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Title: Effect of trace elements addition and alkaline pretreatment on the anaerobic digestion of rice straw

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Abstract: The anaerobic digestion of rice straw using inocula of different origin was investigated in batch tests performed under mesophilic conditions. The trace elements (TEs) Co, Ni and Se were added to the raw rice straw at different dosages. In addition, an alkaline pretreatment, using NaOH, was applied to the rice straw both alone and in combination with the addition of TEs, in order to evaluate potential synergistic effects. The results obtained showed that the alkaline pretreatment was more effective than the TE addition in increasing the cumulative biogas production, causing a 21.4% enhancement of the final biomethane yield, whereas TE dosing resulted only in increases up to 11.6% (obtained with Ni addition). The analysis of volatile fatty acids (VFAs) confirmed that the NaOH pretreatment resulted in a higher production of VFAs, indicating an increased hydrolysis, while TE addition did not cause significant changes in the VFA concentrations.

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Because of her recent prominent critical review about the role of trace elements supplementation in the AD process: "Impacts of trace element supplementation on the performance of anaerobic digestion process: A critical review. Bioresour. Technol. (2016) 209, 369-379".

August 30, 2017

Prof. A. Pandey,
Editor-in-Chief, *Bioresource Technology,*
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Cover letter - manuscript submission

Dear Prof. A. Pandey,

Please find enclosed our manuscript entitled "*Effect of trace elements addition and alkaline pretreatment on the anaerobic digestion of rice straw"* by Gabriele Mancini, Stefano Papirio, Gerardo Riccardelli, Piet N.L. Lens and Giovanni Esposito. The present manuscript is an original work of the authors, which has not been submitted earlier to Bi.Te. nor is any part of it under consideration for publication in another journal.

This paper aims to investigate the improvement of the biogas production obtained from the anaerobic digestion (AD) of rice straw by trace elements (TE) addition and alkaline pretreatment. Rice straw, one of the most abundant lignocellulosic residues, has low levels of TE concentrations and the lack of bioavailable TEs in the raw substrates has been considered as the main limitation for the AD process by several studies. However, only a few studies focused on the TE requirements of anaerobic digesters fed with lignocellulosic residues. To our knowledge, this is the first investigation aimed to assess the effect of adding different TEs (i.e. Co, Ni, and Se) on the AD of rice straw.

Nonetheless, the enhancement of the biogas production yield was not significant when TEs were added to the raw rice straw in the biochemical methane potential tests performed. On the other hand, the use of the alkaline pretreatment caused a considerable increase of the biogas production yield. This led to the conclusion that an enhancement of the hydrolysis stage, rather than the methanogenesis, is required for increasing the biomethane potential of complex lignocellulosic materials such as rice straw. These observations were further supported by monitoring the VFA concentration, which was significantly increased by the pretreatment, whereas negligible effects were produced by the TE addition.

The co-authors and I agree that the current manuscript meets the targets of the journal and can be submitted to *Bioresource Technology*. The subject is classified as "20.030 Anaerobic Digestion".

Should you need to contact me, please use the below address, phone or e-mail address.

Sincerely Yours,

Gabriele Mancini

On behalf of the co-authors

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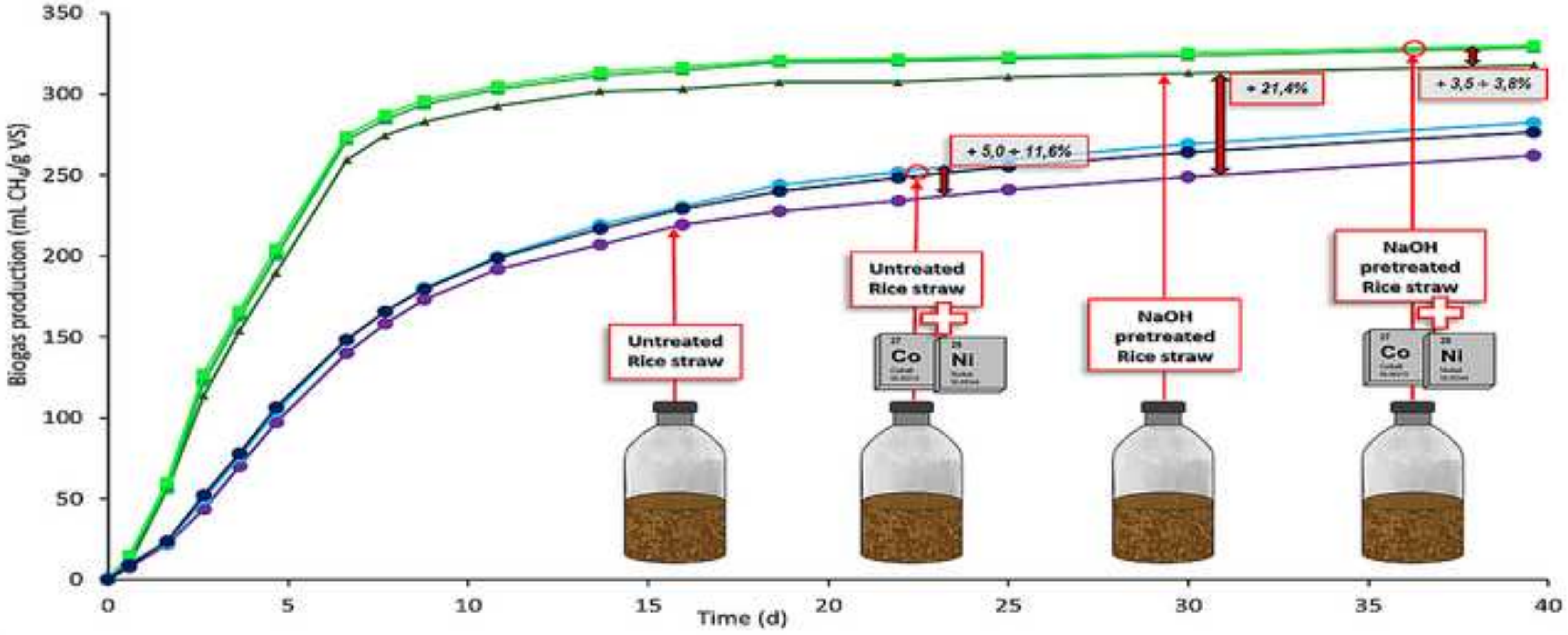
Graphical Abstract (with colors)



