Anaerobic digestion of wastewater rich in sulfate and sulfide: Effects of metallic waste addition and micro-aeration on process performance and methane production

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Abstract

This work explores the effect of two metallic wastes (mining wastes, MW; fly ashes, FA) and micro-aeration (MA) on the anaerobic digestion of wastewater which is rich in sulfate and sulfide. Two initial COD concentrations (5000 and 10000 mg/L) were studied under both conditions in batch systems at 35 °C, with a fixed COD/SO_4^{2-} ratio = 10, with 100 mg/L of S^{2-}. It was observed that the use of MW and FA in the assays with an initial COD concentration of 10000 mg/L resulted in a simultaneous increase in COD removal, sulfate removal, sulfide removal and methane generation, while MA only improved the COD and

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sulfide removals in comparison with the control system. On the contrary, the use of MW, FA or MA in systems with initial COD concentrations equal to or lower than 5000 mg/L did not show any improvement with respect to the control system in terms of COD removal, sulfate removal or methane generation, with only sulfide removal being positively affected by MW and FA.

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Introduction

At present, the anaerobic digestion of industrial wastewater is a process with low operational costs, which also allows obtaining sub-products such as biogas with an important energetic value. [1-3] Nevertheless, several of these industrial wastewaters coming from fishery, tannery, food processing, distillery, pulp and mill, mining, metallurgical, chemical, pharmaceutical, and oil refinery industries and livestock farming have compounds which are problematic for biological processes, [4, 5] such as sulfates and sulfides, [6] which cause serious problems not only in biological processes, but also in the use of its products, namely biogas. [7-9] Sulfates are reduced to sulfides by sulfate-reducing bacteria (SRB) that use a wide variety of organic and inorganic substrates as electron-

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acceptors such as H_2, ethanol, fatty acids, etc. [10, 11] Several of these compounds are intermediates of the anaerobic process, and therefore, a competition for substrate is generated by the different anaerobic microorganisms (acidogenic, acetogenic and methanogenic biomass). From a thermodynamic and kinetic point of view, a sulfate reduction process is more favorable than methanogenesis. This fact implies that SRB can out-compete with methanogenic biomass when the ratio COD/SO_4^{2-} is low, a situation that decreases methane generation. [12] Reducing 1 g of SO_4^{2-} equals 0.67 g COD which means that for every kg of SO_4^{2-} that is reduced the production of CH_4 decreases in 0.23 m^3. [13] Using the COD/sulfate ratio as a reference parameter, performance losses on both CH_4 production and organic matter removal should not be observed for values higher than 10.[14] On the other hand, the product of this reaction is sulfide, a compound that generates problems not only in the biological processes (as inhibitor), but also in the combustion of biogas in engines. There is a general consensus that anaerobic inhibition begins to occur at values of 50-250 mg sulfur (from sulfide)/L that it is observed at influent sulfate concentrations higher than 2 g SO_4^{2-}/L. [15] Indeed, sulfide is commonly undesired in wastewater treatment processes due to: i) potential corrosion; ii) interference with other biological/chemical processes; iii) health and safety risks to workers. Therefore, it is very important to seek other alternatives that permit a decrease in the concentration of these compounds in anaerobic processes.

Among the technologies proposed for decreasing the sulfide concentration in anaerobic reactors are the addition of Fe for the precipitation of it, [16, 17] aerobic biofiltration and micro-aeration for the oxidation of it to elemental sulfur or sulfate. [18] Wastes rich in Fe such as waste iron powder [19] or rusty scrap iron [20, 21] have been used for the removal of

H$_2$S with good results, not only in H$_2$S removal, but also for improving methane generation. On the other hand, micro-aeration has been applied as a biological alternative even at full scale, with good results for sulfide removal. [22] Until now, there has been no research work that compares these technologies in wastewater which is rich in sulfates and sulfide. A comparison is necessary, not only in terms of sulfide removal or methane generation, but it is also important to know the effects of the sulfate-reducing process.

Even though metallic wastes rich in Fe have been explored for sulfide removal, some other metallic wastes that can be used for this purpose such as mining wastes or fly ashes from thermoelectrical plants have not been proposed. Mining wastes and fly ashes can contain not only Fe for precipitation of H$_2$S, but also other trace elements that can be useful for the stimulation of anaerobic digestion processes. [4, 23] Some experiments have been reported for the use of mining wastes [24, 25] and fly ashes [25-27] as stimulatory elements for anaerobic digestion. However, to the best of our knowledge, no comparative study has been carried out on the effects of these wastes and micro aeration on dissolved hydrogen sulfide (H$_2$S) reduction in digester or anaerobic sulfate removal.

