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Short Communication

Micronutrient dynamics after thermal pretreatment of olive mill solid waste

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HIGHLIGHTS

- Thermal pretreated OMSW has a higher methane production rate than unpretreated OMSW.
- Metal deficiency limits methane production.
- Metal dynamics in pretreated OMSW was studied using metal extraction scheme.
- Increase of available Co was coupled to the increase of methane production rate.
- Increase of bioavailable cobalt might be a good strategy to optimize biogas production.

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ABSTRACT

This study investigated metal dynamics, and their bioavailability, before and after thermal pretreatment of olive mill solid waste (OMSW), using a sequential metal extraction scheme. The 11.5% increase of cobalt in the most available fraction after the pretreatment coupled to the increase of methane production rate have been a good indicator that the OMSW anaerobic digestion might be metal limited due to the lack of cobalt.

1. Introduction

Olive mill solid waste (OMSW) is the main waste produced by the two-phase centrifugation olive oil extraction system. In Spain, the main European producer, 98% of olive oil factories use this extraction system producing from 3 to 4 million tons of OMSW annually. OMSW is a high-humidity residue with a thick sludge consistency that contains 80% of the olive fruit, including skin, seed, pulp and pieces of stones (Rincon et al., 2013).

The high quantity of organic matter contained in the OMSW makes of it a substrate susceptible to be treated with anaerobic digestion. However, the presence of recalcitrant and toxic components, such as lignin, hemicellulose, phenolic compounds, etc., has been used as a common excuse for not applying bioprocesses. Until now, efforts focused on detoxifying these wastes prior to disposal, feeding, or fertilisation/composting, being the major disposal option its use as biomass for cogeneration units (Rodríguez-Gutiérrez and Fernández-Bolaños, 2010).

Anaerobic digestibility of two-phase OMSW has been already shown as a promising option (Rincon et al., 2013). In a previous study, conducted in the same research group than this study, application of thermal pretreatment to OMSW was studied (Rincon et al., 2013). Biochemical methane potential (BMP) tests of untreated and thermal pretreated OMSW showed two different stages: a first exponential stage and a sigmoidal stage after a lag period. No influence of the pretreatment was observed on the kinetic constant of the first-stage. However, clear difference was observed in the maximum methane production rate of the second stage, which achieved a value of 76.8 mL CH_4/(g VS day) for pretreated OMSW, which was 22% higher than that obtained for untreated OMSW. Neither increase in the methane yield nor in the organic matter solubilisation for the pretreated OMSW compared to the untreated OMSW was observed (Rincon et al., 2013). The effects of the thermal pretreatment on the recalcitrant or toxic compounds have not been studied in detail. On one hand, a slightly

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decrease on the lignin and hemicellulose content has been reported (Rincon et al., 2013) which may increase digestibility. On the other hand, thermal pretreatment is known to favor solubilisation of polyphenols (Rubio-Senent et al., 2013), which may decrease digestibility.

Several studies have shown limitation in the methane production rate due to metal deficiency in the supplemented substrate, especially with mono substrates (Wall et al., 2014). Considerable decreases in biogas productions and process instability have been observed in lab-scale and full-scale anaerobic digesters that could be attributed to the lack of trace elements such as iron, nickel or cobalt among others (Pobeheim et al., 2011; Shakeri Yekta et al., 2014a,b). The addition of small amounts of trace elements to anaerobic reactors has been shown to stimulate and stabilize the anaerobic process performance and biogas production in several occasions (Banks et al., 2012; Gustavsson et al., 2013; Pobeheim et al., 2011). Several studies have shown different "critical concentrations" of nickel and cobalt. Critical Ni and Co concentrations of between 0.2–1 μM and 2 μM were reported for an adequate performance of hydrogenotrophic and acetate utilizing methanogens, respectively (Zandvoort et al., 2006). In the same way, Ni and Co concentrations of 0.6 and 0.05 mg/kg fresh matter (FM) respectively were considered optimal for an adequate process stability and fast metabolism of acetic and propionic acids during semi-continuous anaerobic digestion of maize silage (Pobeheim et al., 2011). While a minimum Co concentration of 0.22 mg/kg FM was established as critical for anaerobic digestion of food wastes at moderate organic loading rates (OLR) of 5 g VS/(L d) (Banks et al., 2012).

Bioavailability of these trace elements is significantly lower than their total content in the anaerobic medium. The bioavailability of trace metals for microbial metabolism and growth depends on the total metal concentration, metal speciation, reactor conditions such as pH, temperature, organic loading rate and redox-potential, and chemical processes such as precipitation and complexation (Gustavsson et al., 2013; Pobeheim et al., 2011).

