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# Anaerobic co-digestion of recalcitrant agricultural wastes: Characterizing of biochemical parameters of digestate and its impacts on soil ecosystem

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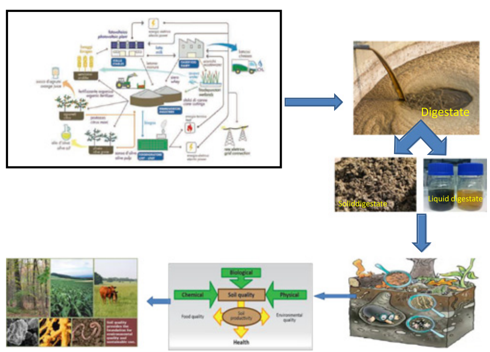
## HIGHLIGHTS

- Agricultural recalcitrant wastes show good potential for anaerobic co-digestion.
- A specificity between feedstock and digestate attributes was really evident.
- The effects of digestates on soil properties depended on their characteristics
- FDA and CAT activities can be used as marker to assess the quality of treated soils.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Anaerobic digestion (AD) of organic wastes is a promising alternative to landfilling for reducing Greenhouse Gas Emission (GHG) and it is encouraged by current regulation in Europe. Biogas-AD produced, represents a useful source of green energy, while its by-product (digestate) is a waste, that needs to be safely disposal. The sustainability of anaerobic digestion plants partly depends on the management of their digestion residues. This study has been focused on the environmental and economic benefits of co-digest recalcitrant agricultural wastes such olive wastes and citrus pulp, in combination with livestock wastes, straw and cheese whey for biogas production. The aim of this work was to investigate the effects of two different bioenergy by-products on soil carbon stock, enzymes involved in nutrient cycling and microbial content. The two digestates were obtained from two plants differently fed: the first plant (Uliva) was powered with 60% of recalcitrant agricultural wastes, and 40% of livestock manure milk serum and maize silage. The second one (Fattoria) was fed with 40% of recalcitrant agricultural wastes and 60% of livestock manure, milk serum and maize silage. Each digestate, separated in liquid and solid fractions, was added to the soil at different concentrations. Our results evidenced that mixing and type of input feedstock affected the composition of digestates. Three months after treatments, our results showed that changes in soil chemical and biochemical characteristics depended on the source of digestate, the type of fraction and the concentration used. The mainly affected soil parameters were: Soil Organic Matter (SOM), Microbial Biomass Carbon (MBC), Fluorescein Diacetate Hydrolysis (FDA), Water Soluble Phenol (WSP) and Catalase (CAT) that can be used to assess the digestate agronomical feasibility. These results show that the agronomic quality of a digestate is strictly dependent on percentage and type of feedstocks that will be used to power the digester.


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## 1. Introduction

Organic waste removal has become an ecological problem, brought to light as a result of an increase in public health concerns and environmental awareness. Recently, the organic wastes have been recognized as a valuable resource that can be converted into useful products via microbially mediated transformations (Yu and Huang, 2009; Lesteur et al., 2010). There are various methods available for the treatment of organic wastes but the anaerobic digestion (AD) appears to be one of the most promising approach (Lee et al., 2009) for producing environmental and socio-economic benefit, in terms of renewable energy (biogas), reduction of organic wastes going to landfills and abatement of GHG emissions (Dennehy et al., 2016). While biogas-AD produced, represents an ascertained useful source of green energy, the residue is a waste, that needs to be sustainably used for improving the economical profitability of AD plants (Iacovidou et al., 2013; Pivato et al., 2016). The digestate in comparison with undigested wastes has greater microbial stability and hygiene and higher amount of nitrogen in the form of ammonium (Alburquerque et al., 2012; Holm-Nielsen et al., 2009). Moller and Muller (2012) demonstrated that digestate contains high levels of macro and micro nutrients and as such represents an environmentally sound alternative to the mineral fertilizers, with the potential to improve soil fertility and quality. Wager-Baumann (2011) suggested also that digestate may reduce the need for irrigation by improving soil moisture retention properties. Agricultural wastes and livestock manures are highly polluting residues with a high cost of disposal for farmers (Panuccio et al., 2016), therefore their anaerobic digestion can represent a reliable and advantageous practice to convert refuse in resource. Anaerobic mono-digestion of animal manure and animal slurry is carried out in many Mediterranean areas with intensive animal production and high density of manure per hectare, as a sustainable option for manure treatment and manure management (Monou et al., 2009). The co-digestion of animal manure with organic wastes, is less frequent, even if Al Seadi and Lukehurst (2012) and Ebner et al. (2016) demonstrated that it produces more biogas with high methane percentage than manure alone, improving the profitability of biogas plants. Most existing studies on co-digestion have been based on biomass mixtures using either sewage sludge or a variety of animal manures together with materials such as food waste, energy crops or crop residues. Examples of key studies are: Kim et al. (2003), Koch et al. (2015) and Murto et al. (2004), who used sewage sludge mixed with residential or industrial food waste; Adelard and Poulsen (2015), Ashekuzzaman and Poulsen (2011), Lansing et al. (2010a, 2010b), Li et al. (2015), Magbanua et al. (2001), Wang et al. (2012, 2013), Zarkadas et al. (2015), used mixtures of animal manure such as cow dung, pig manure or poultry manure in combination with food waste or crop residues (straw). Ogejo and Li (2010), Owamah et al. (2014) Pagés-Díaz et al. (2015) and Rico et al. (2015) investigated the co-digestion of industrial wastes such as cheese whey, food waste, and slaughter house wastes combined with municipal solid wastes and animal manures. No previous studies have been focused on the potential benefits of the co-digestion of animal manures, straw and cheese whey with olive wastes and citrus pulp, recalcitrant pollutant wastes commonly produced in Mediterranean countries. This research investigated on the benefit of co-digest recalcitrant agriculture wastes (olive wastes and citrus pulps), mixed in different proportions with livestock manures, milk serum and maize silage in the production of more stable digestate with compatible soil use as fertilizer. The aim was to elucidate the effects of unprocessed digestates on soil ecosystem functioning. The impact of two digestates different in composition, each separated in liquid and solid fractions, was assessed 3 months after starting treatments, evaluating the effects on SOM, nutrient cycling, MBC, enzyme activities and soil physic-chemical properties (pH, EC and water soluble phenols). The main aims were to relate the chemical composition of the digestates to the quality and percentage of the feedstock used, to evaluate differences in influencing belowground processes in respect to their attributes, and to test their capacity in maximizing the organic carbon for restoring soil fertility.