Thus, the goal of this work was to determine the effect of metallic wastes such as mining wastes and fly ashes and micro-aeration on the anaerobic digestion of wastewater which is rich in sulfates and sulfide. The effects on COD, sulfate and sulfide removals were evaluated, including their influence on methane generation.

Materials and methods

Experimental setup

The anaerobic reactors used were glass mini-vessels of 250 mL total volume and 200 mL effective volume. Each reactor was filled with 40 mL of inoculum and 160 mL of synthetic wastewater, which correspond to 20% and 80% of the effective volume, respectively. [28] All the reactors were sealed and the headspace of each flask was flushed with nitrogen at the beginning of each assay. The produced biogas was passed through a 3% NaOH solution to capture CO_2, and the remaining gas was assumed to be methane. This system for measuring methane production is commonly used in this kind of experiments. [29] Due to the importance of maintaining the homogeneity of the sludge within the reactors, they were subjected to a moderate manual stirring several times per day for several seconds. In addition, the biogas generated inside the reactors also allowed for maintaining the agitation of the reactor contents. The anaerobic digester temperature was kept at 35 ± 2 °C using automatically controlled aquarium heaters.

Characteristics of metallic wastes

The mining wastes were obtained from an industry of Nickel mineral processing, where a solid waste known as "Cola" is produced, which was used in this work. 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 by the combustion of bituminous coal, which is placed before the gaseous effluents that leave the plant. The main characteristics of these wastes are shown in Table 1. The particulate diameter of the residues was 1 – 1.4 mm. [28]

Inoculum, substrate and experimental design

The inoculum was obtained from an anaerobic reactor located in the La Farfana Water Treatment Plant of Aguas Andinas in Santiago, Chile. It had a specific methanogenic activity of 0.32 g CH_4-COD/(g VSS·d). The inoculum had the following characteristics: 16,696 ± 936 mg/L volatile suspended solids (VSS); 12-15 mg/L S^{2-}; pH = 7.4. The experimental design tested consisted of two conditions: Low and High load. The main difference between each condition was the initial soluble Chemical Oxygen Demand (COD) and sulfate concentrations. Low load had initial concentrations of soluble COD and sulfate of 5,000 and 500 mg/L, respectively; high load had initial concentrations of soluble COD and sulfate of 10,000 and 1000 mg/L, respectively. The COD/ S-SO_4^{2-} ratio of 10 was maintained in all the assays, in order to favor the methanogenesis. [14] The rest of the compounds from synthetic wastewater were kept constant in both conditions, as is shown in Table 2.

In both conditions, all the treatments proposed were performed in triplicate: Mining wastes (MW), Fly ashes (FA) and micro-aeration (MA). Furthermore, a control assay was done for each condition, also in triplicate. The control reactors contained the same amounts of inoculum and substrate (low or high load) than those used in each experiment performed, but without addition of MW, FA or MA. The assay with MW consisted of an experiment where 131.6 mg/L of "Cola" were added (5 mg/L of Ni) to each reactor; in the assay with FA, 50 mg/L of fly ash coming from a thermoelectric plant were added to the reactors; finally, the assay with MA consisted of bioreactors aerated continuously with an air-flow

rate of 0.008 vvm (volume air/volume liquid per min) throughout the digestion period. All these conditions were selected in accordance with the literature and taking into account previous experiments. [25, 27, 30] For each condition or group of experiments, 54 mini digesters (in duplicate) were used and from time to time a couple of reactors were taken from the system, and the corresponding analyses were performed, which would determine representative results for that day of digestion. In this way, each value of the analyzed samples represented a point in the evolution curves corresponding to the different physicochemical parameters evaluated. The reactors operated in batch mode until methane accumulation remained constant. Methane production was monitored daily throughout the process.

