Micronutrient dynamics after thermal pretreatment of olive mill solid waste

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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.

KEYWORDS: Sequential metal extraction; Olive mill solid waste; Metal bioavailability; Anaerobic digestion

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

1 focused on detoxifying these wastes prior to disposal, feeding, or
2 fertilisation/composting, being the major disposal option its use as biomass for
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5 cogenerated units (Rodríguez-Gutiérrez & Fernández-Bolaños, 2010).
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7 Anaerobic digestibility of two-phase OMSW has been already shown as a promising
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9 option (Rincon et al., 2013). In a previous study, conducted in the same research group
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11 than this study, application of thermal pretreatment to OMSW was studied (Rincon et
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13 al., 2013). Biochemical methane potential (BMP) tests of untreated and thermal
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15 pretreated OMSW showed two different stages: a first exponential stage and a
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17 sigmoidal stage after a lag period. No influence of the pretreatment was observed on the
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19 kinetic constant of the first-stage. However, clear difference was observed in the
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21 maximum methane production rate of the second stage, which achieved a value of 76.8
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23 mL CH₄/(g VS day) for pretreated OMSW, which was 22% higher than that obtained
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25 for untreated OMSW. Neither increase in the methane yield nor in the organic matter
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27 solubilisation for the pretreated OMSW compared to the untreated OMSW was
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29 observed (Rincon et al., 2013). The effects of the thermal pretreatment on the
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31 recalcitrant or toxic compounds have not been studied in detail. On one hand, a slightly
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33 decrease on the lignin and hemicellulose content has been reported (Rincon et al., 2013)
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35 which may increase digestibility. On the other hand, thermal pretreatment is known to
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37 favor solubilisation of polyphenols (Rubio-Senent et al., 2013), which may decrease
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39 digestibility.
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48 Several studies have shown limitation in the methane production rate due to metal
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50 deficiency in the supplemented substrate, especially with mono substrates (Wall et al.,
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52 2014). Considerable decreases in biogas productions and process instability have been
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54 observed in lab-scale and full-scale anaerobic digesters that could be attributed to the
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56 lack of trace elements such as iron, nickel or cobalt among others (Pobeheim et al.,
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2011, Shakeri Yekta et al., 2014a and 2014b). 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. MATERIALS AND 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

1 based on the release and liquid extraction of metals, by modification of pH and the
2 added extraction reagent. The lower the applied pH the lower the possibility to be
3 released and therefore being available. The more available fraction is the exchangeable,
4 followed by the reductible, the oxidizable and finalizing with the less available fraction,
5 the residual one. Each fraction can be linked to a certain metal specie (Fuentes et al.,
6 2008). The exchangeable fraction can be linked to metal-phosphate precipitates, metal-
7 carbonate precipitates, weakly bound metal compounds and adsorbed metals. Reductive
8 fraction can linked to metals incorporated within Fe and Mn oxides and metal-oxide
9 precipitates. Oxidizable fraction can be linked to metal-organic complexes and metal-
10 sulfide precipitates. Residual fraction is usually linked to unknown strongly bound
11 metal compounds. Being aware that is an operationally defined technique based on
12 decreasing pH, therefore the connection between specie and fraction should be taken as
13 an estimation. The extractions were carried out over a period of 4 days. All extractions
14 were performed in triplicate. The detailed used protocol is reported in González-Flores
15 et al. (2009). As a control, the deviation of the sum of the fractions against the total
16 metal concentration of each element was checked (Table 1). Regarding the potential
17 errors, a deviation of 10 % was regarded as plausible, mainly due to a loss of material
18 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 5220D²¹. 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-NH₃E (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 HNO₃; 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. Fe²⁺ and Fe³⁺. For untreated OMSW, all Fe²⁺ is found as FeHS⁺, while in the case of pretreated OMSW Fe⁺² is mostly found as Fe (OH)₃⁻ and traces of Fe (OH)₂, FeHS⁺ were not found. Iron hydroxides are more likely to be present in the pretreated OMSW and therefore more available for microorganisms. In the case of Fe³⁺, it was observed the presence of the following compounds in the untreated OMSW modelling: 98.17% of Fe(OH)²⁺, 1.70% of FeHPO₄, 0.05% of Fe(OH)²⁺ and finally 0.07% of Fe(OH)₃, while for the pretreated OMW all Fe³⁺ was found as Fe(OH)₄⁻. Although the change on the temperature has induced a swift to one type of hydroxide, there is no a significant change in metal availability.

