INCREASE IN BIOGAS PRODUCTION IN ANAEROBIC SLUDGE DIGESTION BY COMBINING AEROBIC HYDROLYSIS AND ADDITION OF METALLIC WASTES

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Abstract

The objective of this work was to determine the effect of a controlled micro-aeration as a pretreatment or hydrolytic stage of mixed sewage sludge and the incorporation of solid wastes as a source of trace metals in the anaerobic digestion of this pretreated sludge. Three experimental runs were carried out under the same conditions in laboratory-scale anaerobic reactors, to which a previously aerated mixed sludge was added as a substrate and anaerobic sludge as the inoculum. Two anaerobic digesters (blank) were also operated without aerobic pretreatment and without the addition of solid wastes. The aerobic pretreatment was performed with an aeration flow of 0.35 vvm, time of 48 hours and temperature of 35 °C. All anaerobic reactors were operated at the mesophilic temperature

of 35 ± 2 °C. Fly ash or Copper mining residues were added to the anaerobic reactors as trace metal supplementation. The aggregated concentrations were 250 mg.L⁻¹ fly ash, 25 mg.L⁻¹ Copper mining residues and 0 mg/L. The blank reactors produced 38% less methane than those generated in the reactors operating with the pre-aerobic treatment without addition of solid wastes (controls). It was found that the reactors with micro-aerobic pretreated sludge and the addition of fly ash gave the best yields of methane, producing a 201.6% increase in methane with respect to the blank reactors. On the other hand, the pretreatment of micro-aerobic hydrolysis and the addition of mining residues generated an increase of 185.8% in methane production compared to the blank reactors.

Key words: anaerobic digestion; copper mining residues; fly ash; methane production; micro-aeration; sewage sludge

1. INTRODUCTION

One of the great problems that occur in sewage treatment plants is the enormous amount of sludge that is generated from the primary sedimentation of wastewaters and the production of the waste activated sludge (WAS) [1,2]. These sludges have a great amount of organic matter that must be stabilized before its final disposal [3]. Anaerobic digestion is widely applied for effective sludge stabilization and biogas production and it involves four steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis [4].

The hydrolysis step (particulate organic matter conversion into soluble substances) and the methanogenesis step (conversion of acetic acid, CO₂, H₂, and others to methane) are believed to be the rate-limiting steps of anaerobic digestion [5,6].

Several physical and chemical methods have been applied as hydrolytic pre-treatments such as ultrasonication, alkaline hydrolysis, high pressure extruding, ozonization, enzymatic hydrolysis and thermal hydrolysis, and these pre-treatments have been applied individually or in combination [7-11]. Among them, thermal hydrolysis has proven to be a successful approach to making sewage sludge more amenable to anaerobic digestion and there are nearly 80 facilities either in operation or in planning around the world, with the first installation in 1995 [12]. The reported benefits of thermal hydrolysis are related to: increased digestion loading rate due to altered rheological properties, improved biodegradation of (especially activated) sludge, pathogen reduction and enhanced dewaterability [13,14]. Also, the energy input needed for the hydrolysis process is thermal energy and could be satisfied from the energy production of the process itself, resulting in an energetically self-sufficient process [15]. In spite of the advantages that thermal hydrolysis presents, it also has some disadvantages or limitations, being the main ones: investment costs are relatively high because several tank - reactors must be installed that operate at temperatures of 150 – 180 °C and pressures of 0.37-0.95 MPa [16-18]. These operational conditions demand extreme care by imposing on the treatment plant an important operational pressure. A constant threat for anaerobic digestion following the thermal hydrolysis process is related to the possible ammonium inhibition of the digestion process. Thermal hydrolysis allows an increase in loading rate due to altered rheology, increases the solubility of proteins, and improves the breakdown of those proteins [19], which causes an increase in ammonia and also in alkalinity, resulting in a rise in pH. The increase in pH (and also temperature) shifts the equilibrium position away from ammonium to its free state. Having no charge, free ammonia diffuses easily into the cells and once

there, it ionizes to form ammonium resulting in an intracellular pH imbalance, causing the inhibition of methanogenic archaea [20,21].