Chemical and statistical analyses

The following chemical parameters were determined: soluble chemical oxygen demand (COD_s), total volatile solids (TVS), volatile suspended solids (VSS), alkalinity, sulfate, sulfide and pH. All these parameters were analyzed according to APHA Standard Methods. [31] All analytical determinations were made at least in duplicate with a frequency of two or three times per week, except methane volume, which was measured daily. The measurements of Total alkalinity (TA) and Bicarbonate alkalinity (BA) permitted the calculation of alkalinity ratio α:

$$\alpha = \frac{\text{Bicarbonate Alkalinity}}{\text{Total Alkalinity}} \qquad (1)$$

Values of α ratio higher than 0.5 indicated a good performance and an adequate stability of the system. [32] The determination of metal concentrations was made using a Perkin Elmer

Optima 3000 ICP according to standard protocols based on official methods of the US-EPA. [33]

The statistical analysis used in order to compare data between the control system and the applied treatments was the *t-test*, with a significance level = 0.05. To determine the differences between each treatment a one-factor analysis of variance (ANOVA) was applied. All these analyses were done using the Excel 2010 toolbox.

The removal efficiencies of COD, sulfate and sulfide were determined by the following equation:

$$Efficiency \ (\%) = \left(\frac{c_{initial} - c_{final}}{c_{initial}} \right) \times 100 \qquad (2)$$

where: $c_{initial}$ is the initial concentration of each component, and c_{final} is the concentration of each component at the end of the batch assay.

Results and discussion

Effect of mining wastes (MW), fly ashes (FA) and micro-aeration (MA) on COD removal and methane generation

The effect of MW, FA and MA on CODs degradation can be seen in Figure 1. For low load (Fig. 1A), the CODs removal was high and quick, obtaining up to 97% after 20 days of reaction, with no effect of the three treatments on this parameter. Even though the CODs degradation rate at the beginning of the assays appeared faster for the MA treatment, the statistical analysis (*t-student*) showed that there were no statistically significant differences

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between the profiles. At a high load (Fig. 1B) the situation was quite different, with a clear effect of all the treatments on the CODs removal, although the kinetics appeared to be similar. The statistical analysis confirmed this situation, showing that there were statistically significant differences between the CODs profiles of the control and each treatment ($p < 0.05$). The highest CODs removal was achieved using MA (91.5 %), which was 38.4% higher than the control one (66.1%). For MW and FA, the CODs removal was 79.8 and 85.4% higher, respectively, than for the control. This higher CODs removal using MA can be attributed to the better S^{-2} removal under this condition (see Fig. 3B), allowing better environmental conditions for the methanogenic *archaea* metabolism and sulfate-reducing bacteria.

Comparing the two conditions studied (Fig. 1A and Fig. 1B), it can be clearly observed that the treatments were much more necessary and effective for high initial CODs concentrations. In higher CODs concentrations, the competition between methanogenic and sulfate –reducing bacteria was lower even though the COD/SO_4^{2-} was kept constant in both conditions, allowing the sulfate-reducing bacteria to generate H_2S, which at high concentrations could inhibit the methanogenic microorganisms and decrease the process efficiency.

Therefore, it is necessary to find appropriate strategies to simultaneously enhance the CODs removal and methane yield, reducing H_2S production. An efficient strategy has been proposed recently by Dai et al.[8], which consisted of pretreating the substrate (waste activated sludge) at pH 10 for 8 d and adjusting the system at neutral pH to produce methane for 20 d. This procedure allowed the synchronous enhancement of COD removal and methane production and reduction of H_2S production during the anaerobic digestion of

waste activated sludge. These experimental results showed that the methane yield of sludge pretreated at pH 10 in semi-continuous stirred anaerobic reactors for 84 d was 49.6% higher than that obtained in the control. Meanwhile, the production of H_2S was 54.2% lower than that detected in the control. [8]

The effect of MW, FA and MA on the accumulated methane volume production is shown in Figure 2.

It is important to note that the methane volume measurement in the assay with MA was neglected due to the air flow-rate, which could have modified the methane volume value; however, the injection of air at low flow-rate in an anaerobic bioreactor did not affect the calorific value of biogas. Indeed, Porpatham et al., [34] demonstrated that "diluted" biogas could be used in a combustion engine, and they found that a decrease in methane concentration from 70% to 50% only reduced the spark-ignition engine's energetic performance by 0.9% for the same mass methane flow. At low load (Fig. 2A), the methane production was similar between the control system and the assays with treatment, without statistical significant differences between the treatments and the control system ($p > 0.05$). This behavior agrees with the COD removal values obtained in these assays (Fig. 1A). The methane production in all these assays was very fast, obtaining the greatest amount of methane within the first 10 days in all cases, and achieving its steady-state after 30 days. At high load (Fig. 2B), there was an effect of MW and FA on the process, a situation that was also reflected in the statistical analysis ($p < 0.05$). The systems with FA generated a slightly higher volume in comparison to the MW, both being higher than the control system; the accumulated methane volume was 41% higher than the control for the system with FA, while it was 31% higher than the control for the system with MW. This higher methane

