than three times its weight in water and makes this blend suitable for use as a peat alternative (Goldstein, 2014).

7.4.2 Algal treatment of digestate

Algal treatment of digestate is an innovative approach for enhancement of the digestate liquid fraction. Liquid digestate can be combined with carbon dioxide to proliferate some microalgae until they can be harvested and used for the production of biochemicals and biofuels. Because of their easy production, growth rate, short lifecycles and independence from fertile agricultural land (land requirement for microalgae cultivation is estimated at 3% of traditional direct land application of digestate; Xia & Murphy, 2016), algae have great potential for energy use compared with conventional plants. Microalgae can fully use nutrients from liquid digestate, and CO_2 that is otherwise emitted to the atmosphere. The results of some recent works demonstrate the possibility of improving biomass accumulation (Xia & Murphy, 2016) and/or lipid production (Zuliani *et al.*, 2016) using different anaerobic digestates.

7.4.3 Bioenergy production

7.4.3.1 Bioethanol production

Valorisation of both solid and liquid digestate fractions can be achieved through biological fermentation and bioethanol production. The solid fraction has recently attracted attention for bioethanol production due to its high content of cellulose fibres (Xia & Murphy, 2016). In order to solubilise lignin that can limit carbohydrate availability and increase the cellulose content, treatments (mostly dilute-alkali treatment) have to be applied prior to enzymatic hydrolysis and fermentation.

Digestate shows several advantages for bioethanol production (Xia & Murphy, 2016): (i) enriched in easily accessible cellulose; (ii) better enzymatic digestibility than raw material (contains less hemicelluloses and more cellulose); (iii) AD process could improve the energy efficiency in traditional bioethanol production (reduce the energy requirement for the biomass milling).

The liquid digestate can also be used as a culture medium to replace freshwater and nutrients in bioethanol production process. Compounds, such as nutrients (N, P and K) and minerals (Mg, Zn, Cu) are essential for the enzymatic activity and yeast growth. Besides that, liquid digestate contains reduced amounts of potentially inhibitory compounds (i.e., furans and phenolics) for ethanol fermentation, since those compounds can be degraded in the AD process.

7.4.3.2 Thermal processes

Thermal digestate applications use heat (via incineration, combustion, hydrothermal carbonization or pyrolysis) in order to recover energy from the digestate and improve the overall energy efficiency of AD processes. Incineration is applicable for digestates with a high calorific value or where land-based application is not financially practical. Combustion is a thermochemical process with the complete oxidation of organic wastes to heat energy. The calorific value of digestate pellets was found to be similar to the calorific value of wood: 16.5 and 17.3 MJ kg^{-1} DM, respectively (Kratzeisen *et al.*, 2010). The residual ash can be used as a construction material for roads or for concrete production, and phosphorus can be recovered from the ash by acid leaching (WRAP, 2012).

Hydrothermal carbonization is a technique where wet organic material is converted into carbon-rich products called ''hydrochars'' with physicochemical properties close to fossil coal (Hoffmann *et al.*, 2013). Within the pyrolysis process, the digestate is heated under an oxygen-free atmosphere, producing biochar and vapour. By cooling the vapour phase, liquid is condensed (bio-oil composed of a large range of compounds including mainly sugars, acids, ketones, phenols and furans compounds) and the remaining gas phase (syngas) consists of mainly hydrogen, methane and carbon monoxide (Wang *et al.*, 2014). Incineration, pyrolysis and combustion require a solid digestate with a low moisture content, and thus a severe drying pre-treatment, so using heat from CHP facilities for efficient operation.

7.4.3.3 Bioelectricity

Microbial fuel cells are an application of fuel cells with the potential to remove nutrients and produce bioelectricity by the biological oxidation of organic matter from different wastes, as well as anaerobic digestate (Di Domenico *et al.*, 2015). The reactions take place under anaerobic conditions, and currently, this process is operational only at laboratory and pilot scales.

7.5 GAPS AND CHALLENGES

Trace element fluxes in the soils have been widely studied by phytomanagement. Research has shown that over time and under specific environmental conditions, but not in all studied cases, trace elements accumulate in soils. It is important to make the distinction between trace elements that interact with plants (phytoavailable) and trace elements that interact with other organisms (bioavailable). Physical contact between trace elements and plant roots is necessary for phytoavailability and affects root growth and plant uptake. High concentrations of trace elements in soils can damage plant tissues (oxidative stress) and hinder essential nutrients paths (Robinson *et al.*, 2009).

There is currently no general rule on whether ongoing digestate applications will result in constantly improved soil functions in the long run. Therefore, the measurement for assessing the health of a soil by determining diversity of the soil microbial community on structural and functional levels is essential for the sustainable production of crops and stability of arable land ecosystems (Riding *et al.*, 2015).

One of the major limitations to current research is the point-to-point exploration of strategies with no unified strategy (Murovec *et al.*, 2015). Using a diluted approach in which each the researcher can use his or her own approaches to studying the problem at hand, with little or no overlap from other researchers, has limited potential to unravel the cross correlations between various parts of the system and hence results in systematically contradicting results.

There is a chain of system characteristics that govern decision-making policy of digestate disposal: (i) geological characteristics of soils underpinning the production of plethora of biogas substrates; (ii) the substrate mixtures and ratios used, WWS characteristics, annual variations; (iii) anaerobic process characteristics; (iv) all of the previous points pivoting on digestate characteristics that affects the projected area of disposal; and finally (v) returning again to the geological characteristics of soils, which might be well different from those from which the original substrates were either grown or farmed or chemically produced.

Anaerobic digestion and the fate of its concentrated end products are characterized by a complex interplay of multiple factors acting over multiple scales, for example, landscape to nano-scale of metal environmental-matrix interactions. This is an emerging interdisciplinary framework that aims to improve our understanding, prevention of undesired environmental effects, and improve the use of crucial nutrients by integrating knowledge and data across multiple levels of life sciences (chemical, agricultural, engineering, microbiolgical, biotechnological and medical). As this is a multiscale system, the ultimate challenge and vision is a radical paradigm shift from a plethora of scale-specific reductionistic approaches to a more unified multiscale anaerobic systems science integrating past lessons and synchronizing research approaches, similar to current initiatives in medicine and physics.

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