Biological hydrolysis has also been studied [22-24]. The biological process that has given better results is micro aerobic hydrolysis [25-27]. Lim and Wang [28] suggested that the added oxygen was consumed fully by facultative microorganisms and a reducing environment for organic matter degradation was maintained. Other than higher COD solubilization, micro-aeration pretreatment led to greater VFA accumulation and to the conversion of other short chain fatty acids to acetate. This could be due to the enhanced activities of hydrolytic and acidogenic bacteria and the degradation of slowly biodegradable compounds under microaerobic conditions. Recently, Montalvo et al. [29,30] found that by means of an air supply to mixed sewage sludge prior to anaerobic digestion the methane yield value increased by 114% with respect to that obtained with the non-aerated sludge. In the micro-aeration process carried out at an aeration level of 0.35 vvm, increases in soluble proteins and total sugar concentrations of 185% and 192% with respect to their initial values were found, respectively, after 48 h of aeration. At the above micro-aerobic conditions, soluble chemical oxygen demand (COD_s) augmented 150%, whereas the volatile suspended solids (VSS) content decreased to 40% of their initial respective values. For aeration times of 60 h the above-mentioned parameters did not vary significantly with respect to those observed at 48 h.

Methanogenic archaea are microorganisms that carry out methane formation in anaerobic processes. It is a specialized group of obligate anaerobic microorganisms that decompose organic matter to form methane and for carrying out this biochemical reaction they require some heavy metals and cations as nutritional requirements [31,32]. It has also

been found that the absence of these micronutrients has caused problems in anaerobic processes [33,34]. On the other hand, it has been proven that the use of metallic compounds improves anaerobic biodegradability and biogas production [35,36]. Zhang et al. [37] fed anaerobic reactors with a model trace element solution (Fe, B, Zn, Cu, Mn, Mo, Co, Ni, Se) and found a better performance in terms of higher and stable methane productivity, higher methane content, constant pH value, and relatively lower VFA level than reactors operated without a trace element solution. Kim et al. [38] observed that an efficient removal of propionate at high levels of VFA required supplementation of Ca, Fe, Ni, and Co in a thermophilic non-mixed reactor.

In spite of these obvious advantages of the application of traces of metals to the anaerobic digestion, this procedure must be applied taking into account that trace element supplementation anaerobic digestion can both stimulate or inhibit the process depending, basically, on their concentrations [39,40]. Also, it must be taken into account that typically, trace metal-requirements have been reported with pure cultures with a simple substrate, such as acetate, hydrogen, or methanol. However, for more complex substrates and real wastewaters, trace nutrient requirements appear to have been satisfied empirically without the solid knowledge of minimum requirements [41].

The addition of solid wastes containing metals has been evaluated by some researchers using different residues such as municipal solid waste incinerator (MSWI) fly, refuse and nickel solid mining residues in the anaerobic digestion of the organic fraction of municipal solid waste and synthetic wastes obtaining very favourable results [42-45]. This alternative not only proves to be an interesting economic route from the point of view of the

source of metals, but it is also a significant contribution to reducing the environmental liabilities that constitute the waste used as a source of metals giving a use value to them.

In combustion processes in thermal power plants, a large amount of fly-ash products (FAP) is generated. The FAP produced from power plants is taken to landfills or stored in ash lagoons [46]. These disposal strategies not only increase the burden on landfills, but they also have a significant impact on the surrounding habitats and ecosystems [47]. But fly ash has an important content in several metals which are necessary for methanogenic archaea [48]. Other solid residues that have several metals come from copper mining extraction. Due to their compositions, they are attractive for use as nutrient and trace metal suppliers in anaerobic digestion processes. Moreover, given that they are wastes from the mining industry, they do not represent an additional cost for the process.

Thus, the aim of the present work, related to the biomass conversion into renewable energy, was to evaluate the influence of applying micro-aeration to improve the hydrolysis step of mixed sewage sludge and adding metals from solid residues such as fly ash or copper mining residues to enhance methanogenesis yield in the anaerobic digestion process of the mentioned sludge carried out at a mesophilic temperature. This is the first report that appears in the literature on the use of copper mining residues in the anaerobic digestion process and also is the first report showing the combination of the application of pre-aerobic hydrolysis with subsequent anaerobic digestion applying these residues.

2. MATERIALS AND METHODS

The study consisted of the realization of two experimental series (I and II). In the experimental series I, the behaviour of the micro-aeration in the hydrolysis of mixed sludge

was evaluated by performing three experimental runs with different samples of these sludges to obtain representative results. All experimental runs were performed in duplicate. In the experimental series II, the behaviour of anaerobic digestion of sludge was evaluated using mixed sludge, with or without aerobic pretreatment and with or without solid residues containing traces of metals. In the series II, three experimental runs were also performed and each assay was carried out in duplicate.