production also agrees with the slightly higher COD removal achieved using FA. A possible explanation for this result could be the greater trace element bio- availability in the system with FA, which is reflected in better values for α ratio and pH (Fig. 5B and 6B). Specifically, the higher contents in Fe, Cu, Al, Ba, Mn and Zn of the FA compared to the values present in MW could entail a higher stimulation of the growth and metabolism of the methanogens, causing a higher final methane production in the reactors with FA. Moreover, the higher content of Fe in FA (3083 mg/kg) compared to MW (306 mg/kg) could also explain the higher methane production found in the reactors with FA. Reported Fe advantages include: its capacity to decrease the oxidative-reductive potential (ORP) of the anaerobic media and, therefore, provide a more favorable environment for anaerobic digestion; and its role as co-factor of several key enzymatic activities, such as pyruvate-ferrodoxin oxidoreductase, which contain Fe-S clusters and play a key role in fermentation. [35] On the other hand, although the sulfide concentration in the system with FA was always higher than that detected in the system with MW, the sulfide concentration values were not high enough to inhibit methane production in this case. [12]

Figure 2 also shows that the methane generation at high load was slower than in the process at low load, and showed a longer lag-phase at high load. This also shows that high load required more time for stabilization and methane generation.

Thus, it is possible to say that the three treatments studied improved the CODs removal and the methane generation at high load conditions. Initial CODs concentrations equal to or lower than 5000 mg/L did not require any treatment for improving COD removal and methane generation.

Effect of treatments on the sulfur compounds

The effect of MW, FA and MA on the concentrations of both sulfide and sulfate are shown in Figures 3 and 4, respectively. Figure 3 shows that the sulfide was removed under both conditions, high and low load. At low load (Fig. 3A) the control system maintained the sulfide concentration at values superior to 90 mg/L, while the systems with the different treatments decreased the concentrations by up to 18 mg/L, with the MA the treatment being more effective in the sulfide removal. In the cases of MW and FA, the sulfide removal was probably carried out by sulfide precipitation, because the sulfate concentration was not increased in these systems (Fig. 4A). Even though the MA allowed for obtaining a lower sulfide concentration in the liquid phase, the *ANOVA* analysis showed that there were no significant statistical differences between the concentrations obtained by the application of MW, FA and MA ($p > 0.05$).

For the case of high load (Fig. 3B), the situation was different. In this case, the control system presented a decrease in sulfide concentration the first 12 days of digestion, increasing later to up to 90 mg/L. This fact could be attributed to the pH (Fig. 6A), whose value (around 7.3) could shift the equilibrium toward the volatile form of sulfide (H_2S), allowing for the stripping of the H_2S (gaseous) and, therefore, decreasing its total concentration.

In presence of MW, FA and MA there was a fast reduction in sulfide concentration during the first 6 days and, then, there was a production of H_2S due to the performance and operation of the sulfate-reducing bacteria. The highest increase in sulfide production between days 5 and 25 was achieved in the system with FA, followed by the system with MW. The system with MA allowed the sulfide concentration to be kept at values lower than

30 mg/L in almost all the assays, with a small increase on the 18th day. The higher sulfide production in the systems with FA and MW could be due to the stimulation of sulfate-reducing bacteria by trace elements present in these wastes, which also allowed the higher activity of methanogenic archaea. [9,24] On the other hand, the rapid sulfide reduction at the beginning of the assays with FA and MW also showed that these wastes allowed a decrease in sulfide concentration, possibly by precipitation. Finally, at the end of the assays the sulfide concentration decreased to values lower than 20 mg/L in all experiments. This last reduction of sulfide (after day 25) could be attributed to the presence of biological sulfide oxidation, which also agreed with the slight increase in sulfate concentration in these assays (Fig. 4B).

