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Research article

Methodological approach for trace elements supplementation in anaerobic digestion: Experience from full-scale agricultural biogas plants

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ABSTRACT

Trace metals play a very important role on the performance and stability of agricultural biogas digesters. The purpose of this study was to develop a methodological approach to quickly detect limiting conditions due to Trace Elements (TE) concentration in full-scale biogas plants. The work was based on long-term process monitoring in two full-scale agricultural biogas plants and on the correlation between their performance and TE concentration in the digesters.

Monitoring and analysis of data from two different case studies allowed to understand the effect of the TE added on biogas plant performance. Furthermore, over-dosage has been avoided, minimizing the risk of biological inhibition and excess of heavy metal concentration in the effluent digestate according to regulation for land fertilization.

TE supplementation has been successfully applied to optimize the biogas production, when a slight volatile organic acid accumulation has been detected (from about 3515 mg CH_3COOH_{eq} L^{-1} to 4530 mg CH_3COOH_{eq} L^{-1}), and to recover the biogas production after a strong organic acid accumulation (up to 7779 mgCH_3COOH_{eq} L^{-1}).

Molybdenum, nickel, cobalt, and selenium concentrations above the stimulatory level identified in this study showed similar effects in both case studies: a temporary increase of the methane content in the biogas by 15 – 20% and a provisional improvement of the specific methane production. This allowed to decrease the organic loading rate by 10 – 20%, due to rapid degradation of accumulated volatile organic acids.

Further, the residual methane potential of the biogas plant in TE limiting conditions reached values up to 4.8% in comparison to the 1.3% residual methane potential achieved when TE concentration was not a limiting factor, proving that a proper use of TE could help in reducing greenhouse gases emission.

1. Introduction

Nowadays, one of the most important challenge of society regarding all economical sector is related to natural resources management and environmental impact of production systems. Waste prevention and reduction, renewable energy despite fossil fuels utilization, reduction of greenhouse gases (GHG) emissions to mitigate global climate changes are becoming priorities that will drive major research and innovation project on the application of the circular economy also across the agri-food sector (Toop et al., 2017).

Agriculture and land-use changes contribute greatly to anthropogenic GHG emissions and are expected to remain relevant issues during the 21st century (Smith et al., 2014). Additionally, total emissions from the livestock sector in 2000 were estimated to be 2.45 Gt $CO_{2\ eq}$ year^{-1} (Herrero et al., 2013). Therefore, valuable management practices and mitigation of GHG emissions in the agriculture would be challenging.

Generation of biogas through Anaerobic Digestion (AD) of manure and slurries as well as of a wide range of other digestible organic wastes, converts these substrates into renewable energy, reducing CH_4 emission in manure management and producing digestate to use as natural fertilizer for soils.

Furthermore, recent studies showed the sustainability of innovative practices for on-farm biogas production, such as the application of Carbon Capture and Sequestration (CCS) system to renewable fuel production, consisting in *i)* growing of agricultural biomass by sequential cropping to produce both food and energy, ii) using animal manures and agricultural residues, *iii*) recycling digestate to the farm using innovative techniques to substitute mineral fertilizers and increasing carbon sequestration in the soil by highly stable forms (Valli

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et al., 2017).

However, the use of energy crops or other agricultural substrates without a complete anaerobic degradation could arise risks of increase in methane emissions in the atmosphere. Therefore, for an efficient and environmental friendly biogas process, it is necessary to ensure a minimum Residual Methane Potential (RMP) to thereby reduce the methane emissions (Ahlberg-Eliasson et al., 2017; Ruile et al., 2015) and to guarantee the environmental sustainability of the process.

Possible inhibitors that commonly could affect anaerobic process, including ammonia, organic acid accumulation, electrical conductivity, salinity, pH, temperature fluctuations, bacterial competition for metabolic intermediate, Carbon to Nitrogen (C/N) ratio and Trace Element (TE) concentration, are widely described in literature (Chen et al., 2008; Jha and Schmidt, 2017). The role of optimal and limiting trace metal concentrations in anaerobic digestion performance has been addressed by numerous studies (Braga et al., 2017; Wintsche et al., 2016). Anaerobic fermentation process, microbial growth, dynamics of microbial communities and metabolic pathways are dependent on the bioavailability and/or optimal supply of micronutrients (Fermoso et al., 2015). Among trace elements, it is well known the importance of TE such as molybdenum (Mo), nickel (Ni), cobalt (Co), selenium (Se), and iron (Fe) and their crucial role in enzymatic reactions (Choong et al., 2016; Zandvoort et al., 2006; Zhang et al., 2003).

However, literature analysis showed a wide range of recommended TE concentrations in the AD process as following summarized: 0.005 – 50 mg Mo kg_{ww}^{-1}, 0.005 – 5 mg Ni kg_{ww}^{-1}, 0.024 – 10 mg Co kg_{ww}^{-1}, 0.079 – 0.79 mg Se kg_{ww}^{-1}, and 0.16 – 1000 mg Fe kg_{ww}^{-1} (Demirel and Scherer, 2011; Khatri et al., 2015; Lindorfer et al., 2012; Repinc et al., 2018; Schattauer et al., 2011). Other studies pointed out that TE content lower than 0.048 mg Mo kg_{ww}^{-1}, 0.0048 mg Ni kg_{ww}^{-1}, 0.030 mg Co kg_{ww}^{-1}, 0.079 mg Se kg_{ww}^{-1}, and 0.00132 mg Fe kg_{ww}^{-1}started to limit the growth of methanogen culture (Scherer and Sahm, 1981; Zhang et al., 2003). Several orders of magnitude make uncertain and controversial the definition of stimulatory and inhibitory concentrations of metals for each anaerobic digestion plant. These differences could be attributable to several aspects, like digester type and geometry, operating parameters, inoculum origin, feedstock composition, sampling and analytical methods, chemical speciation and bioavailability of metals (Cestonaro do Amaral et al., 2014; Thanh et al., 2016; van Hullebusch et al., 2016).