2.1. Raw materials

The substrate for all the assays was a mixture of primary sludge (60%) and secondary sludge (waste activated sludge, WAS) (40%). This mixture is called mixed sludge and it comes from “La Farfana”, a municipal wastewater treatment plant that is operated by Aguas Andinas, located in Santiago de Chile. The initial values of the Physico-chemical parameters of the reactors (inoculum + mixed sludge, IMS) are summarized in Table 1. The three different values included corresponded to different samples of mixed sludge.

The inoculum for anaerobic assays was obtained from a sludge anaerobic reactor operated in “La Farfana” and had a specific methanogenic activity of $0.34 \text{ g CH}_4\text{-COD}\cdot\text{g VSS}^{-1}\cdot\text{L}^{-1}$; VSS of $95\text{-}105 \text{ g}\cdot\text{L}^{-1}$, and pH of 7.4. In the micro-aeration tests no inoculum was required since the mixed sludge contained aerobic microorganisms from the WAS.

The fly ash was obtained from a thermoelectric power plant located in the north of Chile. Ash was taken from electrostatic precipitators used to collect particulate matter generated in the combustion of bituminous coal in thermoelectric power plants, which are placed before the gaseous effluents leave the plant. Mining solid residues from copper

extraction were obtained from a copper mining located in the north of Chile. Table 2 shows the main chemical characteristics of both solid residues.

Table 2 shows that the mining residues possess a greater amount of Mn, Mo, Co, Fe and Cu compounds indicated in the literature as stimulants of the anaerobic process, in particular the latter, in relation to the ashes, due to the origin of the material [37]. However, the ashes contain more nickel and a good amount of iron. It should also be noted that the fly ashes are generated by a high temperature oxidation process, so the metals that are originally in the fuel are mainly converted into oxides that are poorly soluble compounds [48].

2.2. Experimental design and set up.

Figure 1 shows a scheme of the experiment flow chart.

The micro aerobic hydrolysis tests (Series I) were carried out in flasks of 900 mL of effective volume, where air was supplied by fish tank pumps through a hose that had a passage valve for regulating the air flow to 0.35 volume of air per reactor volume per minute (vvm) for 48 hours. The process temperature was kept at 35 °C by temperature-regulated baths [29]. In each pretreatment air was injected continuously into the bioreactors by mini-compressors (0–10 L per minute, Lpm) and distributed by small diffusers placed almost at the bottom of each reactor. The air flow rate (AFR) was calibrated before the pretreatment assays using the volume variation method.

The performance of a micro-aerobic hydrolysis of mixed sludge and its influence as a pre-treatment of sludge for its subsequent anaerobic digestion was previously evaluated.

Three experimental series were carried out to evaluate the optimum micro-aeration levels in the range from 0.1 to 0.5 air volume/min. reactor volume (vvm) and operation times within the range of 24–60 h. The maximum methane yield [$35 \text{ mL CH}_4/\text{g VSS added}^{-1}$] was obtained for an aeration level of 0.35 vvm. In other study the effect of air flow rate (AFR), pre-treatment time, and temperature on a microaerobic pre-treatment were determined, including its effect on CH_4 generation. For this, four AFR (0.1, 0.3, 0.5, and 1 vvm), three temperatures (20, 25 and 35°C), and three aeration times (24, 48 and 60 h) were evaluated in 1-L and 5-L bioreactors. The effect on CH_4 production was evaluated in 280-mL bioreactors, using previously aerated sewage sludge. It was found that the micro-aerobic pre-treatment improves the hydrolytic process, with an increase of proteins, total sugars, soluble chemical oxygen demand (COD), and a greater removal of volatile suspended solids (VSS) compared to a system without aeration. It was determined that an AFR = 0.3 vvm, 48 h of aeration time, and a temperature of 35°C were the best operational conditions for increasing hydrolysis rate.

In the Series II glass reactors of 200 mL effective volume were used. Each reactor was filled with 40 mL of anaerobic inoculum and 160 mL of mixed sludge, which corresponded to 20% and 80% of the effective volume of the reactor, respectively.