Figure 4 shows the sulfate concentration profiles under low and high load. Under low load condition (Fig. 4A), sulfate was virtually removed in the control system, while in the systems with FA and MW, sulfate removal efficiencies of between 96.7 and 88% were achieved. Under MA conditions, sulfate removal was lower and reached a final value of only 22%. This low removal can be attributed to the inhibition of SRB due to the oxygen present in the medium. [36] This previous research indicated that SRB are inhibited by the presence of electron acceptors such as oxygen, nitrate and nitrite. Among them, oxygen was the most inhibiting electron acceptor regardless of the carbon source used. This same study showed that after exposure to oxygen and when feeding acetate an inactivation time in the sulfate reduction activity was observed. Once the sulfate reduction activity was resumed, only 60% of the original activity was recovered. Although the presence of MW and FA allowed a high sulfate removal, the highest removal obtained at low load was achieved in the control system, with a 96.7% reduction; however, the simultaneous removal of sulfide

and sulfate in the presence of MW and FA allowed not only for good performance of the process with high sulfate and COD removals, but also improved methane production.

At high load (Figure 4B), the performance in terms of sulfate removal was similar, with the lowest removal in the system with MA (76.4%); however, at higher initial SO_4^{2-} and COD concentrations, there was better sulfate removal in comparison to the system with low load, increasing the average removal by 336% with respect to that condition. This can be attributed to the higher bioavailability of substrate for sulfate-reducing bacteria, which allowed a better and more effective biodegradation of this more concentrated substrate.

Piña-Salazar et al. [37] also demonstrated that in sulfate-reducing reactors (down-flow fluidized bed) the sulfate removal efficiency increased when the COD/SO_4^{2-} ratio increased, achieving a maximum sulfate removal of 66.1% at a COD/SO_4^{2-} ratio of 2.5.

According to the results obtained in the present work, the use of metallic wastes (MW and FA) in the anaerobic digestion improves the global performance (COD removal, methane production, sulfide removal, sulfate removal) of this process, especially under conditions of high load. In the same way, the addition of sweetmeat waste as nutrient supplement in anaerobic upflow packed bed reactors treating sulfate rich wastewater resulted in a prompt reactivation of SO_4^{2-} removal. [38] This research demonstrated that SO_4^{2-} removal was proportional to COD/SO_4^{2-} ratio up to 4, at which a maximum sulfate removal (99%) was achieved. [38]

Effect of WM, FA and MA on pH and alkalinity ratio

Alkalinity and pH are two important parameters in anaerobic digestion processes; therefore, it is interesting to know the effect of these three treatments on them in order to determine

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their influence on process stability. Figure 5 shows the variation of the α ratio with time, while Figure 6 shows the pH values observed as a function of time in each assay. For α ratio, at low load (Fig. 5A), the process was always performed under good conditions of alkalinity, with low accumulation of volatile fatty acids (VFAs) (data not shown). This behavior agrees with the high COD and sulfate removals, and also with the high methane production obtained in all these assays.

Regarding the α ratio under high load condition (Fig. 5B), the results showed an effect of MW, FA and MA on this ratio, because under these three treatments the α ratio increased with respect to its value found in the control system. Indeed, the control system obtained values of α ratio in the lower limit of a good and stable operation. According to the literature, [28] α ratio must be superior to 0.5 in order to ensure that the anaerobic system is not producing too many VFAs, which could stop the methane generation by acidification. Thus, the treatments studied allowed an improvement in the alkalinity ratio, decreasing the VFAs in the medium, a situation which also explains the higher methane production in these cases compared to the control. In addition, FA and MW make an important contribution to these alkalinity ratios, taking into account that they contain a suitable liming material derived primarily from Cao, MgO and other alkaline metal oxides that react with water to generate net alkalinity. [28] According to the statistical analysis, there was no significant differences among the α ratio values for the different treatments tested (ANOVA, $p > 0.05$); however, there were statistically significant differences between the α ratio values obtained in the control and those found for each treatment (*t-student*, $p < 0.05$).

For pH values, Figure 6 shows the results for all the conditions studied. At low load (Fig. 6A), the pH for all the assays was kept within the optimal range for methanogenesis, with

values between 7.3 and 7.45, without differences between the control system and the systems with MW, FA and MA. Statistical analysis confirmed this fact, showing that there were no statistically significant differences between the control pH value and the pH values in the assays with treatments. Therefore, at low load (low initial COD and sulfate concentrations), the pH was not affected by the addition of WM, FA or MA.