Nickel is only present in nature as Ni²⁺ and, therefore, it appears with this oxidation state. For untreated OMSW modelling, all Ni²⁺ is forming NiHS⁺, while for pretreated OMSW Ni²⁺ is forming a variety of hydroxides with the following percentages: Ni(OH)₃⁻, 97.02%; Ni(OH)₂, 2.21 %; NiHS⁺, 0.70 % and NiOH⁺, 0.06%. Similarly as happened in the case of iron, nickel hydroxides are more likely to be present in the pretreated OMSW and therefore more available for microorganisms.

1 For Cobalt in untreated OMSW, most of this metal is forming CoHS^+ with a 98%, while
2 the remaining amount was found as free cobalt Co^{2+} and 0.96% forming $\text{Co}(\text{OH})_2$. After
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4 pretreatment an important change in the cobalt compounds was observed, and only
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6 5.2% of CoHS^+ was detected, while the remaining cobalt was found forming different
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8 types of cobalt hydroxides such as $\text{Co}(\text{OH})_2$ (50.53%), $\text{Co}(\text{OH})_3^-$ (44.25%) and
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10 $\text{Co}(\text{OH})^+$ (0.02%).
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13 The three studied metal shown a similar behaviour, within the same amount of sulfur
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15 anions, at 25 °C most of the metal cations are found on a sulfide form, however at 180°C
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17 most of the metals are found on a more bioavailable hydroxide form. It should be
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19 considered that this simulation might be significantly changed if the unknown organics
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21 present in the OMSW are taken into account in the initial conditions.
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25 3.2. Sequential metal extraction 26

27 3.2.1. Iron 28

29 For untreated OMSW 86.85% of the iron was found in the residual fraction, being the
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31 major fraction (Fig. 1A). It was followed by the reducible fraction (4.32%) and the
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33 exchangeable fraction (2.8%), being the oxidizable fraction the minority one with
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35 1.74%.
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38 For pretreated OMSW (Fig. 1B) the majority fraction is again the residual one with
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40 89.26%, followed by the interchangeable (3.47%), the reducible (2.75%) and finally the
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42 oxidizable fraction with 2.52%.
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45 There is not significant change on the iron distribution for the untreated and pretreated
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47 OMSW. After pretreatment the percentages of the exchangeable and oxidizable
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49 fractions were slightly increased by 0.6% and 0.8%, respectively. The reducible fraction
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51 decreased by 1.57%, while the residual fraction was kept virtually constant. It is worth
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53 to mention the high percentage of iron remaining in the residual phase, iron was
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1 expected to be in major proportion in the oxidizable fraction where the organic material
2 is removed and the associated metal released.
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4 3.2.2. Nickel 5 6

7 For untreated OMSW, the residual fraction was the majority one (Fig. 1A) followed by
8 the exchangeable and reducible fractions with 16.93% and 6.2% respectively, being in
9 this case the oxidizable fraction the minor one with 2.26%.
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12 The same trend was observed for pretreated OMSW (Fig. 1B). In this case, the residual
13 fraction was the major one with 74.43% followed by the exchangeable and reducible
14 fractions with 17.67% and 3.66% respectively, being the oxidizable fraction the minor
15 one with only 2.24% of total.
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18 There is not a significant change on the nickel distribution for the untreated and
19 pretreated OMSW. After pretreatment the exchangeable and residual fractions increased
20 by 0.74% and 1.82% respectively, while the reducible fraction decreased by 2.54%,
21 keeping the oxidizable fraction virtually constant. Similar to iron, the residual fraction
22 is the highest one.
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25 3.2.3. Cobalt 26 27