The anaerobic digesters were sealed and the headspace was flushed with N_2 at the beginning of the tests. The produced biogas was measured by liquid displacement after going through a 3% (w/w) NaOH solution to capture the produced CO_2 ; the remaining gas was assumed to be only methane [49,50]. The anaerobic tests were carried out for a period of approximately 20–25 days until the accumulated gas production remained essentially unchanged, i.e. on the last day production was lower than 3% of the accumulated methane

produced. Due to the importance of maintaining homogeneity of the sludge within the reactors, they were subjected to a moderate manual stirring several times per day for several seconds. The anaerobic digester temperature was kept at 35 ± 2 °C using automatically controlled aquarium heaters.

The concentrations of fly ash and copper mining residues used in the anaerobic assays were $250 \text{ mg}\cdot\text{L}^{-1}$ and $25 \text{ mg Cu}\cdot\text{L}^{-1}$, respectively. In addition, a reactor without metal addition was also used as the control. An experimental run without aerobic pretreatment and without metal addition was also carried out as a blank assay.

A schematic diagram of the experimental design used is illustrated in Figure 2.

2.3 Chemical and statistical analyses

All chemical analyses were determined according to the Standard Methods of the American Public Health Association Standard Methods [51]. Specifically, COD and VSS were analysed according to the closed digestion and colourimetric method 5220D and 2540B standard methods, respectively. pH was determined using a Crison model 20 Basic pH-meter. The evolution of parameters during the aerobic assays was monitored by samples taken from each reactor at different times, whereas parameter evolution during the anaerobic assays was carried using the following procedure: two or three times a week, two digesters working under the same conditions were taken out of operation and the values of all physical and chemical parameters were determined. The determination of metal concentrations was performed using a Perkin Elmer Optima 3000 ICP according to standard protocols based on official methods of the US-EPA [52].

The statistic processing and analysis of data were carried out using the Minitab 8 software. An analysis of variance (ANOVA) was made, and a comparison of confidence intervals for mean values was made with a confidence level of 95%.

As was previously mentioned in section 2.2, various experimental runs were performed either in experimental series I or II with the aim of assessing the influence of the sludge characteristics and their variations on the reactor behaviour and performance. However, considering that the results obtained in the different tests have variations of the order of 3 - 5%, in some cases only data corresponding to one experimental run will be shown, each one having been performed in duplicate. Each analysis was also performed, at least, in duplicate, which allows the statistical validation of these results.

3. RESULTS AND DISCUSSION

3.1 Series I: Aerobic pretreatment (hydrolysis)

Table 3 shows the main results obtained in the experimental Series I. Table 3 also shows the variation (increase or decrease) in different parameters during the micro-aerobic process (results from three assays with three different mixed sludge samples). It can be observed that VSS decreases while soluble organic matter (COD_S) increases significantly. This significant increase in the soluble organic matter can be related to an increased solubility of this material, allowing to augment its content in simpler soluble compounds. The pH increase is mainly due to the increase in total ammonia between 170% and 350%, as shown in Table 3. In this table are presented the results of three assays carried out with three different mixed sludge samples. As was mentioned previously it was convenient to submit to study three samples of sludge taken at different times in order to obtain more

reliable results. From this table can be observed the range of values of the different parameters analyzed, both at the beginning and at the end of the micro aeration experiments as well as the percentages of increase or decrease of these values.

The dissolved oxygen concentration at the end of micro-aeration was zero in all the processes assayed.

As shown in Table 3, the values of COD_S, soluble protein and total sugars present a significant increase at the end of the aerobic pretreatment stage, indicating that micro-aeration improves the hydrolysis step, since it increases the solubility and the conversion of complex organic particles into simpler soluble compounds. Simultaneously, a degradation of the organic matter occurs and as expected a decrease in the VTS and VSS contents was achieved at the end of the process. The pH undergoes a slight increase during micro-aeration, which may be mainly due to the increase in the ammoniacal nitrogen caused by the rupture of the complex organic matter such as aminoacids and proteins.

3.2 Series II: Anaerobic assays

As was previously explained in this experimental series only the results corresponding to one of the three experimental runs carried out will be shown.

Figure 3 illustrates the pH evolution during the anaerobic processes.

