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Multi-approach characterization of organic sediment produced by an anaerobic digestion plant fed with pig slurry and stored for a long term in a lagoon

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HIGHLIGHTS

- The aged organic sediment derived from pig slurry digestate is characterised by chemical and spectroscopic methods.
- High concentrations of Cu, Zn, K and Na elements are found in the sediment.
- Sediment is mainly made by recalcitrant organic matter as cellulose.
- By spectroscopy speciation, the two main Zn forms are Zn phosphate and Zn sulfide.
- In the sediment, most of the Zn and Cu are in very stable forms.

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ABSTRACT

This study combined different approaches to characterize organic sediments produced by an anaerobic digestion plant feed with pig slurry, and accumulated for many years in a lagoon. The results of all analyses identified a certain homogeneity of the sediments. As a consequence of the pig diet, the sediment contained an high concentration of Zn (about 4 g kg^{-1}) and Cu (about 1.2 g kg^{-1}), which were mostly associated to the particles with a size ranging from 2 to 53 μm. The sediment was made of large amount of organic matter, mostly cellulose and recalcitrant molecules, and 30–40% mineral fraction. XANES and XES spectroscopies indicated the presence of zinc phosphate (38%), zinc sulfide (32%), zinc carbonate (19%), and zinc oxide (11%). The presence in the sediment of forms characterized by a very scarce solubility, as also confirmed by the Zn and Cu chemical speciation, indicated a low bioavailability of these metals. However, although their low mobility, the high concentrations of Zn and Cu allowed to consider the sediment not suitable to use as a fertiliser due to the potential risk of metal interaction with the food chain.

1. Introduction

The EU eco-sustainable policies and growing demand for energy have determined an interest to new forms of energy production, which can contribute to the replacing of fossil fuel. One of these forms is the biogas production from anaerobic digestion (AD) of different feedstocks in plants, which differ for types and sizes. In 2014, 1681 biogas plants operated in Italy, defined the third EU country for the energy produced from biogas, after Germany and United Kingdom [1]. After the AD process, the organic matter (OM) of the digestate withstands some important modifications, mostly related to the increasing of low degradable organic compounds [2]. However, as metal concentration of the organic wastes feeding the plant is generally conserved at the end of the digestion process, so the addition of matrices like pig slurries, which are usually characterized by a high content of Zn and Cu, can contribute to the total amount of heavy metals in the digestate. Therefore, the agronomic use of pig slurries or their digestate [3,4] is paying attention

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to the problem of the introduction in the environment of Cu and, in particular, Zn bearing compounds.

The AD process has been extensively studied by considering, for example, the factors which affected the process and their optimizations, the introduction of additives as accelerants, the technologies of the reactors, the evaluation of feedstocks and mixtures, and the evolution of microbial communities [5,6]. Furthermore, AD-related studies deal with the co-digestion of pig slurries with other biomass as well as the post-treatments of pig slurry digestate [7,8].

However, as far as we know, no studies exist about the characterisation of the organic sediments produced during the activity of an AD plant and accumulated in collecting reservoirs for a long time, and their possible agronomical use.

Our study focused on an AD plant, which operated from 1989 to 2009 in the Central Italy. Nowadays, this plant is characterized by different critical areas of pollution hazards. The main one is the storage lagoon, which was designated to contain the liquid fraction of the digestate, and that today is filled up with a sludge that gradually accumulated during the time of plant activity. This lagoon is probably unique for its history and its characteristics and, as just few AD plants actually in function, operated for more than 20 years. This situation may represent a case study to evaluate the characteristics of the lagoon sediments but also to give some information to AD plant operators to correctly manage the digestate production and storage, in order to avoid the accumulation of potentially dangerous materials in the environment. Hence, the aim of our research was to characterize the lagoon sediment, stocked for many years in partially anaerobic conditions, in order to evaluate the best environmental safe management of the digestate derived mainly by pig slurries. To reach our goal we used a multi-approach based on a thorough evaluation of the physical, mineralogical and chemical analyses of this sediment stored in the plant reservoir. Specifically, we performed *i)* a chemical and mineralogical characterization of the sediment from different points and depths of the lagoon; *ii)* a chemical speciation of Zn and Cu by using two different sequential extractions (SeqE); and *iii*) an identification of the possible chemical Zn forms by two X-ray spectroscopies techniques: X-ray Absorption Near Edge Structure (XANES) and X-ray emission spectroscopy (XES). Sequential extractions coupled with XANES and XES allowed us to evaluate how metals were lead off into different fractions and to obtain information on their chemical species, and to predict the mobility or stability of the Zn and Cu which in turn may affect their bioavailability.