Highlights

- NaOH pretreatment was more effective than TE addition in improving AD of rice straw
- 21.4% enhancement of the biogas production yield was obtained by NaOH pretreatment
- The highest increase with TE (11.6%) was obtained adding 45 µg Ni/g TS rice straw
- Higher VFA concentrations were obtained with pretreatment than with TE addition
- No synergistic effects were obtained by combining pretreatment with TE addition

Effect of trace elements addition and alkaline pretreatment on the anaerobic digestion of rice straw

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Abstract

The anaerobic digestion of rice straw using inocula of different origin was investigated in batch tests performed under mesophilic conditions. The trace elements (TEs) Co, Ni and Se were added to the raw rice straw at different dosages. In addition, an alkaline pretreatment, using NaOH, was applied to the rice straw both alone and in combination with the addition of TEs, in order to evaluate potential synergistic effects. The results obtained showed that the alkaline pretreatment was more effective than the TE addition in increasing the cumulative biogas production, causing a 21.4% enhancement of the final biomethane yield, whereas TE dosing resulted only in increases up to 11.6% (obtained with Ni addition). The analysis of volatile fatty acids (VFAs) confirmed that the NaOH pretreatment resulted in a higher production of VFAs, indicating an increased hydrolysis, while TE addition did not cause significant changes in the VFA concentrations.

Keywords: anaerobic digestion; biogas; rice straw; trace elements; alkaline pretreatment.

1. Introduction

In recent years, the search for alternative renewable energy sources to fossil fuels has caused a growing interest in anaerobic digestion (AD). This process combines the dual benefits of generating biogas and reducing greenhouse gases emissions and landfill waste (Holm-Nielsen et al., 2009). Methane-rich biogas can be obtained from several organic substrates and used to produce electricity and heat, or as a transport fuel after an upgrade to biomethane (Pöschl et al., 2010). Among the wide range of feedstocks, lignocellulosic materials are particularly attractive, due to their high carbohydrate content and large abundance worldwide (Kabir et al., 2015). In particular, the AD of agricultural residues, such as rice straw, can be a sustainable process for future energy generation, despite the limitation caused by its recalcitrant structure to biodegradation, which can be overcome by a pretreatment step (Mancini et al., 2016a). Alkaline pretreatment, using NaOH, has been applied to pretreat different lignocellulosic materials (Salehian et al., 2013; Sambusiti et al., 2012). This improved the biodegradability of the raw material due to the removal of lignin and increased the porosity, which led to enhanced hydrolysis and thus higher biogas production yields.

In addition to the complex nature of the material, the biogas production from lignocellulosic residues might be restricted by the lack of bioavailable essential trace elements (TEs) (Thanh et al., 2016). Lignocellulosic residues usually contain low concentrations of TEs and limitations of any required TE could disturb the overall AD process (Evranos and Demirel, 2015). TEs such as iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), molybdenum (Mo), selenium (Se) and tungsten (W) are fundamental components of enzymes and cofactors involved in the biochemistry of methane formation, and their role in anaerobic processes has been investigated extensively (Choong et al., 2016; Demirel and Scherer, 2011; Romero-Güiza et al., 2016). Adequate dosing of TEs is required to maintain an effective AD process by sustaining the growth and metabolism of anaerobic microorganisms (Zandvoort et al., 2006a).