This figure 3 shows a decrease in pH during the early days of the process, which is caused by the action of acidogenic bacteria [53]. After the first three days, a trend of increasing pH associated with protein hydrolysis can be seen which can be confirmed by the increase in ammonium nitrogen as shown in Table 4. Finally, pH stabilises between 6.6

and 6.8, suitable values for a smooth trouble-free functioning of the process. Lim and Wang [28], who worked with previously aerated sludge, obtained very similar pH profiles to those found in this study. The pH profile obtained in the Lim and Wang [28] studies are very similar to those obtained in the present research. These authors found that, starting from pH 6.5, it decreased to 5.7 on the third day of anaerobic digestion, something that also occurred in the present investigation, starting with the same pH 6.5, and reaching a pH of 5.6 on the third day, with the pH risin from that day on, reaching pH 7.2 at 17 days of digestion. However, Lim and Wang reached pH 7.2 at 38 days of anaerobic digestion, and that may be due to the different characteristics of the substrates used in both studies, since these authors used co-digestion of brown water and food waste.

This means that despite the hydrolysis carried out by micro aeration, remaining materials are able to be hydrolysed during the early stages of the anaerobic process. After that, the pH may also rise because there are several acidophilic methanogenic *Archaea* such as *Methanosarcina* sp. which are favourable for consuming organic acids and preventing excessive pH decline [54]. There were no statistically significant differences in pH evolution between the different anaerobic processes operated. The ANOVA analysis showed that the $F_{cal} = F_{tab}$ so the hypothesis, with a significance level $p = 0.05$, is approved, that none of the mean values of the different processes differ. A more detailed analysis was performed with tStudent tests for the contrast of two means, finding no condition showed statistically significant differences between them.

Table 4 shows the amounts of ammonium that are achieved at the end of anaerobic processes. As can be seen, none of them can be considered toxic or inhibitory concentrations for anaerobic processes as indicated above.

Figure 4 shows the COD_S evolution during the anaerobic processes. It can be seen how the COD_S decreases with time, and in the early days this decrease is very small, a time period corresponding to the acclimatization stage. Final COD_S removals in anaerobic processes were 58 %, 68% and 69% for the control, copper mining residues and fly ash, respectively. There were no statistically significant differences between the results obtained for fly ash and mining residues.

Figure 5 shows how the volatile suspended solids (VSS) decreased with time, but from the 25th day onwards there was virtually no change in the VSS concentration. This behaviour matches with that observed in Figure 6 regarding the production of methane, which also practically ceases around the 25th day. VSS removals in the anaerobic processes were 38%, 59% and 61% for the control, copper mining residues and fly ash, respectively. There were no statistically significant differences between the results obtained for fly ash and mining residues.

Figure 6 shows the variation in the cumulative methane production ($\text{mLCH}_4 \cdot \text{gVSS added}^{-1}$) with digestion time. It can be seen that methane production increased by 50%, 162% and 200% for the control, copper mining residues and fly ash, respectively, compared to the anaerobic digestion of the blank. Huiliñir et al. [48] also found an increase of 135% in methane production in the batch anaerobic digestion process for residual sludge from the paper industry water treatment when fly ash was added to the digesters as suppliers of trace metals.

The significant increase in methane production when ash and mining waste were added to the digesters may be due to two factors: on the one hand, the inclusion of solids could contribute to an increase in the contact surface between microorganisms and substrate. However, given the high concentrations of suspended solids in the reactors this mechanism contributes little to the increase in process efficiency because much of these are inorganic suspended solids that tend to clog this contact surface. In some studies it has been shown that the addition of zeolites to the anaerobic digestion of piggery wastewaters (more diluted than mixed sludge) from certain doses has a negative influence on anaerobic digestion [55]. These authors found that up to $4 \text{ g of zeolite} \cdot \text{L}^{-1}$ the anaerobic process was favoured, but for doses higher than $8 \text{ g of zeolite} \cdot \text{L}^{-1}$ a significant reduction in methane production was observed. These researchers pointed out that the increase in total solid concentration also increases the apparent viscosity of the medium, thereby hindering mass transfer between the substrate and microorganisms responsible for the process, decelerating the anaerobiosis. In the same way, doses of $5 \text{ mg} \cdot \text{L}^{-1}$ of mining residues from Ni extraction (Cola) that contain a certain amount of Ni, Fe and Co allowed stimulating the batch anaerobic digestion of a synthetic substrate (composed of volatile fatty acids, VFA, and sucrose) increasing methane yield in relation to a control. By contrast, when the residue doses increased to $7 \text{ mg} \cdot \text{L}^{-1}$ the methane production decreased [43]. On the other hand, the two residues studied in the present work (fly ash and mining residues) have several metals that can contribute to enhancing the anaerobic process and to increasing methane production. While it is true that individual metal concentrations used in this study appear to be only stimulants for copper mining waste (according to Table 2) it is also known that combining several metals even at concentrations lower than those reported as stimulants

may enhance anaerobic digestion [54,56]. Another contribution that can be important to the increase in methane production is the presence of alkaline substances in anaerobic digestion processes. Lo [43] showed that the released alkali metals contained in bottom ashes from municipal solid waste seemed to exert a beneficial effect on anaerobic digesters within which the volatile acids were buffered by the increase in compounds with neutralizing capacity.