## 2. Materials and methods

### 2.1. Biogas plants: process temperature and retention time

This research was carried out in collaboration with two cooperatives Fattoria della Piana soc. Agricola, and Uliva Srl soc. Agricola, owners of biogas plants. Each biogas energy plant has an installed power of 998 kWel. The two biogas plants were differently supplied: the first one named Fattoria (F) was powered with 60% animal manures (poultry, cow and sheep), milk serum, maize silage and in minor amount with olive waste (20%) and citrus pulp (20%). The second one named Uliva (U) was mainly powered with olive waste 30%, and citrus pulp 30% and in minor amount (40%) with animal manure and maize silage (Panuccio et al., 2016).

Process temperatures and retention times are appropriate for the sanitation and are calibrated on the basis of the feedstock that had to be digested.

Fattoria: process temperature: 40 °C, pH 7.8, total volume of the two digesters: 7500 $m^3$ (2500 DIG.1 + 5000 DIG.2), total volume loaded per day: 120 $m^3$/day, hydraulic retention time (HRT): 60 days, minimum guaranteed retention time (MGRT) 16 h at 40 °C.

Uliva: process temperature: 40 °C, pH 8.0, total volume of the two digesters: 7420 $m^3$ (3180 DIG.1 + 4240 DIG.2), total volume loaded per day: 120 $m^3$/day, hydraulic retention time (HRT) 60 days, minimum guaranteed retention time (MGRT) 16 h at 40 °C.

As reported in Panuccio et al. (2016), the digestates coming from both plants were separated in liquid and solid fractions (Solid Uliva, SU; Liquid Uliva, LU; Solid Fattoria, SF; Liquid Fattoria, LF) a desirable upstream operation in the treatment process since dewatering the solid fraction reduces the cost of transport and facilitates its addition to soil (Holm-Nielsen et al., 2009). The obtained fractions were analyzed for chemical and biological characteristics.

### 2.2. Digestate chemical analysis

Chemical parameters of the two digestates, each separated in liquid and solid fractions, were determined in three replicates as follow. Dry matter (dm) content was determined at 105 °C until the mass loss of the sample during 24 h was lower than 0.5% of its weight (AFNOR, 2001); moisture content, after drying to constant weight at 105 °C; volatile solids, reflect the content of OM which can be decomposed by combustion at 550 °C for 24 h up to constant weight; pH was measured in distilled water using a 1:2.5 (digestate/water) suspension; organic carbon was determined by the Walkley–Black procedure (Nelson and Sommers, 1982), and it was converted to organic matter by multiplying the percentage of carbon by 1.72; total nitrogen was measured by Kjeldahl method (Bremner and Mulvaney, 1982); electric conductibility was determined in distilled water by using 1:5 digestate:water suspension, mechanically shaken at 15 rpm for 1 h to dissolve soluble salts, and then detected by Hanna instrument conductivity meter. Available P was determined by the Bray II method (Bray and Kurtz, 1992). Exchangeable K was extracted with 1 M $NH_4OAc$, and determined using a flame-photometer. The $NO_3$–N was measured using a nitrate-ion selective electrode (U.S. EPA, 2011), while $NH_4$–N was determined by a colorimetric method based on Berthelot's reaction (Sommer et al., 1992). All values refer to material dried at 105 °C for 24 h. The 5-day biochemical oxygen demand (BOD) was measured with a respirometric Oxitop® IS 6 (WTW, Germany) based on pressure measurement, which is automatically transformed into mg $O_2$ $L^{-1}$. In the Oxitop® system, cumulative oxygen consumption measurements were made each day during a 5-day period. COD was determined by dichromate oxidation of dried ground samples, according to an