One of the major effects of TE addition on the AD process is the decrease of the level of volatile fatty acids (VFAs) within the anaerobic reactor, which is generally associated with a consequent increase of the biogas production (Lindorfer et al., 2012). Choong et al. (2016) highlighted that substrates such as food waste have a greater response to TE supplementation than complex feedstocks, such as lignocellulosic materials. However, information about TE requirements of anaerobic digesters fed with lignocellulosic residues is scarce (Demirel and Scherer, 2011). Leaving aside silages from energy crops, the effects of TE dosing on the AD of agricultural byproducts have so far been investigated only by a few studies in the literature (Table 1).

This study aimed to assess the effect of adding different TEs, i.e. Co, Ni, and Se, on the AD of rice straw. Two different inocula were employed to evaluate the effect of different TE background levels. The effect of the TE addition was also studied in combination with an alkaline pretreatment to evaluate potential synergistic effects. Biomethane potential (BMP) tests were conducted under mesophilic conditions to determine the biogas production yields from each configuration adopted. The production of volatile fatty acids was monitored along the AD process to further assess the impact of TE addition on the anaerobic biodegradation of rice straw.

2. Materials and methods

2.1 Substrate and inocula

Rice (*Oryza sativa*) straw, obtained from agricultural fields in Pavia (Italy), was used as the sole substrate in this work. After collection, the straw was manually cut down to a particle size smaller than 4 mm. Part of the rice straw was pretreated with sodium hydroxide by soaking 16 g of rice straw in 100 mL of 1.6% (w/w) NaOH solution inside a 500 mL bottle. The bottle was incubated at 30°C for 24 h. Then, the rice straw was filtered and air dried, until further use.

Two types of inocula, with different background levels of TEs, were used in the BMP tests. The first inoculum was an anaerobic granular sludge, collected from a paper mill wastewater treatment plant located in Eerbeek (the Netherlands), its characteristics are described by Roest et al. (2005). The second inoculum was a digestate from a full-scale AD plant treating buffalo manure and milk whey from a mozzarella factory located in Capaccio (Italy), its characteristics are detailed in Ariunbaatar et al. (2015). Both inocula were degassed by incubating them at mesophilic conditions (37 ± 2°C) for 4 d before starting the experiments. The physicochemical characterization of the rice straw and the inocula is reported in Table 2.

2.2 Trace elements dosing strategy

Table 2 presents the representative concentrations of Co, Ni and Se, together with some other TE found in the rice straw, the granular sludge and the buffalo manure. The TE concentrations observed in the rice straw were compared with the recommended values from the literature (Hinken et al., 2008). The differences between the amount of Co, Ni and Se in the rice straw used in this study and the recommended values were then used to calculate the amount of each TE to be added in the BMP tests (Table 3). In addition to this optimal concentration, representing the 100% of the calculated requirement, two other amounts were tested, i.e. 200 and 500% of the calculated requirement. The amount of TE present in the two inocula was not taken into account in the calculations, in order to evaluate if different TE background levels could result in different effects on the biogas production yields.

The selected TEs were individually supplemented in different serum bottles, injecting different amounts of stock solutions prepared using the following salts: $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and Na_2SeO_3 (analytical grade, Sigma-Aldrich, Germany).

2.3 BMP tests

BMP tests were performed in triplicate under mesophilic conditions (37 ± 2°C). The biomethane production was measured by the liquid displacement method, as described by Esposito et al. (2012) and modified as in Mancini et al. (2016b). The inoculum to substrate ratio was maintained at 2.0 g VS/g VS. Therefore, the 250 mL glass bottles employed in the BMP tests were loaded with 2.5 g of rice straw and 36.0 g of granular sludge or 142.0 g of buffalo manure inoculum, respectively. Tap water was added to reach 150 mL of working volume into each bottle. Triplicates of blank samples containing only inoculum and tap water were also prepared in order to determine the biomethane production of the two inocula, which was then subtracted from the production of the rice straw. For VFA analysis, 1.0 mL of the liquid phase was sampled daily from each bottle during the first 10 d of the BMP tests.

2.4 Analytical methods

Total solids (TS) and volatile solids (VS) were determined according to the method described by Sluiter et al. (2008a). Total Kjeldahl nitrogen (TKN) was measured according to the Kjeldahl method (Pansu and Gautheyrou, 2007). The rice straw was analyzed for its structural carbohydrates and lignin content according to the procedure described by Sluiter et al. (2008b).

TE analysis was carried out by using inductively coupled mass spectroscopy (ICP-MS) (X-Series, Thermo Fisher Scientific, USA). The total TE content was determined after drying the samples at 105°C and digesting 0.5 g TS with 10.0 mL HNO_3 in a microwave accelerated reaction system (MARS5, CEM Corp., USA). VFAs were determined by gas chromatography (GC) (Varian 430-GC, Varian Inc., USA) equipped with a CP WAX-58 CB column (25 m × 0.32 mm × 0.2 µm) and a flame ionization (FID) detector. Helium was used as the carrier gas.