For the case of high load (Fig. 6B), there was an initial small decrease in pH from 7.2 to around 7.0 during the first 6 days of digestion. This decrease can be attributed to a simultaneous decrease in the alkalinity α ratio (Fig. 5B) during this period, which affected the buffering capacity of the systems during this time interval, decreasing the pH values. From the 6th day, the alkalinity α ratio increased again, causing a rise in pH up to values in the range of 7.5-7.7. Even though the values and tendency of pH in the control system and the systems with MW, FA and MA were similar, the statistical analysis showed that there was a statistically significant difference between the pH values of control system and the pH values of the system with MA ($p < 0.05$); the rest of the treatments (MW and FA) did not show statistically significant differences from the control system. The increase in pH in the systems with treatment agreed with the improvement in alkalinity ratio, COD removal and methane generation. A similar range of pH values (7.0-7.8) was found in the anaerobic digestion process of maize straw carried out in continuously stirred tank reactors (CSTR) at 38 ºC, when a natural clay mineral mixture (containing basically Fe, Ni, Co and Mn) was added to the reactors. [24] These pH values guaranteed a well-balanced anaerobic digestion process operating at OLRs in the range of 0.5-2 g VS/(L·d).

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Thus, it is shown that the use of MW, FA or MA improved the anaerobic digestion process, improving the alkalinity ratio and avoiding the acidification of the bioreactors, while maintaining the pH values around the optimal range for methanogenesis.

Conclusions

The use of mining wastes (MW), fly ashes (FA) or micro-aeration (MA) in the anaerobic digestion of wastewater rich in sulfate and sulfide improved the COD and sulfide removals, methane generation, alkalinity and pH for wastewater with high initial COD and sulfate concentrations. The use of MW and FA allowed the simultaneous increase of COD removal, sulfate removal, sulfide removal and methane generation, while MA only improved the COD and sulfide removals in comparison to the control system. Therefore, the use of metallic wastes as nutrient supplement resulted in an increase in the SO_4^{2-} removal. Operational parameters such as alkalinity α ratio and pH also showed improved its values in comparison to the control system when WM, FA and MA were used. The use of WM, FA or MA in a system with initial CODs concentrations equal to or lower than 5000 mg/L with COD/SO_4^{2-} ratio = 10 did not show any improvement with respect to control system in terms of COD removal, sulfate removal or methane generation. Only sulfide removal showed an improvement when WM, FA or MA were used under these conditions. In sulfate reducing reactors, the sulfate removal efficiency increased when the COD/SO_4^{2-} ratio augmented up to certain values.

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FIGURE CAPTIONS

Figure 1: Effect of WM, FA and MA on CODs concentration. A) Low load; B) High load.

Figure 2: Accumulated methane volume for the different conditions studied. A) Low load; B) High load.

Figure 3: Sulfide concentrations for the different conditions studied. A) Low load; B) High load.
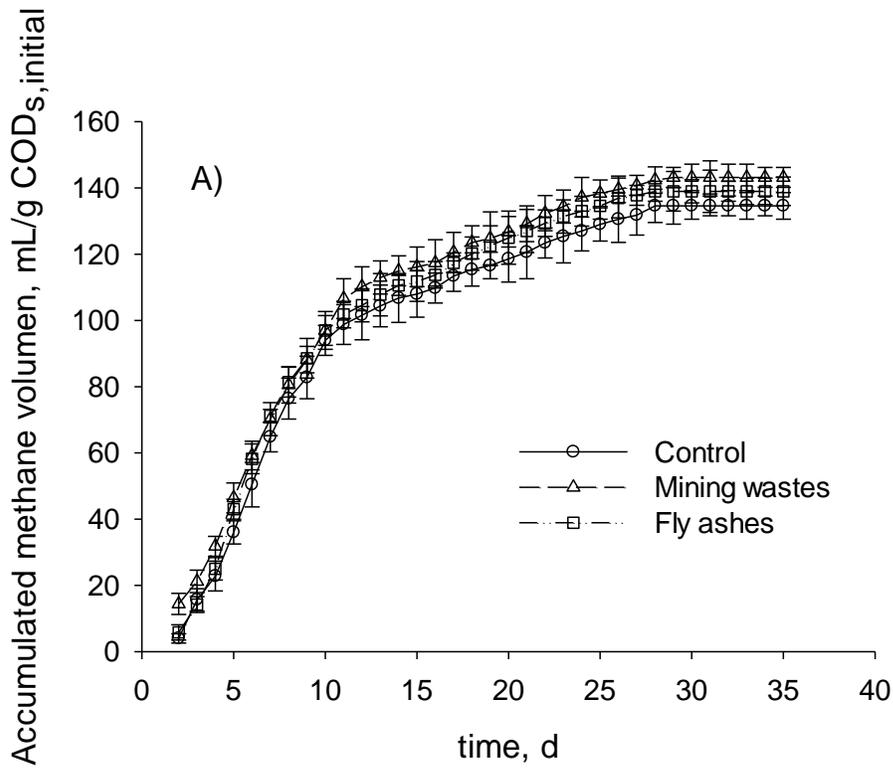
Figure 4: Sulfate concentrations for the different conditions studied. A) Low load; B) High load.