28 For untreated OMSW (Fig. 1A) the majority fraction of cobalt was the oxidizable one
29 with 40.3%, followed by the exchangeable fraction (39.15%), reducible fraction
30 (10.81%), representing the residual fraction the minor one (7.74%). Most of cobalt is
31 mainly divided into two fractions: the exchangeable and the oxidizable one.
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34 For pretreated OMSW (Fig. 1B), the majority fraction is the exchangeable with 50.61%
35 followed by the oxidizable and reducible fractions with 40.9% and 4.34% respectively,
36 being the residual fraction the minor one with 1.16%.
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39 There is a significant change on cobalt distribution after pretreatment. There is a
40 movement of cobalt to more available fractions, contrary to iron and nickel, which were
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more related to the residual fraction. Cobalt is more related to the organic fraction, being more easily exchangeable after pretreatment as observed in the results, and therefore might be more available for microorganisms.

3.3 Metal bioavailability

Iron, nickel and cobalt have been shown as essential trace metals for anaerobic microorganism in numerous studies. There are several studies dealing with metal limitation (Fermoso et al., 2008b; Munk et al., 2010) and some other dealing with metal supplementation (Banks et al., 2012; Fermoso et al., 2010; Shakeri Yekta et al., 2014a). However, there are few studies about metal bioavailability improvement of the already presented metals. Modification of metal fractioning in an active mode needs an input of energy or chemicals which most probably be unfavorable for the overall operation of the treatment plant. Addition of organic chelants, such EDTA (Fermoso et al., 2008a), or decreasing pH in the system are approaches that most probably will lead to unstable operation of the bioreactor.

Pretreatment of the substrate is shown in the present study as a possible strategy to improve metal availability. Iron and nickel did not shown a significant change in the studied distribution. However, cobalt showed a significant change to more available fractions. Cobalt has been shown as an essential metal for methanogens in solid waste anaerobic digestion (Banks et al., 2012; Gustavsson et al., 2013). In the present study, cobalt content of the OMSW is rather low, i.e. 0.4 mg Co/ kg ST. Similar cobalt concentration has been reported in cobalt limited substrates (Gustavsson et al., 2013; Pobeheim et al., 2011). Therefore, cobalt limitation can be expected on OMSW anaerobic digestion.

The previous study done by Rincon et al. (2013), with the same OMSW used in this study, shown that BMP tests of untreated and pretreated OMSW showed two different

1 stages: a first exponential stage and a sigmoidal stage after a lag period. A clear
2 difference was observed in the maximum methane production rate of the second stage,
3 which achieved a value of 76.8 mL CH₄/(g VS day) for pretreated OMSW, which was
4 22% higher than that obtained for untreated OMSW. Neither increase in the methane
5 yield nor in the organic matter solubilisation for the pretreated OMSW compared to the
6 untreated OMSW was observed. Therefore, increase of organic matter solubilization
7 most probably is not the cause of the kinetic improvement. Cobalt addition studies have
8 shown that mostly the observed process improvement is not based on the methane yield
9 but in the degradation kinetics (Fermoso et al., 2008b; Pobeheim et al., 2010), as shown
10 similarly in the present study.
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24 It has to be noted that iron or nickel limitation can be still an important issue on the
25 anaerobic digestion of OMSW as it is for other substrates (Gustavsson et al., 2013;
26 Shakeri Yekta et al., 2014b; Zandvoort et al., 2003). However, the thermal pretreatment
27 did not clearly improve their accessibility and therefore their bioavailability.
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34 Addition of trace metals as micronutrients is being a big concern for biogas operators,
35 e.g. see <http://www.omex.com/environmental/NewsItem.aspx?id=644> (seen on
36 30/January/2015). Costly trace metal liquors are added to anaerobic digesters. As
37 suggested in the present study, modification of the already presented metal in the
38 substrate might be another possibility to overcome metal limitation.
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46 4. CONCLUSIONS