2.5 Statistical analysis

Statistically significant differences between the biomethane production from the BMP tests with and without addition of TEs were determined by a paired t-test. The same method was used to assess differences between the VFA concentrations recorded in the BMP tests. The Microsoft Excel 2016 (Microsoft Corporation, USA) statistical package was used, applying a 95% confidence interval.

3. Results and discussion

3.1 Substrate and inocula characterization

The total Ni content in the rice straw was 2.0 µg/g TS, while Co was below the ICP-MS detection limit of 1.0 µg/g TS (Table 2). Se was not detectable in the rice straw, nor in the two inocula used. The concentrations of TEs found in the rice straw, granular sludge and buffalo manure were comparable to those determined by Mussoline et al. (2014), Zandvoort et al. (2006b) and Ariunbaatar et al. (2016), respectively.

The characteristics of the two inocula used were appreciably different. The granular sludge had a higher TS and VS concentration than the buffalo manure. At the same time, the background concentration of TEs was higher in the granular sludge than in the buffalo manure (Table 2). The factor of TE background level should be taken into account before supplementing TE, in order to avoid overdosing that can inhibit the AD process. This aspect was elucidated by Facchin et al. (2013), who showed that TE supplementation to food waste inoculated with a sludge having a high TE background level negatively impacted the AD process, decreasing the methane production yield.

Determining the total TE concentration is considered the first step to evaluate possible deficiencies that could hinder the AD process (van Hullebusch et al., 2016). However, the TE bioavailability, defined as the degree to which TE are available for metabolic activities (Marcato et al., 2009), is more representative than the total TE content, since it allows to consider only the TE fractions that can be directly taken up by microorganisms (Thanh et al., 2016). Despite a sequential extraction technique was not applied in this study to assess bioavailability, the soluble fraction, which is considered highly bioavailable, was analyzed in the two inocula used to determine the amount of dissolved TE. The amount of Co in the supernatants of the granular sludge and buffalo manure inoculum was 0.5 (± 0.1) and 0.2 (± 0.1) µg/L, respectively. The Ni concentration was 2.5 (± 0.1) and 3.3 (± 0.2) µg/L, whereas Se was below the detection limit for both inocula supernatants.

3.2 Effect of TE addition and pretreatment on the biomethane production

Two consecutive runs of BMP tests were carried out at mesophilic temperature (37 ± 2°C). In the first run, the rice straw was inoculated with granular sludge and Co and Ni were individually added at 3 different concentrations, representing 100%, 200% and 500% of the recommended dosage reported in Table 3. The cumulative production obtained, reported in Fig. 1, showed a consistent enhancement of the final biomethane production yields compared to the rice straw without Co and Ni addition. The biomethane production yield was from 5.0 to 11.6% higher (Table 4) when Co and Ni were supplemented to the rice straw inoculated with granular sludge. Similarly, in the second run of BMP tests, Co and Ni were separately added to rice straw inoculated with buffalo manure, using 100% of the recommended dosage (Fig. 2a). The cumulative methane production yield increased by 7.6 and 5.7%, when Co and Ni were respectively added (Table 4). However, the differences between the controls and the BMP tests with supplemented TEs were not statistically significant in all the investigated configurations ($p>0.05$).

The role of Co and Ni in the AD process has been studied extensively in the literature (Gustavsson et al., 2013; Pobeheim et al., 2011; Shakeri Yekta et al., 2014). These two TEs are considered essential cofactors of several enzymes involved in both the acetoclastic and hydrogenotrophic methanogenesis pathways, such as acetyl-CoA decarbonylase, CO dehydrogenase, methyl-CoM reductase and methyl-H4SPT:HS-CoM methyltransferase (Romero-Güiza et al., 2016). Co is a fundamental constituent of a corrinoid, namely vitamin B_{12}, that binds to the coenzyme methylase, catalyzing the methane formation (Kida et al., 2001). Likewise, Ni is required in substantial amounts within the coenzyme F_{430}, which is always present in methanogenic archaea, and involved in the generation of methane through all methanogenic pathways (Friedmann et al., 1990).

When Se was added to the rice straw inoculated with granular sludge (Fig. 3a), among the three tested concentrations, only the recommended dose of 1.0 µg/g TS (Table 3) enhanced the final production (i.e. 7.8% higher than control). In contrast, doubling the recommended dose led to a negligible increase by 0.8%. A negative response (i.e. – 0.4%) was obtained with the highest dose of 5.0 µg of Se/g TS (Table 4). On the other hand, when buffalo manure was used as the inoculum (Fig. 3b), the addition of Se resulted in a consistent improvement of the cumulative production yield with all the selected dosages (Table 4).