3.3 Metals in sludge digested

The Chilean law, and more specifically Article 24 of Presidential Decree N° 4 for handling sludge from sewage treatment plants establishes maximum concentrations for metals in sludge applied to agricultural soils (Class A) and degraded soils (Class B) [57].

Table 5 shows comparative metal values among digested sludge produced in anaerobic reactors and maximum values allowed for sludge Class A and B.

It should be noted that some elements such as Cd and Pb that do not initially appear in the fly ashes are detected, in extremely small amounts, in the sludge generated in the anaerobic process where the ash was added which may be due to the fact that in mixed sludge and in the sludge used as inoculum there would be a small amount of these chemical species

The digested sludge that had higher metal amounts was that derived from the digesters where copper mining residues were applied, the metal concentrations (mg.kg^{-1}) being the following ones: As (2.4); Cd (1.2); Cu (249); Ni (9.8); Pb (14); Zn (484). The requirements

for Class A sludge are the most strict, with the maximum permitted concentration (mg.kg^{-1}) of metals in sludge being as follows: As (20); Cd (1.2); Cu (8); Ni (80); Pb (300); Zn (2000). As can be seen the metal concentration in digested sludge is well below than allowable values by law to use sludge digested as fertilizer.

The use of traces of metals in the anaerobic digestion of residues has been treated to some extent in the literature and the positive influence of these, up to certain levels, on the production of methane has been fully demonstrated [58]. Two aspects must be considered in order to determine the real causes of the effectiveness of the metals on the anaerobic digestion, one is related to the individual effect of the different metals or the combined effect of these ones [59] and the other aspect are related with bioavailability of the metals [60]. On the other hand the improvement of the anaerobic processes has also been observed when certain solids have been added inside the digesters increasing the contact between the microorganisms and the substrates, acting as a kind of biocatalysts [61] or these solids have served as a support medium to immobilize microorganisms and form biofilms with high concentration of biomass and increase the rate of degradation of organic matter with the consequent increase of methane production in digesters [62]. These physical - biological phenomenon will depend on the characteristics of the surface of the materials added to the anaerobic process. In the case of the fly ashes and the mining residues used in this investigation there are different studies where it is shown that these materials can have rough surfaces or not depending on the material of origin or the deposit from where they come [63,64]. The characteristics of the crystalline and amorphous phases in fly ash vary with the operating conditions of the thermal power plant and the types of fuels used. Therefore, it is presumed that these phenomena could be occurring in

the anaerobic processes developed in the present study, however, it is very convenient to make in-depth studies about those aspects

As previously mentioned, the process applied on an industrial scale to improve the hydrolysis of sludge is thermal, and its limitations or disadvantages have been commented, being the aerobic process much simpler it will be possible in the near future to design and implement it at a real scale.

CONCLUSIONS

It was convincingly shown that the application of a small amount of air (micro-aeration) significantly improved the hydrolysis of mixed sewage sludge obtaining a process effluent with suitable characteristics for anaerobic digestion (35°C , $0\text{ mg}\cdot\text{L}^{-1}$ of dissolved oxygen and pH increased). The addition of fly ash or mining waste significantly enhanced the anaerobic digestion of the sludge, thus increasing methane production by more than 100%. A combination of micro aerobic hydrolysis with anaerobic processes carried out with the addition of trace metals from these residues increased methane production by 162%–200%. The digestates obtained after the anaerobic digestion of microaerated sludge with the above metal residues contain minimum metal concentrations that allow its use as fertilizer in agricultural soils.

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Figure captions

Figure 1. Experimental flow chart

Figure 2. Schematic diagram of the experimental design used.

Figure 3. Evolution of pH during the anaerobic processes.

Figure 4. Evolution of CODS during the anaerobic processes.

Figure 5. Variation in the VSS content with time during the anaerobic processes.

Figure 6. Variation in cumulative methane production (mL CH₄.g VSS⁻¹) with digestion time (days).

