Thermophilic Anaerobic Digestion as suitable bioprocess producing organic and chemical renewable fertilizers: a full-scale approach.

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Abstract

This work reports a full-scale study in which organic wastes were transformed by high-solid thermophilic anaerobic digestion (HSAD), into N fertilizers and organic fertilizers, i.e. digestate. The produced fertilizers were characterized over 42 months and their properties were discussed in comparisons with literature data. HSAD coupled with N stripping technology led to ammonia sulphate production having high N concentration (74 ± 2 g kg^{-1} wet weight), neutral pH (6.8 ± 1.3) and low traces of other elements. Digestate showed both higher carbon (C) content (314 ± 30 g kg^{-1} on dry matter (DM) and biological stability than green composts, indicating good amendment properties. Digestate was also interesting for its N (77 ± 3.7 g kg^{-1} dry matter – DM) content, half of it in the ammonia form, and P content (28 ± 4.1 g kg^{-1} DM) that was 43% readily available as soluble P-orthophosphate. K content was low (6.5 ± 1.3 g kg^{-1} DM), indicating poor fertilizing ability of digestate for this element. All organic pollutants investigated were much lower than the limits required for agricultural use and levels of some of them were lower than the content revealed for other organic matrices such as agricultural and energy crop digestates and compost. Emerging pollutants (i.e., pharmaceuticals) were tested as markers and they were found to be below the detection limit (<0.01 mg kg^{-1} DM) indicating very low content. The results obtained showed that HSAD coupled with N stripping allowed transforming sewage sludge into fertilizers and soil improvers exploitable in agriculture.

Keywords: Ammonium sulphate; High Solid Anaerobic Digestion; Digestate; Fertilizer properties; Sewage sludge.

1 Introduction

With the increase of the global population, the production of organic wastes is likewise increasing. Sewage sludges (SS), in particular, which are the semi-solid residual materials left over after municipal and industrial wastewater treatment processes (Raheem et al., 2018), have been produced at the rate of 181 and 1,850 Gg dry matter (DM) $year^{-1}$, i.e. 21 ± 4 kg DM $person^{-1}$ $year^{-1}$ in Europe's top 13 producing countries for the period 2010 -2017 (Di Capua et al., 2020), i.e. 8 million m^3 $year^{-1}$ (https://ec.europa.eu/environment/waste/sludge/), posing environmental and economic problems for their management.

Population expansion not only causes an increase of waste production but also an escalation of food demand and consequently of fertilizer requirements. It has been estimated that the world demand for fertilizer will increase by 7.9% in 5 years (from 2017 to 2022) according to Food and Agriculture Organization (FAO) (FAO, 2019). Producing fertilizers requires energy and/or fossil-origin raw material. The nitrogen production industry as a whole uses more than 1% of the world's total energy and emits more than 300 million Mg of CO_2 per year (Cherkasov et al., 2015). Most of the phosphate rock mines sites are concentrated in a few countries (Morocco, China, USA, Jordan and South Africa) which can cause supply issues especially for Europe. Moreover, the quality of these sources is decreasing, causing a higher content of pollutants (e.g. for P-based fertilizers) (Günther et al., 2018). P and N are also dangerous pollutants in both deep and fresh waters and especially in the latter, in which they can cause eutrophication and consequent death zones (Conley et al., 2009) if misused.

Soil contains the largest pool of active C, about 1,500 – 2,000 Pg C (considering one-meter-depth) (Janzen, 2004). This fraction is important because it directly affects soil fertility, but also the world C stocking capacity (Ayuke et al., 2011; Lal, 2009; Smith et al., 2018). Furthermore, C content in soil is decreasing because of both land use changes and intensive agriculture depleting soil C. Therefore, there is a need to recover nutrients but also organic matter from organic matrices contributing to soil C balance.

Although there are different pathways for sewage sludge disposal, i.e. landfill, incineration, land reclamation, composting, pyrolysis, gasification and co-incineration, the use of sewage sludge in agriculture represents the most common practice, taking almost 40% of sewage sludge in EU (European Commission, 2009). This is because sewage sludge contains both organic matter (OM) and nutrients, it can act as both an organic amendment and as fertilizer (Di Capua et al., 2020). Sewage sludge's fertilizer properties can be enhanced by SS pre-treatment such as anaerobic digestion (AD), which also brings other benefits (Di Capua et al., 2020). The AD process produces a substrate, called digestate, that has different characteristics from the feedstock of the digester. The AD, by promoting organic matter (OM) degradation of easily decomposable organic components, leads to relative high biological stability of the digestate, increasing its amendment properties (Tambone et al., 2010) and nullifying phytoxicity (i.e. high maturity); moreover, by promoting OM mineralization it increases nutrient availability for plants (Tambone et al., 2010), reducing, also, potential odour production (Orzi et al., 2015). The OM stabilization, at a right

combination of temperature, microbial competition and ammonia production, reduces or annuls pathogen contents above all under thermophilic conditions (Orzi et al., 2015; Qi et al., 2018; Scaglia et al., 2014) guaranteeing hygienic products and avoiding pathogens ending up in the soil (Bonetta et al., 2014). Therefore, digestate can be proposed as both organic amendment and fertilizer, as it can provide both OM to replace soil OM losses (Tambone et al., 2010) and nutrients, replacing mineral synthetic fertilizers (Riva et al., 2016). However, in many cases there are dangers that nutrients can overload crop requirements or digestate may not prove to be directly suitable for fertilizer use (e.g. nutrient imbalance in the product compared to crop requirements, limits imposed by law for a specific component - e.g. Nitrate directive in EU - and topdressing fertilization). Therefore, nutrient recovery from digestate may be necessary to produce new biobased fertilizers, which can be easily be used and/or transported. AD has been reported to be a useful biotechnology for facilitating the subsequent nutrient recovery to produce fertilizers, because of nutrient speciation (e.g. organic N to mineral N(Amekan, 2020; Ledda et al., 2013)).
One of the most studied and exploited digestate post-treatments for recovering a nutrient is ammonia stripping (Sigurnjak et al., 2019a). Ammonium is often the most represented mineral N form in digestate and at high pH and/or high temperatures, ammonia can volatilize from digestate and extracted by exploiting a gas (air, biogas or N_2). The ammonia rich gas can be scrubbed with an acid substance (most often sulphuric acid or nitric acid), recovering N and producing an N-salt solution having high N content (N of 6-8 % weight/weight). This technique can also enhance biogas production, avoiding ammonia inhibition during the AD process (Zhang and Jahng, 2010; Abouelenien et al., 2010; Walker et al., 2011; Bousek et al., 2016).

This work aims to describe amendment and fertilizer properties of bio-fertilizers obtained from a full-scale thermophilic high-solid thermophilic anaerobic digestion (THSAD plant) designed to produce fertilizers, i.e. digestate and ammonium sulphate, starting from organic wastes represented mainly by sewage sludge. The fertilizers obtained were analysed throughout 2017-

2020, comparing analytical data with those of other bio-fertilizers (agricultural digestates and composts) and with the legal limits in force for agricultural use.

Potentially, both inorganic and organic pollutants can affect the safe use of digestate in agriculture, especially because the AD process degrading the OM can cause an increase in the relative concentration of pollutants (Al Seadi et al., 2013; Kupper et al., 2014). On the other hand, literature has reported the ability of AD to degrade organic pollutants (Verlicchi and Zambello, 2015). As consequence of that, in addition to agronomic properties, inorganic and organic pollutants have been detected, introducing, also, some emerging organic pollutants as markers.