The importance of Se for microbial growth has long been recognized, due to the fundamental catalytic role of selenoproteins in bacteria and archaea (Stock and Rother, 2009). Nonetheless, limited information about the effect of Se addition on the AD process is available in the literature. Studies showed that a lack of Se in anaerobic processes leads to a decrease of microbial activities (Lebuhn et al., 2008; Worm et al., 2009). During the AD of food waste, the addition of Se enhanced the biomethane production by more than 30% (Ariunbaatar et al., 2016; Facchin et al., 2013).

In this study, rice straw was pretreated using NaOH and inoculated with buffalo manure. The final biomethane production yield (i.e. 318 mL CH_4/g VS) obtained from rice straw pretreated using NaOH and inoculated with buffalo manure showed a significant (i.e. $p = 0.018$) enhancement, equal to 21.4%, compared to that achieved with the untreated substrate (Table 4, Fig. 2b). Co and Ni were separately added to the pretreated rice straw in order to investigate possible synergistic effects of combining the alkaline pretreatment with TE addition. The specific biomethane production yield was further increased by only 3.5 and 3.8% through Co and Ni dosing, respectively (Table 4, Fig. 2b). This extra enhancement due to TE addition was, however, not statistically significant compared to the result obtained with the pretreatment alone. The increase of the biogas production yield caused by the NaOH pretreatment remained the only statistically significant enhancement (i.e. $p = 0.018$) observed in this study.

Alkaline pretreatment has proven to be successful in increasing the biodegradability of lignocellulosic materials, thus enhancing the biogas yields (Sambusiti et al., 2012). Breaking the linkages between carbohydrates and lignin, the alkaline pretreatment provokes an increased porosity and a delignification of the raw material (Zheng et al., 2014).

3.3 Effect of TE addition and pretreatment on the volatile fatty acids production

The effect of TE addition and alkaline pretreatment was further assessed by monitoring the VFA evolution during the first 10 d of AD. The concentrations of the total VFAs recorded during the 2 runs of BMP tests are reported in Fig. 4. The total VFA concentration, expressed as mg/L of acetic acid, was given by the sum of acetic, propionic, iso-butyric and butyric acids, with the first two being the predominant VFAs produced during the BMP tests.

The total VFA concentration was constantly below 500 mg/L during the AD of rice straw inoculated with granular sludge (Fig. 4a) and the addition of Co or Ni did not cause statistically significant differences ($p > 0.05$) in the total VFA concentrations. On the other hand, the production of VFAs was markedly enhanced by the alkaline pretreatment (Fig. 4b), with peaks of total VFAs around 900 mg/L recorded on the third day of AD. This relevant increase, compared with the untreated straw, indicated that the alkaline pretreatment enhanced the hydrolysis of the rice straw, which consequently caused a higher methane production yield from the pretreated straw (Table 4). Despite the larger amount of available VFAs after the NaOH pretreatment, the addition of Co and Ni to the pretreated straw produced only a slight supplementary increase of the final methane production. The VFA production achieved with the pretreated straw was similar with and without TE addition, resulting in no synergistic effects.

Previous studies showed the importance of TE addition to stabilize the AD process in case of VFA accumulation. Se is particularly important to prevent propionic acid accumulation by providing the co-enzymes necessary for the oxidation of formate, which is a breakdown product of propionate (Banks et al., 2012). Pobeheim et al. (2011) reported that Co and Ni addition was able to stabilize a continuous digester performance during the AD of maize silage, when a deficit of the two TEs caused VFAs to accumulate. An increase of the VFA utilization rate by TE addition was observed also by Espinosa et al. (1995) and Ariunbaatar et al. (2016) during the AD of cane molasses stillage and food waste, respectively. In those studies, the total VFA accumulated to concentrations of 1500 – 10000 mg/L in the absence of TE supplementation, whereas a reduction to levels around 500 – 1000 mg/L was observed when TEs were provided. In contrast, in the present study the VFA concentrations never exceeded 500 mg/L during the AD of rice straw. This could be attributed to the hydrolysis being the limiting step for lignocellulosic materials, rather than methanogenesis as for more easily degradable substrates (Mata-Alvarez et al., 2000). The pretreatment was more effective than the TE addition in increasing the hydrolysis of rice straw and this resulted in a higher production of VFAs. The methanogenic archaea populations present in both the inocula were able to efficiently convert the acetic acid produced to methane. Even when the VFA concentration was increased as a result of the pretreatment, the addition of TE was not necessary to achieve a complete acetate conversion.