Table 1

Table 1. Initial mean values of physico-chemical parameters of reactors.

Parameters						
IMS	VTS ^a (mg·L ⁻¹)	VSS ^b (mg·L ⁻¹)	COD _T ^c (mg·L ⁻¹)	COD _S ^d (mg·L ⁻¹)	pH	TAN ^e (mg·L ⁻¹)
1	34000	31000	39700	7600	6.04	232
2	32100	32100	39200	8000	6.03	129
3	35300	32600	40200	7200	6.05	237

^aVolatile total solids; ^bVolatile suspended solids; ^cTotal Chemical Oxygen Demand;

^dSoluble Chemical Oxygen Demand; ^eTotal ammonia nitrogen

Table 2

Table 2. Metal composition of the solid residues used as trace metal suppliers.

Element	Fly ash (mg.kg⁻¹)	Mining residues (mg.kg⁻¹)
Cd	<DL	2.38 ± 0.2
Zn	5.40 ± 0.5	19.09 ± 2.4
Cr	2.92 ± 0.3	1.94 ± 0.3
As	<DL	1.89 ± 0.2
Cu	2.21 ± 0.2	2321.14 ± 198
Ni	6.17 ± 0.4	3.43 ± 0.3
Pb	<DL	11.86 ± 1.4
Al	1315.42 ± 112	1678.16 ± 120
Se	<DL	<DL
Mn	21.05 ± 2.0	66.10 ± 5.9
Ag	<DL	<DL
V	13.36 ± 0.9	3.95 ± 0.4
Ba	44.36 ± 3.8	4.52 ± 0.3
Co	<DL	6.35 ± 0.5
Mo	<DL	11.67 ± 0.9
Be	<DL	<DL
B	35.03 ± 2.9	100.42 ± 12
Fe	3083.58 ± 287	17421.06 ± 1812

DL: Detection Limit

Table 3

Table 3. Variation in different parameters during the micro-aerobic processes*.

Parameters	Initial values	Final values (48 hours)	Increase (+) or decrease (-) (%)
VTs ($\text{mg}\cdot\text{L}^{-1}$)	35300-32100 $\pm$ 1200	28593-26001 $\pm$ 750	19 (-) $\pm$ 2
VSS ($\text{mg}\cdot\text{L}^{-1}$)	32600-31000 $\pm$ 1000	26406-25110 $\pm$ 680	29 (-) $\pm$ 3
COD _s ($\text{mg}\cdot\text{L}^{-1}$)	8000-7600 $\pm$ 700	13200-13800 $\pm$ 900	78 (+) $\pm$ 2
Soluble protein ($\mu\text{g BSA}^{\text{a}}\cdot\text{L}^{-1}$)	0.4-1.8 $\pm$ 0.2	2.5-4.0 $\pm$ 0.2	525 (+) $\pm$ 50
Total sugars ($\mu\text{g Glucose}\cdot\text{L}^{-1}$)	180-200 $\pm$ 85	500-600 $\pm$ 100	200 (+) $\pm$ 21
TAN($\text{mg}\cdot\text{L}^{-1}$)	129-237 $\pm$ 56	580-640 $\pm$ 100	170 (+) $\pm$ 15
pH	6.03-6.05 $\pm$ 0.02	6.20 $\pm$ 0.05	2 (+) $\pm$ 0.3

^aBovine Serum Albumin.

Table 4

Table 4. Initial and final ammonium nitrogen concentrations ($\text{mg}\cdot\text{L}^{-1}$) in anaerobic reactors.

	Influent	Effluent	Increase (%)
Control	639 ± 0	2175 ± 71	240
Mining residues	639 ± 0	2407 ± 311	277
Fly ash	639 ± 0	2356 ± 61	269

Table 5

Table 5. Comparative mean values (mg.kg^{-1}) among digested sludge produced in anaerobic reactors and maximum values allowed for sludge Class A and B.

Sludge	As	Cd	Cu	Ni	Pb	Zn
With Fly Ash	2.6 ± 0.3	1.14 ± 0.1	156.98 ± 17	9.05 ± 0.8	12.75 ± 0.9	455.22 ± 48
With Mining Residues	2.36 ± 0.3	1.23 ± 0.1	248.85 ± 20	9.79 ± 0.7	13.98 ± 1.4	484.19 ± 52
Class A	20	8	1000	80	300	2000
Class B	40	40	1200	420	400	2800

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6