This paper represents a rare case in which a detailed description of chemical and biological properties of biofertilizer obtained at full scale plant monitored for long time (years) have been done, becoming data collected very useful to give a detailed description of the biofertilizer properties. No many data exist with reference to ammonia sulfate charateristics and their variability with time. Again there is no so detailed description of digestate that included the use of both common and less common analytical approaches (e.g. biological stability, ^{13}C-and ^{31}P-NMR) helping in tracing amendment and fertilizers properties. In addition becasue biofertilizers were produced treating organic wastes, environmental issues have been considered making a great analytical effort in the investigation of common pollutants, i.e. heavy metals, but also organic pollutants, including emerging pollutant, and pathogens. All these allowed giving a full picture of biofertilizers produced by anaerobis digestion at full scale to be used in agricultrue in substitution of conventional fertilizers.

2 Materials and methods

2.1 Plant description

The THSAD plant, located in Lombardy Region (northern Italy), transform different types of wastes, mainly sewage sludge, into a useful soil improver (i.e. digestate) and N-based mineral fertilizer (i.e. ammonium sulphate), i.e. renewable fertilizers, and the electrical and thermal energy needs of the plant.

The data reported in the present paper refer to a period covering 42 months (2017, 2018, 2019 and the first 6 months of 2020).

2.1.1 Anaerobic Digestion section.

High-solid anaerobic digestion (Di Capua et al., 2020) took place in three reactors in series of 4,500 m^3 each, made of carbon steel (Giordano et al., 2019) and it was performed under thermophilic conditions (55 °C) using hot water and steam as thermal energy carriers. The biogas produced by the plant is fed to a combined heat and power (CHP) unit in order to recover heat and electrical energy, primarily consumed on-site (about 30%), while the excess is sent to the national grid. During the cold season, an auxiliary boiler fed with methane (starting from month 38 of the observation periods with biogas) can be used if necessary. Reactor tanks have no mechanical mobile part inside, and the feedstock/digestate mixing is guaranteed by continuous circulation through external pumps. Biogas was collected in the headspace of each reactor equipped with a double-membrane gasometer dome maintained at a constant pressure which covers the tanks (Figure 1).

Feedstock was represented by 85% of municipal sewage sludge, 5% by sewage sludge from the agro-food industry and the remaining fraction by the liquid fraction of food waste from separate collection. The feedstock received was first gathered in basins and then transferred into a mixing unit where it was heated (by direct steam injection, to reach 55°C) and homogenized with digestate coming from the third digester and water to obtain a solid content of about 140 g kg^{-1} wet weight (ww) before being fed to the first digester. About 0.3 Mg of water was added per Mg of feed (these data represent both water vapour injected directly into digestate to assure thermophilic conditions and water used to lower DM content). The weekly organic loading rate (OLR) during the whole period was in the range 0.7 – 3 kg VS m^{-3} d^{-1} with a mean value of 2.0 ± 0.5 kg VS m^{-}

^{3} d^{-1}. This means an average Hydraulic Retention time (HRT) of about 50 days. The weekly specific methane production was of about 200 ± 29 CH_4 kg^{-1}VS$_{in}$.

During the 42 months of observation, the AD plant treated about 240,000 Mg of waste producing about 320,000 Mg of digestate and about 13,500 Mg of biogas.

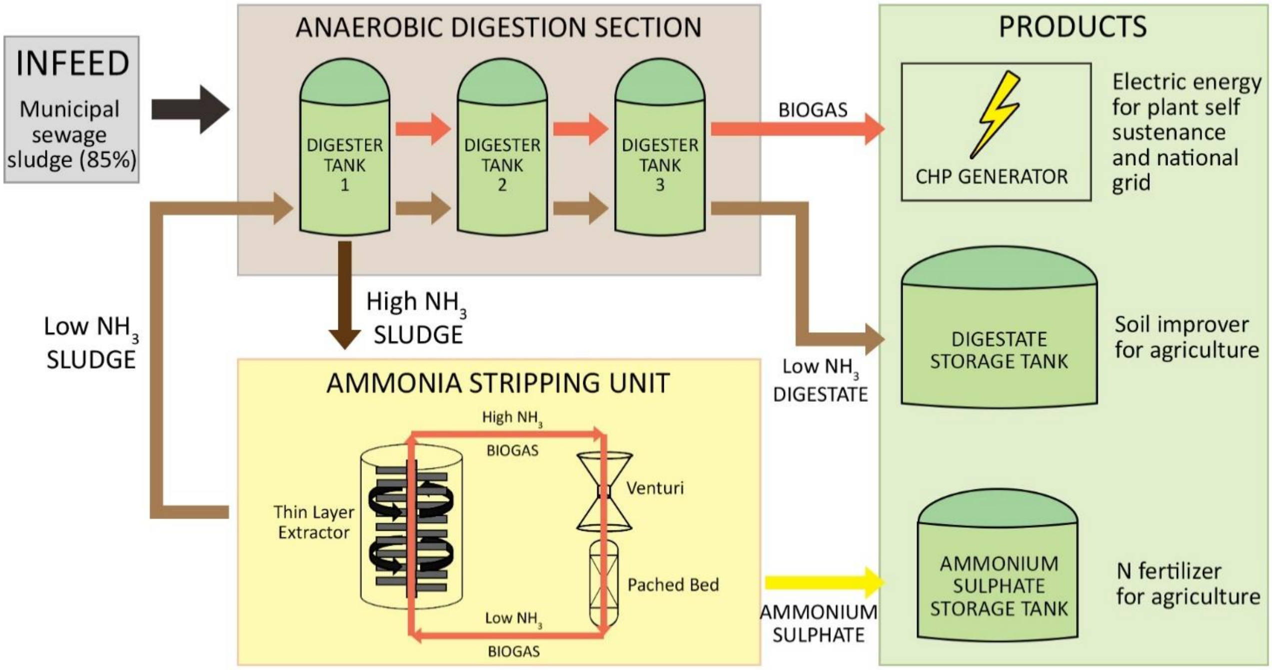

Figure 1. Scheme of the digestion plant and ammonia stripping system. On the left is represented the infeed of the plant. On the right are shown the three main outputs: energy, digested sludge and ammonium sulphate.

2.1.2 Ammonia stripping unit.

The ammonia stripping unit is used to control the total ammonia nitrogen (TAN) level in the digestate to avoid AD inhibition due to TAN accumulation and toxic circumstances for the micro-organisms (Capson-Tojo et al., 2020). The system withdraws sludge from the digester tank to a thin film evaporator (TFE), where ammonia is stripped from digestate by biogas collected from the headspace of the three digesters. Then, biogas is fed to an absorption unit constituted by a Venturi scrubber followed by an upstream packed bed column where ammonia reacts with sulphuric acid producing an ammonium sulphate solution (Costamagna et al., 2020). The resulting low-ammonia digestate is pumped back to the first reactor.

The stripping and adsorption unit was modified in 2020 by increasing the liquid/gas, using air as stripping gas, and finally using three Venturi scrubbers in the absorption section.