4. Conclusions

The addition of Co, Ni and Se did not result in a significant improvement of the AD of rice straw. On the contrary, the use of an alkaline pretreatment with NaOH caused a considerable enhancement of AD, increasing the biogas production yield by 21.4%. The marginal effect observed after TE supplementation on the untreated rice straw could be linked to its complex lignocellulosic structure, which required an enhancement of the hydrolysis, rather than the methanogenesis. This observation was also supported by monitoring the VFA concentration, which was significantly increased by the pretreatment, whereas negligible effects were obtained after TE addition.

Acknowledgments

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Figures captions:

Fig. 1. Impact of different Co (a) and Ni (b) concentrations on the cumulative biomethane production from the AD of rice straw inoculated with anaerobic granular sludge.

Fig. 2. Impact of recommended Co and Ni concentrations on the cumulative biomethane production from the AD of untreated (a) and NaOH pretreated (b) rice straw inoculated with buffalo manure.

Fig. 3. Impact of different Se concentrations on the cumulative biomethane production from the AD of rice straw inoculated with anaerobic granular sludge (a) and buffalo manure (b).

Fig. 4. Total VFA production during the first 10 d of AD of rice straw inoculated with anaerobic granular sludge (a) and buffalo manure (b).

Tables:

Table 1

TE dosing in anaerobic digesters loaded with lignocellulosic residues.

Lignocellulosic residue	TEs added	Concentration	Inoculum used	Experimental configuration	Methane yield enhancement	Reference
Corn stover	Fe, Co, Ni	1.0 (Fe) + 0.4 (Co) + 0.4 (Ni) mg/L	Activated sludge	Batch, 35°C	+62.0%	(Liu et al., 2015)
Maize straw	Fe	50.0, 200.0, 1000.0, 2000.0 mg Fe/L	Chicken manure	Batch, 37°C	+15.0% (with 1000.0 mg Fe/L)	(Khatri et al., 2015)
Mango waste	Fe, Co, Ni	4000.0 (Fe), 125.0 (Co), 125.0 (Ni) mg/L	Cattle dung	Semi-continuous, 15 to 36°C	+ 120.0% (with 4000.0 mg Fe/L)	(Raju et al., 1991)
Napier grass	Co, Ni, Mo, Se	0.25 (Ni) + 0.19 (Co) + 0.30 (Mo) + 0.062 (Se) mg/L/d	Rumen fluid and grass leachate	Continuous, 35°C	+ 40.0%	(Wilkie et al., 1986)
Phragmites straw	Fe	0.5 to 10.0 mg Fe/L	Cow dung	Batch, 35°C	+ 18.1% (with 10.0 mg Fe/L)	(Zhang et al., 2016)
Phragmites straw	Co	0.2 to 2.0 mg Co/L	Cow dung	Batch, 35°C	+ 18.0% (with 0.8 mg Co/L)	(Tian et al., 2017)
Phragmites straw	Cu	30.0 to 500.0 mg Cu/L	Cow dung	Batch, 35°C	+43.6% (with 30.0 mg Cu/L)	(Hao et al., 2017)
Rice straw	Co, Ni, Se	9.0 to 45.0 (Co), 9.0 to 45.0 (Ni), 1.0 to 5.0 (Se) mg/kg TS straw	Buffalo manure, anaerobic granular sludge	Batch, 37°C	+11.6% (with 45.0 mg Ni/kg TS straw	This study

Table 2

Characteristics of the raw rice straw and the two inocula used.

	Rice straw	Inoculum 1 (granular sludge)	Inoculum 2 (buffalo manure)
TS (%)	93.1 ± 0.1	16.1 ± 0.9	5.1 ± 0.1
VS (%)	76.8 ± 1.1	11.0 ± 0.6	3.4 ± 0.0
TKN (g N/kg TS)	11.2 ± 0.2	51.0 ± 0.4	27.1 ± 1.3
Fe (µg/g TS)	476.9 ± 81.3	25476.2 ± 833.1	623.0 ± 4.9
Cu (µg/g TS)	16.7 ± 4.6	318.9 ± 13.1	19.5 ± 0.2
Zn (µg/g TS)	61.9 ± 25.3	323.7 ± 0.3	69.7 ± 2.0
Co (µg/g TS)	< 1.0	10.0 ± 0.3	< 1.0
Ni (µg/g TS)	2.0 ± 0.0	28.1 ± 0.3	10.4 ± 0.1
Se (µg/g TS)	< 1.0	< 1.0	< 1.0
Cellulose (%)	28.6 ± 0.2	-	-
Hemicellulose (%)	19.5 ± 1.2	-	-
Lignin (%)	17.3 ± 0.3	-	-

Table 3

Determination of TE addition in the BMP tests.

Trace element	Recommended supplementation (Hinken et al., 2008) (μg/gTS)	TE in the used rice straw (μg/gTS)	TE addition used in this study (μg/gTS)
Co	9	0	9
Ni	11	2	9
Se	1	0	1

Table 4

Specific methane production obtained from the BMP tests aimed at studying the effect of TE supplementation and pretreatment of rice straw.