Nevertheless, a market for TE additive to use in agricultural biogas plants has been established, but awareness for their utilization at full scale level is not yet so clear for operators and in many cases more knowledge on that field should be required (Kuttner et al., 2015; Lebuhn et al., 2014; Romero-Güiza et al., 2016).

This work provides a methodological approach *i*) to decide if the TE supplementation is required, *ii*) to understand the expected effects of the TE added in terms of process performance and GHG emissions reduction, and *iii*) to avoid over-dosage, minimizing the risk of biological inhibition and the excess of potentially toxic elements concentration in the effluent digestate, according to regulation for land fertilization. The results obtained with this method for two full-scale biogas plant in Italy are shown and discussed, providing useful examples for anaerobic biological process improvement by TE supplementation.

2. Materials and methods

2.1. Monitoring of the full-scale biogas plants

Two mesophilic stirred full-scale AD plants (Italy) were studied for long periods and the findings have been reported in this study providing useful information to develop a methodological approach to quickly identify TE deficiencies in biogas plants, thus improving the anaerobic digestion process.

Feedstocks were analyzed periodically for Total Solid (TS) and Volatile Solid (VS) content; while Biochemical Methane Potential (BMP) was assigned on the basis of our internal database. The results of feedstocks characterization are shown in Table 1. The chemical composition of digestate slurries from primary digesters was analyzed in terms of concentration of Volatile Organic Acids (VOAs), buffer capacity expressed as Total Inorganic Carbon (TIC), Total Ammonium Nitrogen (TAN), TS, VS, Electrical Conductivity (EC), pH, and TE content, such as Mo, Ni, Co, Se, and Fe. The quantities of the material inflows, electricity production and biogas composition were daily obtained from the biogas plant operator.

Table 1
Feedstock characterization.

Feedstock	Total Solids [g kg^{-1} ww]	Volatile Solids [g kg^{-1} ww]	BMP[a] [Nm^3 CH_4 t VS^{-1}]
Case – study A			
Maize silage	354.8 ± 52.6 (323.1; 386.6)	342.9 ± 51 (310.5; 375.3)	355
Triticale silage	267.6 ± 26.5 (249.1; 286.1)	248.5 ± 24.2 (230.0; 267.0)	325
Cow slurry	68.5 ± 11.1 (60.4; 76.7)	52.9 ± 10.1 (44.8; 61.1)	220
Case – study B			
Pig slurry	57.6 ± 30.1 (41.6; 73.7)	45.1 ± 24.7 (31.9; 58.2)	250
Maize silage	311.7 ± 17.2 (295.7; 329.7)	300.4 ± 16.8 (282.7; 318.0)	355
Chicken manure	422.5 ± 153.8 (299.7; 545.2)	302.3 ± 139.3 (179.6; 425.0)	300
Maize grain	880.3 ± 7.1 (887.2; 882.7)	855.0 ± 7.1 (848.1; 861.9)	375

Means ± S.D. during the monitored periods.
Values in parenthesis (−) indicate the 95% CI.
[a] BMP values were assigned on the basis of our internal database.

The first biogas plant represents a case-study for the development of a strategy for the optimization of the biogas production (*case-study A*), while the second biogas plant represents a case-study for the recovery of an unbalanced anaerobic digestion process, after a strong VOA accumulation (*case-study B*). Each biogas plant was fed with a mixture of agricultural substrates, which resulted in a continuous production of methane, valorised in a Combined Heat and Power (CHP) unit of 380 kW_{el} and 999 kW_{el} in the *case-study A* and *B,* respectively. Both biogas plants were conducted at a temperature of 40 – 42 °C, and the produced electrical energy was sold to the public power grid, while the thermal energy was used to heat the biogas plants.

The first full-scale biogas plant (*case-study A*) was monitored for a period of more than 4 years. It consisted of two anaerobic digesters (AD1, AD2) in series with a nominal volume of 2700 m^3 and 1200 m^3, respectively. The effluent digestate was sent to a solid/liquid separation unit; a part of the liquid fraction was allowed to be recycled from the uncovered storage tank to the AD1 (approximately in the range of 0 – 15 t d^{-1}), while the solid fraction and the remained liquid fraction were utilized as a soil conditioner and fertilizer, respectively (Fig. 1, a). The biogas plant was operated with an overall Hydraulic Retention Time (HRT) of 107 ± 18 days and an Organic Loading Rate (OLR) of 1.83 ± 0.16 kg VS m^{-3} d^{-1}. The digester AD1 had a HRT of 74 ± 12 days, and an OLR of 2.65 ± 0.23 kg VS m^{-3} d^{-1}.

The performance of the second full-scale biogas plant (*case-study B*) was monitored and evaluated for a period of 15 months. The set-up of the second biogas plant consisted of two anaerobic digesters (AD1, AD2) in parallel, each with a nominal volume of 2145 m^3, followed by a Post Fermenter (PF) with a nominal volume of 2865 m^3. The digestate was sent to a solid/liquid separation unit, and the solid and liquid fractions were utilized as soil conditioner and fertilizer, respectively (Fig. 1, b). The biogas plant was operated with an overall HRT of 40 ± 2 days and an OLR of 2.33 ± 0.19 kg VS m^{-3} d^{-1}. The AD1 and AD2 digesters had a HRT of 24 ± 1 days, and an OLR of 3.88 ± 0.33 kgVS m^{-3} d^{-1}.