During the first 38 months (30 months of effective work), the stripping unit removed about 6 % of the input N waste, corresponding about to 12% of TAN. In the following 4 months, by tuning the stripping and ammonia trap units, about 12% of the input N-waste was removed, i.e. 22-27% of TAN. During the 42 months of observation, about 2,180 Mg of ammonium sulphate solution (7.2 ± 0.2 % N-NH_4) was produced.

2.2 Renewable fertilizers characterization

2.2.1 Chemical analysis methods

Ingestate, digestate and ammonium sulphate, if not better specified in tables, were sampled during a period of 42 months (from January 2017 to June 2020) and characterized from a chemical point of view according, also, (digestate) to Lombardy Region regulation (Regione Lombardia, 2019) for agricultural use of these products.

The following parameters were determined: pH (EPA 9045D) (EPA, 2004), dry matter at 105°C (DM 105°C), dry matter at 600°C (DM 600°C) and Total Organic Carbon (TOC) (APHA, 1998), total nitrogen (TKN) (EN 13652) (EN 2001). Ammonia-N (NH_4-N) was determined by ISO 5664 method (ISO, 1984) (reagent and grade in Table S1).

In addition, nutrients (P, K, Ca, Mg, Fe, Mo, Mn), heavy metals contents (Cd, Cr tot, Ni, Pb, Cu, Zn), and micropollutants/element (Hg, As, Al, Co, Se, Na) were determined by inductively coupled plasma mass spectrometry (ICP-MS, Varian Inc., Fort Collins, CO, USA) according to DIN EN ISO 11885 (ISO, 2009) (Ca, Mn, Mg, Fe, Mo, Al, Co, Na), and according to UNI-EN 16174 (UNI-EN, 2012) for all the other elements.

Organic micropollutants were detected as follows: C10-C40 hydrocarbons by UNI EN 14039 (UNI, 2005) method, halogenated organic compounds (AOX) by Gas Chromatography (GC) approach (UNI EN ISO 22155:20161) (UNI, 2016) and EPA 8270E 20181 (EPA, 2014) + EPA 3550C 2007) (EPA, 2007a). PCDD/Fs were measured using UNI 11199 (UNI, 2007) method, PCBs through UNI EN 16167 (UNI, 2012) and UNI EN 16167 (UNI, 2019), and DEHP through EPA 3550C (EPA, 2007a) + EPA 8270E (EPA, 2018) methods.

Emerging organic pollutants (pharmaceuticals), i.e. Ciproflaxacin, Sulfamethoxazole, Fenofibrat, Gemfibrozil, Carbamazepine, Metoprolol, Diclofenac, Ethinylestradiol and Estradiol were detected by HPLC-MS following EPA 3550C (EPA, 2007a) and EPA 8321B 2007 methods (EPA, 2007b).

Faecal coliform and *Salmonella* were determined as reported in CNR IRSA 3 (CNR IRSA, 1983) (Fecal coliform) and ISTISAN 14/18 (ISTISAN, 2018) + APAT CNR IRSA 7080 (*Salmonella*) (APAT, 2003).

2.2.2 Biological stability determination

Biological stability of the digestates was evaluated by measuring the oxygen uptake by microorganisms to degrade organic matter and by measuring the residual Biochemical Methane Potential (BMP).

In particular, the Substrate Oxygen Uptake Rate test (SOUR test) was used (Orzi et al., 2010). In brief, 1 g of wet matter sample was placed in a flask with 500 ml of deionized water, and added of 12 mL of phosphate buffer solution (KH_2PO_4 0.062 mol L^{-1}, K_2HPO_4 0.125 mol L^{-1}, $Na_2HPO_4 \cdot 7H_2O$ 0.125 mol L^{-1}), and 5 mL of nutritive solution ($CaCl_2$ 0.25 mol L^{-1}, $FeCl_3$ 0.9 mmol L^{-1}, and $MgSO_4$ 0.09 mol L^{-1}), prepared according to the standard BOD test procedures (Orzi et al., 2010). The oxygen uptake rate was reported as the result of the oxygen demand occurring in a 20-h tests (OD_{20}, mg O_2 g DM^{-1}). All SOUR-OD_{20} tests were performed in triplicate.

Biological stability was determined, also, by a long-term degradation test (60 d) using the anaerobic potential biogas production test (BMP test), performed according to Schievano et al. (2008). In brief, in a 100 mL serum bottle, 0.62 g of dried sample (Ø < 1 mm) was added to 37.5 mL of inoculum and 22 mL of deionized water. The batch tests were carried out with 60 mL samples (about 35 g kg^{-1} TS) and 40 mL of headspace. The fresh feedstock and inoculum percentages of TS were respectively 35% and 65%. Control blanks were prepared using 60 mL of inoculum. All batches were sealed with Teflon hermetic caps, flushed with an N2 atmosphere, and incubated at 37 ± 1°C, until no further biogas production was detected (normally around 60 d).

2.2.3 Cross-Polarization Magic Angle Spinning Carbon-13 Nuclear Magnetic Resonance.

Three samples of digestate were taken directly from the plant at three different times over the years 2018, 2019 and 2020. Before analyses, the samples were dried at 105°C and milled (diameter ≤0.2 mm).

The solid-state Cross-Polarization Magic Angle Spinning Carbon-13 Nuclear Magnetic Resonance (CPMAS ^{13}C NMR) spectra of the digestate samples were acquired at 10 kHz on a Bruker AMX 600 spectrometer (Bruker BioSpin GmbH, Rheinstetten) using a 4-mm CP-MAS probe. The pulse repetition rate was set at 0.5 s, the contact time at 1 ms, and the number of scans was 3200. The chemical shift scale of CPMAS^{13}C NMR spectra were referred to tetramethylsilane (δ = 0 ppm). Spectra were elaborated using TOPSPIN 1.3 software (Bruker BioSpin GmbH, Rheinstetten, Germany).

2.2.4 P fractionation and its characterization by ^{31}P-NMR.

Sequential extraction of phosphorus

The different phosphorus (P) species characterizing the samples of digestate, collected at three different times during the year, were carried out by the sequential extraction suggested by Turner and Leytem (2004). This procedure was able to assess the different P fractions by using $NaHCO_3$, NaOH-EDTA, and HCl solvents. In this way it was possible to extract P considered readily soluble ($NaHCO_3$) and also, poorly soluble P fractions, such as P associated with amorphous iron/aluminium hydroxides and organic matter, and Ca^{2+}, Mg^{2+} and NH_4^+ - phosphates, which were extracted by NaOH-EDTA and HCl.

In brief, the first extraction was performed by using a 0.5 mol L^{-1} $NaHCO_3$ solution (1:60 dry biomass/solution ratio) for 4h. After centrifugation at 10,000 rpm for 30 min and then filtration through a 0.45 µm cellulose-nitrate membrane, the residual fraction was extracted for 16 h with 1 mol L^{-1} HCl solution (1:60 dry biomass/solution ratio) or with a 0.5 mol L^{-1} NaOH plus 50 mmol L^{-1} EDTA (1:20 dry biomass/solution ratio).

An aliquot of each supernatant was frozen at -80°C and lyophilized for NMR spectroscopy characterization. Another aliquot was mineralized and subsequently the P content was detected by ICP-MS analysis.