The aim of the present research was to study the bioavailability dynamics of the trace metals Fe, Co and Ni present in the OMSW before and after thermal pretreatment in order to determine its influence on the anaerobic digestion of this waste. Equilibrium speciation modeling and sequential metal extraction were used with the aim of studying metal fractioning and availability.

2. Methods

2.1. Characterization of OMSW

The two-phase OMSW used in the present study was collected from the Experimental Olive Oil Factory located in the "Instituto de la Grasa (CSIC)" of Sevilla, Spain. Before to be used, the OMSW was sieved through a 2 mm mesh to remove olive stone pieces. The main characteristics of this substrate were: 265.0 ± 2.6 g TS/kg OMSW, 228.4 ± 2.3 g VS/kg OMSW, 331.1 ± 0.7 g COD/kg OMSW, 143.4 ± 3.2 g CODs/kg OMSW, pH 4.9 ± 0.2, 2.5 ± 0.1 g $CaCO_3$-TA/kg OMSW. Being TS, total solids; VS, volatile solids; COD, total chemical oxygen demand; CODs, soluble chemical oxygen demand; TA, total alkalinity. OMSW total metal content were: 1164.54 mg Fe/kg TS, 5.79 mg Ni/kg TS, 0.38 mg Co/kg TS, 17.76 mg Cu/kg TS, 29.11 mg Zn/kg TS, 17.60 mg Mn/kg TS, 1.51 mg Mo/kg TS, 3363.96 mg Ca/kg TS, 8427.70 mg Mg/kg TS, 2650.70 mg P/kg TS, 1534.30 mg S/kg TS. This OMSW was the same than the OMSW used and reported in Rincon et al. (2013).

2.2. Equilibrium speciation modeling

Equilibrium speciation modeling was performed by Visual Minteq software. Visual Minteq is widely used in geochemical modeling (http://www2.lwr.kth.se/English/OurSoftware/vminteq/). It allows modeling the balance and speciation of organic and inorganic solutes. Also allows determining the state of saturation with respect to the different mineral phases in the system. The measured total metal content was used to model metal speciation in the OMSW. The imposed initial conditions for modeling were: no presence of organics, atmospheric pressure, 25 °C for untreated OMSW and 180 °C for thermal pretreated OMSW.

2.3. Sequential metal extraction (SME)

Sequential extraction method used in this research followed the modified method proposed by (González-Flores et al., 2009) for municipal biosolids. This technique is based on the release and liquid extraction of metals, by modification of pH and the added extraction reagent. The lower the applied pH the lower the possibility to be released and therefore being available. The more available fraction is the exchangeable, followed by the reductible, the oxidizable and finalizing with the less available fraction, the residual one. Each fraction can be linked to a certain metal specie (Fuentes et al., 2008). The exchangable fraction can be linked to metal-phosphate precipitates, metal–carbonate precipitates, weakly bound metal compounds and adsorbed metals. Reductive fraction can be linked to metals incorporated within Fe and Mn oxides and metal-oxide precipitates. Oxidizable fraction can be linked to metal–organic complexes and metal–sulfide precipitates. Residual fraction is usually linked to unknown strongly bound metal compounds. Being aware that is an operationally defined technique based on decreasing pH, therefore the connection between specie and fraction should be taken as an estimation. The extractions were carried out over a period of 4 days. All extractions were performed in triplicate. The detailed used protocol is reported in (González-Flores et al., 2009). As a control, the deviation of the sum of the fractions against the total metal concentration of each element was checked (Table 1). Regarding the potential errors, a deviation of 10% was regarded as plausible, mainly due to a loss of material during the successive extraction steps can occur.

2.4. Chemical analyses

TS and VS were determined according to the standard methods 2540 B and 2540E respectively (APHA et al., 2005). COD was determined using the method described by Raposo et al. (2008) and CODs using the closed digestion and the colorimetric standard method 5220D[21]. A pH-metre model Crison 20-Basic was used for pH determination. TA was determinated by pH titration to 4.3 (APHA et al., 2005). TKN was analysed using a method based on the 4500-N_{org} B of standard methods (APHA et al., 2005). Ammonia was determined by distillation and titration according to the standard method 4500-NH_3E (APHA et al., 2005). The total metal and the residual fraction concentration were determined after microwave destruction of dried samples, subjected to a digestion with aqua regia (HCl to HNO_3; 1:3). After digestion samples were filtered and analyzed with ICP-OES. Metal concentration of exchangeable, reductible and oxidizable fractions were analyzed with ICP-OES.

3. Results and discussion

3.1. Equilibrium speciation modeling

Iron was found both in untreated OMSW and pretreated OMSW modelling, in the two forms of oxidation existing in nature, i.e. Fe^{2+} and Fe^{3+}. For untreated OMSW, all Fe^{2+} is found as $FeHS^{+}$, while in the case of pretreated OMSW Fe^{+2} is mostly found as Fe $(OH)_3^-$ and