2. Materials and method

2.1. Description of AD plant and storage lagoon

The AD plant was built in 1989 in Olmeto, Marsciano, Italy (42°59′01.9"N 12°18′27.6"E), within an area characterised by intensive pig farming. For many years, it had been considered as an innovative and avant-garde plant, which produced 5.5 MW by treating 155,000 Mg/year of pig slurries, in two primary digesters with a volume of 6000 m^3 each and in a secondary digester with a volume of 2000 m^3. Some characteristics of the digestate produced by this plant were reported by Provenzano et al. [9]. During AD process, the digestate was separated in a solid and liquid fractions. The solid fraction was utilized to produce an organic amendment after composting, whereas the liquid fraction, usually used as fertiliser, was stored in a lagoon (80,000 m^3) when the crop ferti-irrigation was not possible to realize. However, with time, a progressive deposition of solid material due to the not always perfect separation of the digestate in the two fractions, filled up the reservoir (about 4 m depth). The storage of the sediment was mainly in anaerobic condition.

2.2. Sampling

Thirty samples of the sediment were collected with probes in six different points of the lagoon and at five different depths (0–0.4 m, 0.4–1.0 m, 1.0–2.0 m, 2.0–3.0 m and 3.0–4.0 m). The samples were immediately cooled at 4 °C and, once in the laboratory, an aliquot of each sample was frozen at −20 °C, while another aliquot was dried at room temperature, crushed, sieved to 0.2 mm, and stored until used for the analyses.

2.3. Chemical and mineralogical characterization of the sediment

The chemical and mineralogical characterization was carried out on all samples collected in the lagoon. Total solids (TS) and volatile solids (VS) were determined by weight loss after drying at 105 °C in an oven for 24 h and after ashing at 550 °C for 24 h in a muffle furnace, respectively. The pH and the electric conductivity (EC) were determined potentiometrically in a sediment water extract (solid:liquid ratio of 1:5 w/v) [10]. The cation exchange capacity (CEC) was determined in $BaCl_2$ by Gilman method [11]. The samples were characterised for their contents of total organic carbon [10], total extractable carbon (TEC), humic carbon (HA + FA) and degree of humification (DH) [12], and water extractable organic carbon (WEOC) [13]. Fresh samples were used to determine the Total Kjedahl Nitrogen (TKN) and NH_4^+-N, as described in ANPA methods [10]. Briefly, TKN was determined after mineralization in microwave and Kjeldahl distillation, while NH_4^+-N was determined, after extraction with 6M HCl at room temperature, by Kjeldahl distillation. Organic N was calculated by the difference between total N and NH_4^+-N. Finally, the germination index (GI) was evaluated [13,14].

To determine the metal contents, the samples were digested with HNO_3 and H_2O_2 [15], and the element concentrations in the extracts were determined by flame atomic absorption spectrophotometry by a Shimadzu AA-6800 apparatus (Shimadzu Corp., Tokyo, Japan), with the exception of Hg, determined through a hydride generator coupled with the atomic absorption spectrometer, and Na and K, which were analysed by flame atomic emission spectrophotometry in the same extracted described above. Cr(VI) was determined spectrophotometrically after extraction with KH_2PO_4 at room temperature. Total P was determined spectrophotometrically after the digestion of the samples with H_2SO_4 and $HClO_4$ [10].

The mineralogical investigation was accomplished on powdered specimens after treatment with a 6% NaClO solution to oxidise the organic cements and clean the mineral surfaces from organics. The analyses was run by a Philips PW1830 X-ray diffractometer, using the Fe-filtered Kα1 radiation produced by a Co anode, and operating at 35 kV and 25 mA. Diffractograms were acquired in the range 3–80°2θ, with a step size of 0.02°2θ and scanning speed of 1 s per step. The mineralogical assemblage was qualitatively determined on the basis of the peak position using the Brindley and Brown [16] and Dixon and Schulze [17] databases.

2.4. XANES and XES

Three samples collected at different points and depths of the lagoon [0.4–1.0 m (6B), 1.0–2.0 m (4C) and 3.0–4.0 m (5E)] were used for the synchrotron analyses performed at European Synchrotron Radiation Facility (ESRF). With regard to the Zn speciation, different model systems were considered: zinc oxide (ZnO), basic zinc carbonate ($(ZnCO_3)_2{\cdot}(Zn(OH)_2)_3$), zinc phosphate ($(Zn_3(PO_4)_2$), zinc citrate dehydrate ($(C_6H_5O_7)_2Zn_3{\cdot}2H_2O$), IDRANAL II–zinc disodium salt tetrahydrate (EDTA-Na_2 zinc-$C_{10}H_{12}N_2Na_2O_8Zn{\cdot}4H_2O$), zinc sulfide (ZnS), and zinc hydroxide ($Zn(OH)_2$). The X-ray absorption and X-ray emission experiments