^{31}P Nuclear Magnetic Resonance Spectroscopy

^{31}P Nuclear Magnetic Resonance Spectroscopy was performed by using 300 mg of lyophilized sample dissolved in 3 mL of a solution made by 1 mol L^{-1} NaOH and 0.1 mol L^{-1} EDTA (H_2O/D_2O 9:1) (pH > 13). The samples were vortexed and centrifuged at 5,000 rpm for 4 minutes at 20 °C. The supernatant was placed in a 10 mm NMR tube and the NMR spectra recorded on a Bruker AV600 spectrometer operating at a frequency of 600.13 MHz and 242.94 MHz for ^{1}H and ^{31}P nuclei, respectively. The ^{31}P spectra were acquired with a 10 mm BB probe at 20 °C and were referenced to external 85% H_3PO_4. $P_{90°}$=15 µs, D1=2 s, SW=7763, 975 Hz, NS ranging from 4,000 to 27,000 depending on the samples; chemical shifts (δ) were measured in ppm. The NMR spectra were transformed with a line broadening (LB=-2 Hz and GB= 0.02) by TOPSPIN software and the baseline was corrected using a polynomial function. All NMR signals were integrated and the sum of the integrals was assigned the value of the total phosphorus concentration (mg kg^{-1}) obtained by the ICP-MS analysis. The complete assignment of phosphorus species was performed following the literature relative to the composition of the phosphorus species in soil, manure and slurry (Turner and Leytem, 2004).

3 Results and discussion

3.1 Renewable fertilizers characterization

3.1.1 Ammonium sulphate solution characterization

A full characterization of the ammonium sulphate solution was made on samples collected during the trial period; every sample was tested in triplicate. This characterization was very important because little information is available in the literature on the complete chemical characteristics of ammonium sulphate solutions produced by ammonia stripping from digestate or effluents. Ammonium sulphate solution (Table 1) appeared as a yellowish/red liquid, with a density of about 1,200 g L^{-1}. Ammonium sulphate solution (ASS) recovered had a NH_4-N average concentration of 7.2 ± 0.1%, electric conductivity of 119 ± 27 mS cm^{-1} (1:2.5 v/v digestate:water at 25°C); the dry matter (DM) content was of 35.5 ± 0.37% and so, higher than that reported in other works, which however reported data with a strong variability. pH of the solution was almost neutral, i.e. 6.8 ± 1.3, and so higher than values found in the literature (average of 3.7 ± 2.2). pH close to neutrality represent an advantage for agricultural purposes, as it allows an easier use as fertilizer, reducing corrosion of machinery and risk of damage for crop plants when it is used as a topdressing; in addition, soil acidification is reduced. As expected, almost all nitrogen (Total N), which had a concentration of 74 ± 2 g kg^{-1} ww was found in ammonia form (i.e. 97%); this value was higher than those found in literature that was, as average, of Total N of 41 ± 32 g kg^{-1} ww (Table 1).

Organic carbon was found only in traces i.e. TOC of <0.1 g kg^{-1}, according to data reported in the literature (Table 1). Other macronutrients, namely P and K, as expected, had no a significant concentration in ammonium sulphate solution, i.e. 11.7 ± 4.7 mg kg^{-1} and 14.2 ± 7.9 mg kg^{-1}, respectively, showing the high purity of the solution produced. Higher concentrations of the elements were found for Ca (68 ± 18 mg kg^{-1} ww), Mg (10 ± 4 mg kg^{-1} ww) and Na (22.4 ± 7.7 mg kg^{-1} ww) with all the other elements being lower than 10 mg kg^{-1} ww. Micronutrients and inorganic micropollutants were found only in traces. Currently there are no other data in the literature on the content of micronutrients or pollutants in ammonium sulphate obtained from biofertilizers from anaerobic digestion, so it was not possible to make any comparisons.

Table 1. Main characteristics (mean ± SD; n=17) of ammonium sulphate - $(NH_4)_2SO_4$ - produced by the plant (all concentrations are expressed on wet basis) - data referred to the period 01/01/2017- 30/06/2020.

	Unit	**Value**	**Literature Comparison**
pH	pH	6.8 ± 1.3	3.7 ± 2.2 [a, b, c]
EC	mS cm^{-1}	119 ± 27 (1:2.5 v/v 25 °C)	192 ± 61 [a, b, c] (dilution not reported)
Dry Matter 105°C	% of ww	35.5 ± 0.4	20 ± 10 [a, b, c, d]
Total Organic Carbon	g kg^{-1} ww	< 0.1	0.4 [a]
Total N	g kg^{-1} ww	74 ± 2	41 ± 32 [a, b, c, d]
N-NH_4	g kg^{-1} ww	71.7 ± 1.9	41 ± 32 [a, b, c, d]
P tot	mg kg^{-1} ww	11.7 ± 4.7	16 ± 28 [a, b, d]
K tot	mg kg^{-1} ww	14.2 ± 7.9	59 ± 93 [a, b, d]
S tot	g kg^{-1} ww	88 ± 2	39 ± 12 [a, b, c]
Ca tot	mg kg^{-1} ww	68 ± 18	
Mg tot	mg kg^{-1} ww	10 ± 4	
Fe tot	mg kg^{-1} ww	< 11	

Mo tot	mg kg^{-1} ww	0.1 ± 0.1	
Cu tot	mg kg^{-1} ww	< 6	0.3[b]
Zn tot	mg kg^{-1} ww	2.5 ± 2.4[e]	2.9[b]
Mn tot	mg kg^{-1} ww	0.7 ± 0.5[e]	
Al tot	mg kg^{-1} ww	3.6 ± 5.5	
Co tot	mg kg^{-1} ww	0.01 ± 0	
Se tot	mg kg^{-1} ww	0.04 ± 0	
Na tot	mg kg^{-1} ww	22.4 ± 7.7	
Cr tot	mg kg^{-1} ww	< 1	
Pb tot	mg kg^{-1} ww	< 1	
As tot	mg kg^{-1} ww	< 1	
Cd tot	mg kg^{-1} ww	< 0.25	
Ni tot	mg kg^{-1} ww	< 1	
Hg tot	mg kg^{-1} ww	< 0.25	
Salmonella		Absent	
E. Coli		Absent	
Enterococcaceae		Absent	

[a] Sigurnjak et al., (2019), ammonium sulphate produced by air scrubbing

[b] Ivona Sigurnjak et al. (2016), air scrubber water from digestate treatment

[c] Vaneeckhaute et al. (2013), air scrubber water from digestate treatment

[d] Ledda, et al. (2013), ammonium sulphate produced by scrubbing with sulfuric acid

[e] Mean and SD calculated considering data below detection limits = 0.

3.2.2 Digestate characterization vs. amendment and fertilizers properties.

Digestate produced represented a fertilizer that contained organic matter (amendment properties) and nutrients (fertilizers properties). Therefore, the next sections are devoted to discussing digestate data in its amendment and fertilizing properties in comparison with other organic matrices, i.e. agriculture order to establish both co-digested (agricultural digestate) and energy crops digestates (Tambone et. al., 2017; Scaglia et al., 2018 and organic amendments, i.e. green composts (Scaglia et al., 2018) (Table 2).

Table 2. Main characteristics of infeed (mean ± SD) and full characterization of digestate in comparison with legal limits for its use as fertilizer in agriculture, and with data from literature for digestate and composts.