47 No significant change in Ni and Fe (bio)availability after thermal pretreatment was
48 observed. In the case of OMSW, anaerobic digestion is limited for lack of these metals,
49 pretreatment does not clearly improve the accessibility of these metals. Increase of
50 11.5% cobalt in the exchangeable fraction coupled to the increase of methane
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1 production rate after thermal pretreatment have been a good indicator that the anaerobic
2 digestion might be metal limited due to the lack of essential cobalt.
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11 Biotechnologies’).
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18 REFERENCES 19

- 20
21 1. APHA, AWWA, WEF. 2005. *Standard Methods for the Examination of Water and*
22 *Wastewater. 21th ed.* American Public Health Association, Washington DC, USA.
23
24
- 25 2. Banks, C.J., Zhang, Y., Jiang, Y., Heaven, S. 2012. Trace element requirements for
26 stable food waste digestion at elevated ammonia concentrations. *Bioresour. Technol.*,
27 **104**, 127-135.
28
29
- 30 3. Fermoso, F.G., Bartacek, J., Chung, L.C., Lens, P. 2008a. Supplementation of cobalt
31 to UASB reactors by pulse dosing: CoCl₂ versus CoEDTA²⁻ pulses. *Biochem. Eng.*
32 *J.*, **42**(2), 111-119.
33
34
- 35 4. Fermoso, F.G., Bartacek, J., Manzano, R., van Leeuwen, H.P., Lens, P.N. 2010.
36 Dosing of anaerobic granular sludge bioreactors with cobalt: impact of cobalt
37 retention on methanogenic activity. *Bioresour. Technol.*, **101**(24), 9429-37.
38
39
- 40 5. Fermoso, F.G., Collins, G., Bartacek, J., O’Flaherty, V., Lens, P. 2008b.
41 Acidification of methanol-fed anaerobic granular sludge bioreactors by cobalt
42 deprivation: Induction and microbial community dynamics. *Biotechnol. Bioeng.*,
43 **99**(1), 49-58.
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6. Fuentes, A., Lloréns, M., Sáez, J., Isabel Aguilar, M., Ortuño, J.F., Meseguer, V.F. 2008. Comparative study of six different sludges by sequential speciation of heavy metals. *Bioresour. Technol.*, **99**(3), 517-525.
7. González-Flores, E., Tornero Campante, M.A., Ángeles Cruz, Y., Bonilla Y Fernández, N. 2009. Total concentration and speciation of heavy metals in urban origin biosolids. *Revista Internacional de Contaminacion Ambiental*, **25**(1), 15-22.
8. Gustavsson, J., Shakeri Yekta, S., Sundberg, C., Karlsson, A., Ejlertsson, J., Skyllberg, U., Svensson, B.H. 2013. Bioavailability of cobalt and nickel during anaerobic digestion of sulfur-rich stillage for biogas formation. *Appl. Energy*, **112**, 473-477.
9. Munk, B., Bauer, C., Gronauer, A., Lebuhn, M. 2010. Population dynamics of methanogens during acidification of biogas fermenters fed with maize silage. *Eng. Life Sci.*, **10**(6), 496-508.
10. Pobeheim, H., Munk, B., Johansson, J., Guebitz, G.M. 2010. Influence of trace elements on methane formation from a synthetic model substrate for maize silage. *Bioresour. Technol.*, **101**(2), 836-839.
11. Pobeheim, H., Munk, B., Lindorfer, H., Guebitz, G.M. 2011. Impact of nickel and cobalt on biogas production and process stability during semi-continuous anaerobic fermentation of a model substrate for maize silage. *Water Res.*, **45**(2), 781-787.
12. Raposo, F., de la Rubia, M.A., Borja, R., Alaiz, M. 2008. Assessment of a modified and optimised method for determining chemical oxygen demand of solid substrates and solutions with high suspended solid content. *Talanta*, **76**(2), 448-453.
13. Rincon, B., Bujalance, L., Feroso, F.G., Martín, A., Borja, R. 2013. Biochemical methane potential of two-phase olive mill solid waste: Influence of thermal pretreatment on the process kinetics. *Bioresour. Technol.*, **140**, 249-255.