TE added	TE concentration (μg/g TS_{straw})	Inoculum	Specific methane production (mL/g VS)	Increase from control (%)
Control run 1	0	Granular sludge	259 ± 5	-
Co	9	Granular sludge	274 ± 22	+ 5.8
Co	18	Granular sludge	275 ± 16	+ 6.2
Co	45	Granular sludge	272 ± 7	+ 5.0
Ni	9	Granular sludge	283 ± 7	+ 9.2
Ni	18	Granular sludge	274 ± 20	+ 5.8
Ni	45	Granular sludge	289 ± 29	+ 11.6
Control run 2	0	Granular sludge	244 ± 11	-
Control run 2	0	Buffalo manure	262 ± 26	-
Co	9	Buffalo manure	282 ± 8	+ 7.6
Ni	9	Buffalo manure	277 ± 10	+ 5.7
Se	1	Granular sludge	263 ± 39	+ 7.8
Se	1	Buffalo manure	282 ± 31	+ 7.6
Se	2	Granular sludge	246 ± 26	+ 0.8
Se	2	Buffalo manure	279 ± 14	+ 6.5
Se	5	Granular sludge	243 ± 17	– 0.4
Se	5	Buffalo manure	276 ± 7	+ 5.3
Pretreated rice straw	0	Buffalo manure	318 ± 9	+ 21.4
Pretreatment + Co	9	Buffalo manure	329 ± 11	+ 25.6 (+ 3.5)
Pretreatment + Ni	9	Buffalo manure	330 ± 12	+ 26.0 (+ 3.8)

Fig. 1 (with colors)

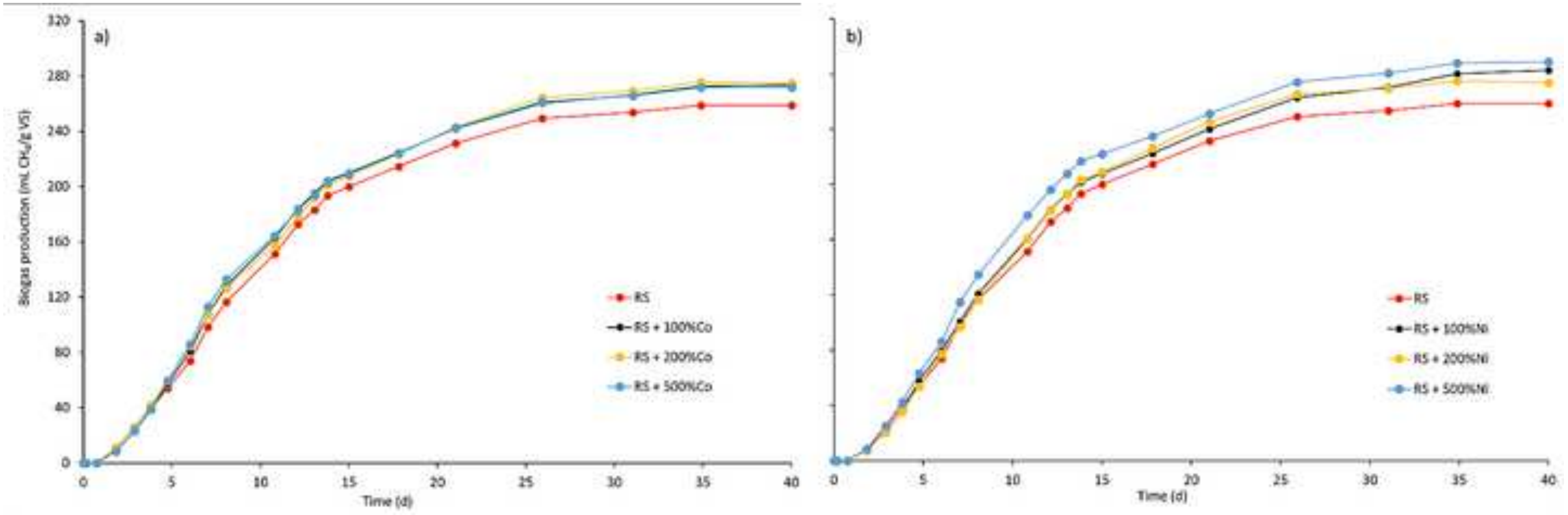
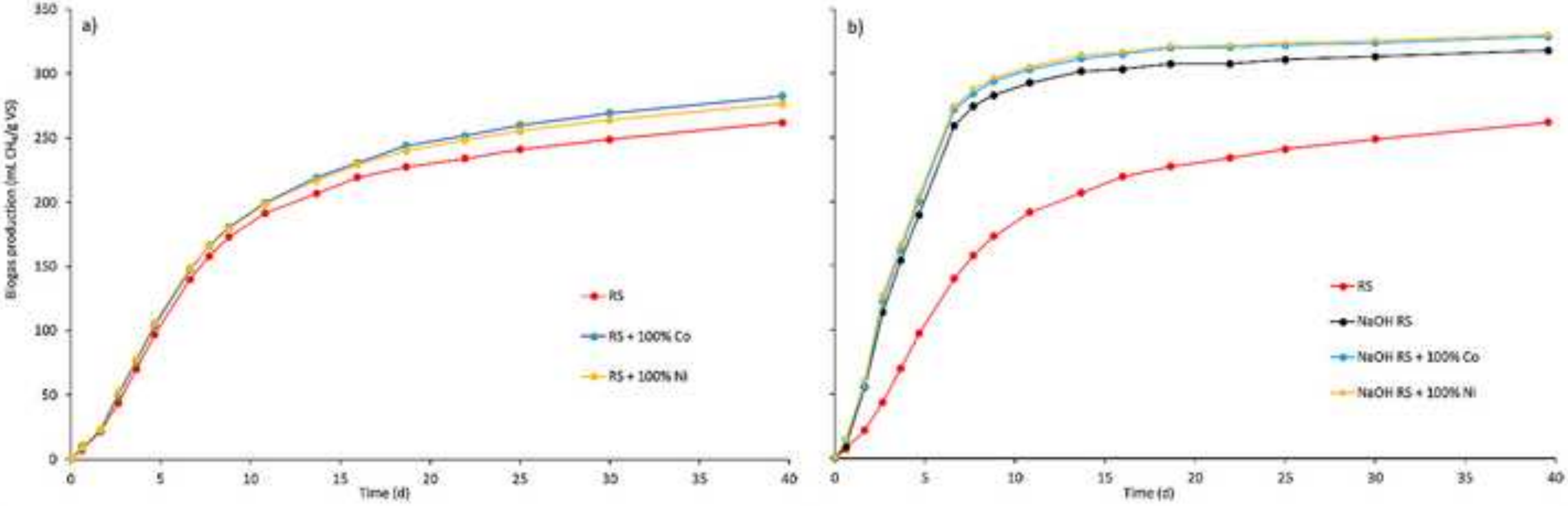