Parameter	**Unit**	**Infeed[a] (this work)**	**Digestate[b] (this work)**	**Lombardy Law N. 6665/2019 – Legal limits[c]**	**Agricultural digestate[d]**	**Energy Crop digestate[e]**	**Green Compost 1[e]**	**Green Compost 2[e]**
pH		7.3 ± 2.5	8.5 ± 0.3	5.5 < pH < 11		8.4 ± 0.1	8.8 ± 0.2	8.9 ± 0.3
Dry Matter 105°C	g kg^{-1} ww[f]	191 ± 45	103 ± 3.7		61.1 ± 12.5			
Dry Matter 600°C	g kg^{-1} ww	60 ± 48	40.4 ± 2.5					
Total Organic Carbon	g kg^{-1} DM[f]	351 ± 78	314 ± 30	> 200		432 ± 14	292 ± 30	210 ± 10
TKN	g kg^{-1} DM	54 ± 20	77 ± 3.7	> 15	80.6 ± 13.3	70.3 ± 0.8	15.2 ± 0.18	15.2 ± 0.6
N-NH_4	g kg^{-1} DM	n.d.[g]	35.9 ± 2.4		48.9 ± 26.7	44.1 ± 3.8	0.12 ± 0.01	0.5 ± 0.0
N-NH_4/TKN	%	n.d.	46.6		60.66	62.27	0.7	3.2
OD_{20}[g]	mg O_2 g^{-1} DM	n.d.	22.6 ± 6.1			66.8 ± 1	15.6 ± 0.3	10.3 ±1.1
BMP[h]	L_{biogas} kg^{-1} DM	n.d.	57 ± 23			229 ± 31	144 ± 3.8	201 ± 20
P	g kg^{-1} DM	19±11	28 ± 4.1	> 4	15 ± 5	13.8 ± 5	3 ± 0	20.75 ± 0.12
K	g kg^{-1} DM	n.d.	6.5 ± 1.3			14.8 ± 3	9.2 ± 0.1	12.01 ± 0.09
Ca	g kg^{-1} DM	n.d	43 ± 7			9.2 ± 0.1	31.47 ± 0.17	30.9 ± 0.2
Mg	g kg^{-1} DM	n.d	5.2 ± 0.6			2.8 ± 4	8.57 ± 165	7.5 ± 17.1

Fe	g kg^{-1} DM	n.d	26.2 ± 6.4			3.4 ± 0.0	10.6 ± 0.1	13.2 ± 0.1
Mo	mg kg^{-1} DM	n.d	10 ± 1					
Cu	mg kg^{-1} DM	277 ± 142	408 ± 60	≤ 1,000	71.1 ± 30.6	83.3 ± 1.1	53.5 ± 1.6	53.5 ± 0.86
Zn	mg kg^{-1} DM	673 ± 413	1,020 ± 120	≤ 2,500	353 ± 204	393 ± 4.4	151 ± 3	159 ± 0.1
Mn	mg kg^{-1} DM	n.d	444 ± 35					
Al	g kg^{-1} DM	n.d	25.8 ± 4.5					
Co	mg kg^{-1} DM	n.d	6.6 ± 2.3					
Se	mg kg^{-1} DM	4[l]	3.7 ± 2.1	≤ 10				
Na	g kg^{-1} DM	n.d	1.9 ± 0.4			11.41 ± 0.034	0.807 ± 0.017	0.571 ± 0.001
Cr	mg kg^{-1} DM	54.2 ± 55.6	95 ± 22	< 200	8.56 ± 1.93	17.24 ± 0.4	88.8 ± 0.9	37.78 ± 0.8
Pb	mg kg^{-1} DM	45 ± 44	64 ± 11	≤ 750	1.97 ± 0.91	2.99 ± 0.04	24 ± 0.2	51.2 ± 0.08
Ni	mg kg^{-1} DM	36.8 ± 36.2	61 ± 13	≤ 300	10.3 ± 3.36	9.55 ± 0.47	41.8 ± 1	26.11 ± 2.2
As	mg kg^{-1} DM	6.3 ± 4.7	9.0 ± 2.2	< 20		1.05 ± 0.02	0.51 ±0.06	0.57 ± 0.15
Cd	mg kg^{-1} DM	0.6 ± 1.1[i]	1 ± 0.5[i]	≤ 20	0.39 ± 0.17	0.37 ± 0.05	0.17 ± 0.03	0.34 ± 0.01
Hg	mg kg^{-1} DM	0.3 ± 0.7[i]	0.1 ± 0.3[i]	≤ 10		0.24 ± 0.1	0.75 ± 0.02	0.22 ± 0.01
PAH	mg kg^{-1} DM	0.2 ± 0.5[i]	0.5 ± 0.5[i]	∑< 6		1.08	0.04	< 0.83

PCB	mg kg^{-1} DM	0.04 ± 0.51[i]	< 0.1	∑< 0.8		0.12	0.008	0.03
PCDD/F+PCB-DL	ng TEQ kg^{-1} DM	2.3 ± 4.4[i]	10.6 ± 2.9[i]	∑≤ 25		0.87	1.02	1.01
DEHP	mg kg^{-1} DM	2.8 ± 7.0[i]	5.7 ± 5.3[i]	< 100		< 1.54	< 0.14	0.15
Hydrocarbon C10-C40	mg kg^{-1} ww mg kg^{-1} DM	807 ± 1,093[i]	284 ± 251[i] (2,757)	≤ 1,000				
AOX	mg kg^{-1} DM	0.4 ± 3.3[i]	< 0.6	∑ < 500		< 0.46	2.75	0.04
Ciproflaxacin	mg kg^{-1} DM		< 0.01[m]					
Sulfamethoxazole	mg kg^{-1} DM		< 0.01[m]					
Fenofibrat	mg kg^{-1} DM		< 0.01[m]					
Gemfibrozil	mg kg^{-1} DM		< 0.01[m]					
Carbamazepine	mg kg^{-1} DM		< 0.01[m]					
Metoprolol	mg kg^{-1} DM		< 0.01[m]					
Diclofenac	mg kg^{-1} DM		< 0.01[m]					
Ethinylestradiol	mg kg^{-1} DM		< 0.01[m]					
Estradiol	mg kg^{-1} DM		< 0.01[m]					
Salmonella	MPN g^{-1} DM	47[n]	Absent	< 100		Absent	Absent	Absent
Faecal coliform	MPN g^{-1} DM	110,000[l]	< 1,000	< 10,000		Absent	Absent	Absent

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[a] Calculated as average of input material: *n* = 1,021; PHA: n = 973; PCB: *n* = 1,000; PCDD/F+PCB-DL: n = 370; DEHP: *n* = 704; Hydrocarbon C10-C40: *n* = 297; AOX: *n* = 717

[b] Mean ± SD: $n=42$, except for Ca, Mn, Mg, Fe, Mo, Al, Co, Na: $n = 9$, and BMP: $n = 10$.

[c] Legal limit referred to the digestate described in this work.

[d] Tambone, et al. (2017) average of n=13 mix of livestock effluent and energy crops.

[e] Scaglia et al., (2018).

[f] ww and DM: wet weight and dry matter, respectively.

[g] n.d.: not determined.

[g] OD_{20}: Oxygen Demand after 20h

[h] BMP: potential biogas production.

[i] Mean and SD calculated considering data below detection limits = 0.

[l] Data from this work.

[m] Analysis performed on 2020; $n=4$.

[n] Mean calculated considering 80th percentile because other data were below detection limits.

Organic matter content vs. amendment properties.