14. Rodríguez-Gutiérrez, G., Fernández-Bolaños, J. 2010. Olive oil and by-products: Mainly components and compounds, effect on health. in: *Olive Oil and Health*, pp. 409-426.
15. Rubio-Senent, F., Lama-Muñoz, A., Rodríguez-Gutiérrez, G., Fernández-Bolaños, J. 2013. Isolation and identification of phenolic glucosides from thermally treated olive oil byproducts. *J. Agric. Food Chem.*, **61**(6), 1235-1248.
16. Shakeri Yekta, S., Lindmark, A., Skyllberg, U., Danielsson, T., Svensson, B.H. 2014a. Importance of reduced sulfur for the equilibrium chemistry and kinetics of Fe(II), Co(II) and Ni(II) supplemented to semi-continuous stirred tank biogas reactors fed with stillage. *J. Hazard. Mater.*, **269**, 83-88.
17. Shakeri Yekta, S., Svensson, B.H., Björn, A., U., S. 2014b. Thermodynamic modeling of iron and trace metal solubility and speciation under sulfidic and ferruginous conditions in full scale continuous stirred tank biogas reactors. *Appl. Geochem.*, **47**, 61-73.
18. Wall, D.M., Allen, E., Straccialini, B., O'Kiely, P., Murphy, J.D. 2014. The effect of trace element addition to mono-digestion of grass silage at high organic loading rates. *Bioresour. Technol.*, **172**, 349-355.
19. Zandvoort, M.H., Lens, P.N.L., van Hullebusch, E.D., Lettinga, G. 2003. Effect of Cobalt and Nickel Speciation on the Performance of Methanogenic Biofilms. *Soil Sediment Contamination*, **12**(5), 679-680.
20. Zandvoort, M.M., van Hullebusch, E.D., Fermoso, F.G., Lens, P. 2006. Trace metals in anaerobic granular sludge reactors: Bioavailability and dosing strategies. *Eng. Life Sci.*, **6**(3), 293-301.

Table 1. Metal concentration found in the different extracted fractions (exchangeable, reducible, oxidizable and residual) and deviation of the sum of the fractions against the total metal concentration. All values are expressed as mg /kg TS.

	Fe in untreated OMSW	Fe in pretreated OMSW	Ni in untreated OMSW	Ni in pretreated OMSW	Co in untreated OMSW	Co in pretreated OMSW
Exchangeable	32.63±1.16	36.83±4.95	0.98±0.03	1.01±0.08	0.143±0.012	0.193±0.015
Reductive	49.37±6.52	32.00±1.00	0.36±0.03	0.21±0.01	0.041±0.010	0.017±0.010
Oxidizable	20.00±1.00	32.22±8.08	0.13±0.28	0.32±0.28	0.150±0.03	0.153±0.012
Residual	1010	1029	3.76	4.00	0.029	0.005
Deviation from total concentration	4.5%	3%	5.5%	5%	3.5%	3%

Figure 1. Percentage of metal fractions in (A) Untreated OMSW and (B) treated OMSW. ■ Exchangeable; □ Reductible; ▨ Oxidizable; and ▩ Residual. Total metal content of Fe, Ni and Co: 1164.5 mg Fe/g TS, 5.79 mg Ni/g TS and 0.38 mg Co/g TS.