Fig. 2 (with colors)



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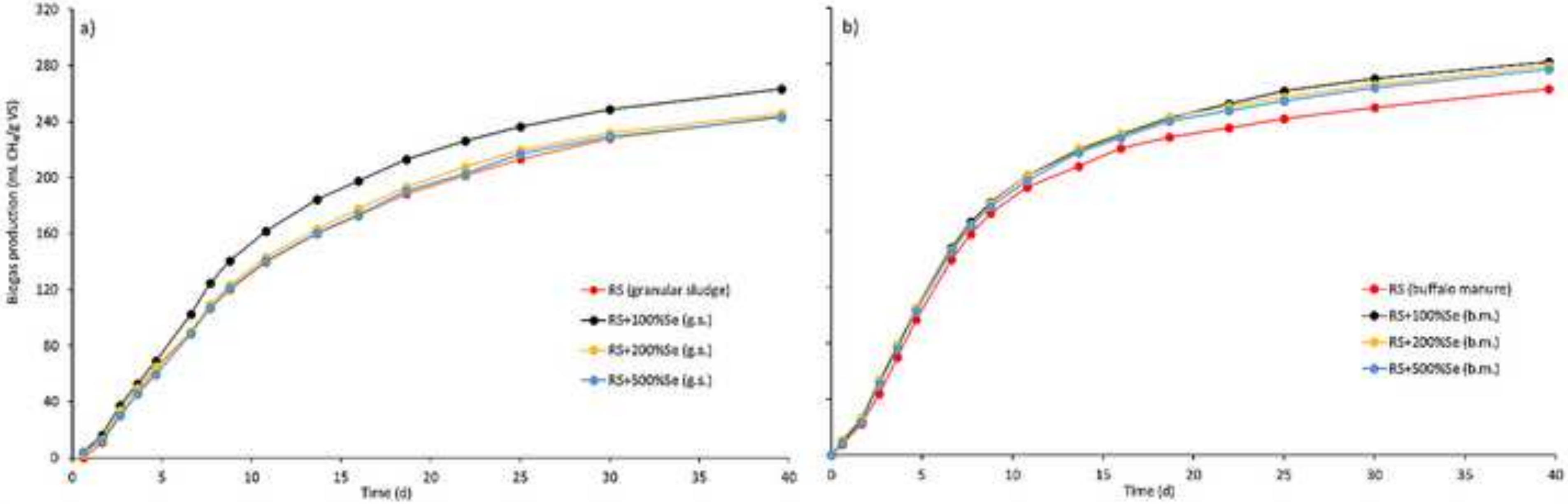

Fig. 4 (with colors)

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