It is widely recognized that conservation of soil organic carbon (SOC) is the result of the combination of three different processes: biochemical, physical and chemical organic matter (OM)-protection (Castellano et al., 2015). Biochemical protection is related to the molecular and chemical recalcitrance of organic substrates to prevent degradation (Papa et al., 2014). Rapid degradation contributes to faster OM turnover (months, years); non-protected OM assumes agronomic relevance, i.e. amendment properties. On the other hand, physical and chemical protection are related to the occlusion of OM by soil microaggregates' surface interaction with soil minerals (Bachmann et al., 2008; Marschner et al., 2005). These latter mechanisms of organic C protection are reported to contribute to long term OM turnover (centuries, millennia), assuming less agronomic importance and its amount is limited in soil and finite (Castellano et al., 2015; Chung et al., 2010).

As discussed above, the ability of an organic matrix to contribute to soil fertility acting as an organic amendment depends on the amount of organic matter (TOC) (quantitative aspect) and its degradability, i.e. biological stability (qualitative aspects).

TOC content of the digestate from sewage sludge produced in this work (314 ± 30 g kg^{-1} DM) (Table 2), was lower than that reported in the literature for digestates obtained from energy crops (432 ± 14 g kg^{-1} DM) (Table 2), but higher than those reported for green compost (292 ± 30 and 210 ± 10 g kg^{-1} DM). These figures suggest good amendment properties for digestate. Amendment properties also depend on TOC biological stability, i.e. TOC degradability (biochemical OM protection). Therefore, digestate studied was characterized also for biological stability and the results obtained (Table 2) were compared with those for agricultural digestates and above all for green composts, since the latter are recognized as very good organic amendments (Adugna, 2016). Specific Oxygen Uptake Rate (OD_{20}) and residual biogas potential (BMP) are two interesting techniques to estimate OM stability of biomasses, as previously recognized (Schievano et al., 2009).

OD_{20} values for digestate studied, i.e. 22.6 ± 6.1 mg O_2 g^{-1} DM, was lower than values reported for energy crop digestate, i.e. 66.8 ± 1 mg O_2 g^{-1} DM, and only slightly higher than those of composts (15.6 ± 0.3 and 10.3 ±1.1 mg O_2 g^{-1} DM) (Table 2), suggesting good biological stability of TOC. BMP gave different figures as data registered for digestate, i.e. 57 ± 23 L_{biogas} kg^{-1} DM was lower than those for energy crop digestate, i.e. 229 ± 31 L_{biogas} kg^{-1} DM, and for green compost, i.e. 144 ± 3.8 and 201 ± 20 L_{biogas} kg^{-1} DM. Differences obtained were due to dissimilarity in methods used with particular reference to length of time of the measurements. OD_{20} was performed for a short time (20h) so that above all only easily degradable OM contributed to the whole oxygen consumption. Because digestate contained volatile fatty acids (VFAs) coming from anaerobic digestion, short time measurement gave an underestimation of the biological stability (higher oxygen consumption to degrade VFAs). On the other hand, BMP took place for a longer time, i.e. 60 d, so that contribution to biogas (anaerobic biodegradation of organic matter) was due to not only due to easily degradable organic matter but also to intermediate types of degradable organic matter such as lignocellulosic material.

Therefore, based on both TOC content and biological stability data it can be concluded that thermophilic digestate is a valuable product to contribute to the maintenance of organic matter content of the soil (Scaglia et al., 2018; Tambone et al., 2010).

In order to complete the description of the amendment properties of digestate, CPMAS ^{13}C NMR was used to better describe organic carbon composition of the digestate (Table 3). Results obtained indicated a constancy in C composition of digestate during the period considered.

The region (Figure S1) between 47 and 115 ppm dominates the ^{13}C NMR spectra of all the samples, with an average of 54.8 ± 10 % of the total integrated area that is typical of polysaccharides and protein. The strong chemical shift at 73 ppm was attributable to O-alkyl-C of cellulose/hemicellulose-like material and the pronounced signal at 105 ppm was related to anomeric-C compounds in C2 and C6 of carbohydrates (Fernandez-Bayo et al., 2018; Kögel-Knabner, 2002). A shoulder centered at 56 ppm represents the metoxhy-C indicating the presence of lignin and lignin-derived molecules, which was confirmed by the presence of aromatic C phenol or phenyl ether C (115-160 ppm), i.e. 7.63 ± 2.5 %. These compounds (hemicellulose, cellulose and lignin) are typically clustered forming a 3D complex characterized by medium-low degradability (Papa et. al, 2013): they are partially preserved and concentrated in relative terms during the anaerobic digestion process (Tambone et al. 2009; Fernandez-Bayo et al. 2018).

Chemical shifts in the region 0-47 ppm constituted the second largest region characterizing digestates spectra (29.2 ± 6.7 %). According to previous work, this region was represented by hydrocarbons (Tambone et al., 2010, 2013, 2009; Baldock et al., 1992). Jardé et al. (2005), studying the lipid fraction in sewage sludge reported that hydrocarbons were mainly constituted by vegetal hydrocarbons derived from the presence of vegetable fragments, oil and human feces containing both microbial and food hydrocarbons. Payet et al. (1999), confirmed the presence of natural hydrocarbons in sewage sludge due to the presence of plant hydrocarbons preserved in the human feces, in agreement with data from Réveillé et al. (2003). The intense signal at 174 ppm in the carbonyl region (160–210 ppm), suggested the contribution of carbonyl groups of peptide bonds of amino acid moieties and carbonyl C of hydrocarbons (Martinez-Balmori et al., 2014).

Comparing the spectroscopic characteristics of these digestates (Table 3) with those of digestates of different origins, the similarity with those originating from animal manure was evident because of the presence of fecal material and vegetable matter (Table 3). On the other hand, digestates derived from the organic fraction of municipal solid waste (OFMSW), were characterized by higher aliphatic carbon, probably due to the high presence in the infeed mixture of vegetable waste and oil/fat (from food) contributing to this fraction (cutin, suberin). More interesting was the fact that ^{13}C-NMR spectra of digestate resembled that of composts (Table 3), apart from the higher presence of aromatic-C and lower presence of alkyl fractions due to biomass origin (lignocellulosic material vs. fecal origin material).

Therefore, taking into consideration total C content, biological stability data and ^{13}C-NMR, it should be noted that digestate was very little different from compost and indeed it contained more

C and the C was more recalcitrant to biological degradation. These results indicate that anaerobic digestion as well as composting degrade the easily degradable organic matter, concentrating most recalcitrant matter, so that digestate can be considered an alternative for giving good organic amendment properties, such as previously suggested by Tambone et al. (2015) that reported that well performed AD was able to achieve high biological stability and that the subsequent composting did not add any notable advantage (Tambone et al., 2015).

Table 3. Spectroscopic (CPMAS 13-C NMR) characteristics of digestate and comparison with other biomasses (literature data).

SAMPLES	**C-type (ppm)**			
	Total aliphatic C (0-47 ppm)	O-CH$_3$ or N-alkyl O-alkyl C di-O-alkyl C (47-115 ppm)	Aromatic C phenol or phenyl ether C (115-160 ppm)	Carboxyl C keto C (160-210 ppm)
Digestate (n=3)[a]	29.2 ± 6.7a[b]	54.8 ± 10b	7.63 ± 2.5a	8.37 ± 2.9a
Farm digestate (n=8)[d, e]	31.1 ± 4.5a	49.9 ± 9.1b	8.85 ± 1.9a	10.13 ± 6.1a
OFMSW digestate (n=12)[c,d]	44 ± 2.1b	36.3 ± 2a	8.13 ± 0.6a	11.61 ± 1.1a
Compost[d]	21.6±3.6a	55.4±1.8b	13.9±1.6b	8.9±0.5a

[a] Digestates of this work.

[b] Values of the same column followed by different letters are statistically different ($P < 0.001$, Gabriel test).

[c] Tambone et al. (2009).

[d] Tambone et al. (2010).

[e] Tambone et al. (2013).

3.2.3 Digestate Nutrient contents

N, P and K

Total N concentration for digestate was of 77 ± 3.7 g kg^{-1} DM, in line with those for agricultural and energy crop digestates, i.e. 80.6 ± 13.3 g kg^{-1} DM and 70.3 ± 0.8 g kg^{-1} DM, respectively (Table 2). Ammonia concentration in the digestate was of 46.6 % of Total N, lower than that found for agricultural and energy crop digestates (Table 2), but much higher, as expected, than those of composts. Lower ammonium content than that of other digestates was related to the fact that it was partially removed by the N stripping unit, as described earlier. On the other hand, because of the high dry matter content, 103 ± 3.7 g kg^{-1} ww, the $N\text{-}NH_4^+$ content of digestate was of 7.9 g kg^{-1} ww and so, much higher than that measured for agricultural digestates, i.e. 2.98 g kg^{-1} ww. About 53.4% of Total N was under organic forms that were recalcitrant to mineralization, as suggested by the high biological stability as discussed before, which was much higher than that of green compost. In this way, organic-N contributed to maintain the soil-N pool.

The P content of the digestate from sewage sludge, i.e. 28 ± 4 g kg^{-1} DM, was higher than that reported for other digestates i.e. 15 ± 5 and 13.8 ± 5 g kg^{-1} DM for agricultural digestate and energy crops, respectively (Table 2). During anaerobic digestion organic P forms becomes modified, depending on the biomass origin, AD condition and chemical and physical properties of ingestate vs. digestate (Mazzini et al., 2020). Therefore, to understand chemical speciation of P in the digestate under study, P fractionation of digestate samples was carried out to assess its fertilizer properties. Data obtained showed good P recoveries, equal to 86 ± 2% of the total P detected for all digestates (Table 4). Average P fractions contents (mg kg^{-1} DM) were, as the average of three replicates, as in the following: P-$NaHCO_3$ of 11,590 ± 1,100, P-HCl of 7,932 ± 913 and P-NaOH-EDTA of 6,891 ± 1,179. This means that, on average, more than the 43% of the total P in digestate can be considered readily soluble, i.e. P-$NaHCO_3$ (Table 4): these data are in line with previous findings (Mazzini et al., 2020).

^{31}P NMR performed on digestate samples allowed us to get more information about different P fractions. In this regard, the NMR spectra of digestate (Table 4) were able to identify the main peaks due to inorganic P-forms, i.e. orthophosphate (6.1 ppm) and pyrophosphate (-4.4 ppm) (Figure S2). Another signal at -0.2 ppm was assigned to P of DNA. Small peaks in the monoester region (4.85 - 4.64 ppm and 5.23 ppm) attributed to α and β –glycerophosphate and phosphatidic acid, respectively, indicated the presence of P organic compounds. Other signals in the phosphate monoesters region (4.95 - 4.10 ppm) were due to inositol-phosphate and mononucleotides originating from the hydrolysis of RNA. Each P-species detected was quantified and the results are reported in Table 4. Data clearly showed that P extracted by $NaHCO_3$ was 100 % inorganic-P made up by orthophosphate P, which is considered soluble and readily available for plants. Inorganic forms also dominated the HCl and NaOH-EDTA fractions, and they were made, above all, by orthophosphate P (Mg/Ca phosphate) (Table 4). The HCl fraction showed, also, low concentrations of phosphate monoester and pyrophosphate P. On the other hand, NaOH-EDTA extracts showed the presence of low amounts of organic P such as DNA and phospholipids.

All these figures were very similar to the average data calculated for agricultural digestate previously studied (Table 4) (Mazzini et al., 2020).

The concentration of K in the digestate produced (6.5 ± 1.3 g kg^{-1} DM) was lower than that reported in the literature both for digestates from energy crops (14.8 ± 3 g kg^{-1} DM) and for green compost (9.16 ± 0.13 and 12.01 ± 0.09 g kg^{-1} DM). This makes the digestate from sewage sludge slightly poorer in K than other bio-fertilizers.

Table 4. Phosphorous fractionation and speciation detected by ^{31}P NMR for digestate studied in this work in comparison with literature.

Digestate	**Extractant**	**P-total**[a]	**P distribution**[b]	**Orthophosphate**	**Phosphate monoesters**	**Pyrophosphate**	**DNA**	**Phospholipid**	**Pi**[c]	**Po**[c]
		mg kg^{-1}	%P$_{tot}$	mg kg^{-1}					(% P for fraction)	
Digestate of this work	P-NaHCO$_3$	11,590 ±1,100	44 ± 3	11,590 ± 1,100	n.d.[d]	n.d.	n.d.	n.d.	100	0
	P-HCl	7,932 ±913	30 ± 2	7,749 ± 899	131±28	52±6	n.d.	n.d.	98.3±0.4	1.65±0,37
	P-NaOH + EDTA	6,891 ±1,179	26 ± 5	6,514 ± 1,106	262±54	61±15	29±6	24±5	95.4±0.4	4.57±0.37
Agricultural digestate[e]	P-NaHCO$_3$	5,139 ± 1,398	44 ± 14	5,097 ± 1,423	21.3 ± 52.2	20.7 ± 25.1	n.d.	n.d.	98.3±2[c]	1.67±1[c]
	P-HCl	3,769 ± 1,461	31 ± 7	3,188 ± 1,539	572 ± 489	8.53 ± 11.1	n.d.	n.d.	100 ± 1	1 ± 1
	P-NaOH + EDTA	3,094 ± 1,400	25 ± 7	2,411 ± 1,583	567 ± 631	32.4 ± 26.0	56.1 ± 27.4	27.8 ± 28.2	86 ± 9	14 ± 9

[a] Quote extracted by the three different solvents.

[b] Quote extracted by the three different solvents reported as % of the total P.

[c] Inorganic (Pi) and organic (Po) phosphorous in each extract calculated on the base of ^{31}P NMR data.

[d] n.d. no detectable

[e] Mazzini et al. (2020), average different agricultural digestates (n=6).

Other meso- and micronutrient nutrients, and inorganic micropollutants

Digestate characterization showed that it contained, also, other meso and microelements useful for plant nutrition (e.g. Ca, Mg, Fe etc.) the presence of which was in line with the other organic matrices indicated for comparison (Table 2). AD processes, because of organic matter degradation, concentrated micro-pollutants contained in the feed matrices (Bloem et al., 2017; Boix et al., 2016) so that detecting and discussing them can be useful in view of the agricultural use. From Table 2, it can be seen that digestate from sewage sludge had a content of pollutants, as expected, higher than those contained in agricultural digestate and compost; on the other hand, they were much lower than the legal limits for the use of this kind of digestate in agriculture (Lombardy Region Law N. 6665/2019). It should be reported, also, that digestate are dosed in order to fulfil nutrient requirements of crops and that doses are about 1/10 of the compost amount used as organic amendment.

Organic micro-pollutants

Persistent Organic Pollutants (POPs) are those organic compounds that can show dangerous effects on people and/or on the environment, and are not easily degraded in soil, water or sediment. These compounds are, also, mostly non-degradable during AD process. For this reason, their content in digestate depends on the quality of the infeed (Al Seadi et al., 2013). Therefore, an AD plant whose products will go to fields must carefully select infeed with very low concentrations of POPs, in order, also, to fulfil the very strict limits required for agricultural use (Table 2). Any non-compliance with rules suggests the need to take a different path such as incineration or pyrolysis.

In this study, several organic pollutants were tested (Table 2). All organic pollutants were much lower than the limits imposed for agricultural use and some were lower than the contents revealed for other organic matrices such as agricultural and energy crop digestate and compost (e.g. PHA, PCB, AOX). Again, it is important to remember that amounts of digestate fertilizer commonly applied is about 8-10 times lower than that of compost used as organic amendment. Unfortunately, no data about hydrocarbons (C10-C40) were available for other biomasses. From Table 2, it can be seen that hydrocarbons reduced a lot after anaerobic digestion indicating a biological origin of hydrocarbons for sewage sludge, as well reported in the literature (Payet et al., 1999). An investigation performed by the Environmental Protection Agency of Veneto Region (Italy) on the presence of hydrocarbons (C>12) (ARPAV, 2013) in 17 agricultural digestates, reported hydrocarbons concentration in the range of 720-4,600 mg kg^{-1} DM and even of 31,800 mg kg^{-1} DM for slaughterhouse derived digestate (high fat content). These values can be compared with data for digestate from this work (Table 2), referring to DM, i.e. 2,757 mg kg^{-1} DM.

Less studied until recently is the presence of emerging pollutants (pharmaceuticals) in digestate. Konradi and Vogel (2013), suggested, taking into consideration parameters related to pollutants such as residence time in the soil, solubility and eco-toxicity, to detect 9 emerging pollutants to be used as markers: antibiotics (Ciproflaxacin and Sulfamethoxazole), lipid regulators (Fenofibrate and Gemfibrozil), psychiatric drugs (Carbamazepine), beta-blockers (Metoprolol), analgesic (Diclorofenac) and hormones (Ethinylestradiol and Estradiol). Results obtained (Table 2) showed a concentration for all compounds below the detection limit (<0.01 mg kg^{-1} DM) indicating low concentration (Konradi and Vogel, 2013). These values were in line with those reported in the literature for the same classes of compounds in digestates from sewage sludge, i.e. 0.001 – 1 mg kg^{-1} DM for antibiotics, 0.0001 – 1 mg kg^{-1} DM for psychiatric drugs, 0.004 – 1 mg kg^{-1} DM for analgesics and 0.001 – 10 mg kg^{-1} DM for hormones (Verlicchi and Zambello, 2015). Low contents can be ascribed, also, to the AD process since it is reported as the most effective type of treatment in reducing the concentration of these compounds in sewage sludge (Verlicchi and Zambello, 2015). Panseri et al., (2013), studying the ability of AD in reducing antibiotics content, reported an 80% of reduction.

Unfortunately, a comparison with similar organic pollutants in other fertilizers is not possible because of the lack of systematic studies on this subject. Furthermore, most of the classes of emerging pollutants analysed in this work were exclusively for human use, and therefore not easily traceable in animal waste or agricultural biomasses, with the exception of antibiotics, that are furthermore considered very toxic for soil organisms (EC_{50} > 1 mg kg^{-1}) (Konradi and Vogel, 2013). Literature reported concentrations of veterinary antibiotics in a range of 0.005 – 7.5 mg kg^{-1} DM in pig slurry (Gros et al., 2019), 2.0 – 22.8 mg kg^{-1} DM in pig manure (Van den Meersche et al., 2016), and 0.02 – 8.0 mg kg^{-1} DM in cattle feces (Berendsen et al., 2015), all of these data reported being much higher than those observed for digestate analysed in this paper (<0.01 mg kg^{-1} DM (Table 2).

Pathogen content

The pathogen contents (Salmonella and Faecal coliform) was detected in both infeed and digestate (Table 2). Salmonella was present in the feed, i.e. 47 MPN g^{-1} DM, but after anaerobic digestion it was absent. AD showed a strong effect also on Faecal coliform that dropped from 110,000 MPN g^{-1} DM (feed) to less than 1,000 MPN g^{-1} DM in the digestate, being this data much lower than Regional legal limits (<10,000 MPN g^{-1} DM) (Regione Lombardia, 2019). Anaerobic digestion has been reported reducing pathogen content thanks to the joined action of alkaline pH, high ammonia concentration and biological process, i.e. microbial competition for organic substrate (Orzi et al, 2015). pH and ammonia actions are magnified under thermophilic condition leading to excellent digestate sanitation such as previously reported (Mendez et al., 2002; Nordin and Nyberg, 2009). Scaglia et al., (2014) studying sewage sludge sanitation by AD, indicated that temperature above 55 °C and ammonia concentration higher than 0.4 g kg^{-1} ww resulted in optimum digestate sanitation. Since process studied in this work showed alkaline pH, i.e. 8.5 ± 0.3 and high ammonia concentration, i.e. 3.7 ± 0.2 g kg^{-1} ww, the reduction of the pathogen contents observe was expected.

Conclusions

Anaerobic digestion is an interesting biotechnology able to produce renewable energy (biogas) but also renewable fertilizers. This work aimed to describe the fertilizer properties of fertilizers produced at full scale starting from a mix of organic wastes (sewage sludge, organic fraction of municipal solid waste and minor food industry wastes). Results indicated that ammonia stripping allowed the production of N mineral fertilizers that can be useful for topdressing purposes. On the other hand, digestate can act as both an organic amendment because of high organic carbon content and high biological stability, i.e. high recalcitrance of biomolecules contained, and as fertilizers because of high nutrient contents (except for K). Inorganic and organic pollutants were much lower than the limits imposed by rules for agricultural use and sometimes lower that those detected for other biomasses. Emerging pollutants were present only at very low levels, emphasizing the role of HSAD in reducing their content. Unfortunately, a systemic comparison with other organic matrices used in agriculture (e.g. agricultural digestate and compost) was not possible because of the lack of literature data regarding emerging pollutants and suggesting further investigation in this direction.

In conclusion, this paper was able describing renewable fertilizers obtained from anaerobic digestion plant and discussing fertilizers properties. A limit of this paper consist in the fact that fertilizers properties have been indirectly studied and no directly tested at full field. In this way, agronomical trials are ongoing within the same European project and three years of experimental data will be presented in next scientific papers.

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Notes

The authors declare no competing financial interest

AP and MZ contributed equally to this work

Credits

FA: designed the project, elaborated data, interpreted the data and wrote the paper

MZ: collected, elaborated, interpreted the data and wrote the paper

AP: collected, elaborated, interpreted the data and wrote the paper

FT: collected the data, 13CNMR analyses and wrote the paper

SM: 31P-NMR analyses

MS: Full scale plant collection and management

AD: Full scale plant collection and management

EM and OS: Scientific contribution and manuscript correction.

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