Figure 5: Alkalinity ratio (α) for the different conditions studied. A) Low load; B) High load.

Figure 6: pH profiles for the different conditions studied. A) Low load; B) High load.
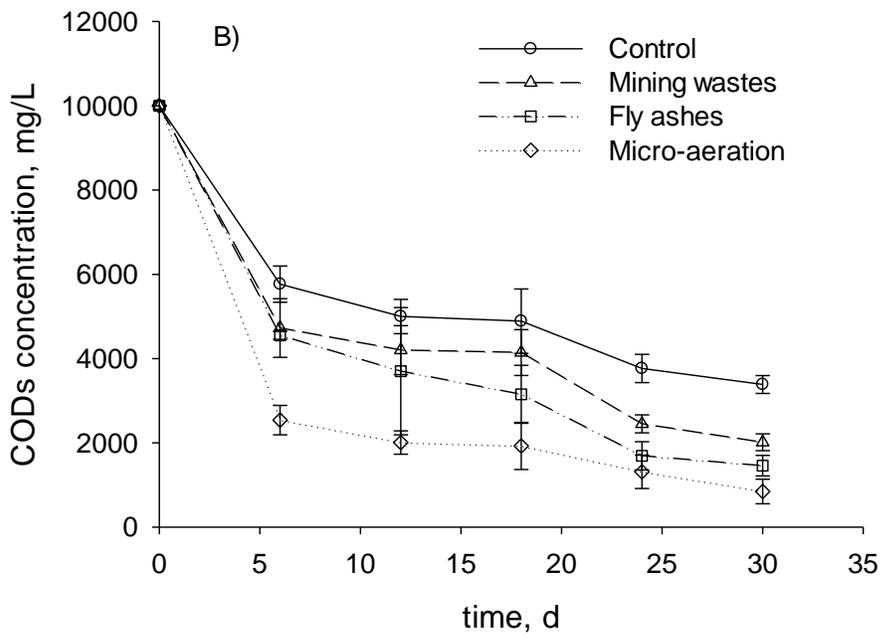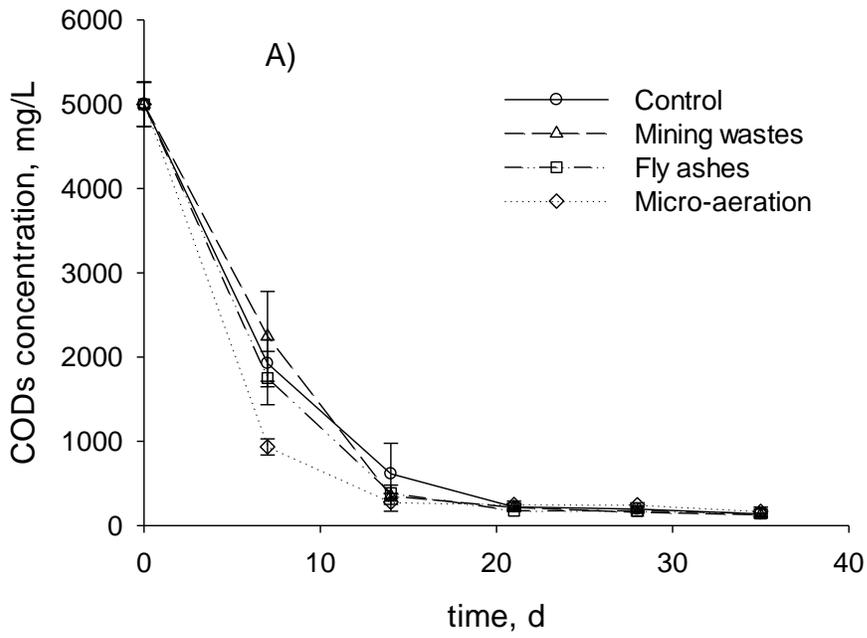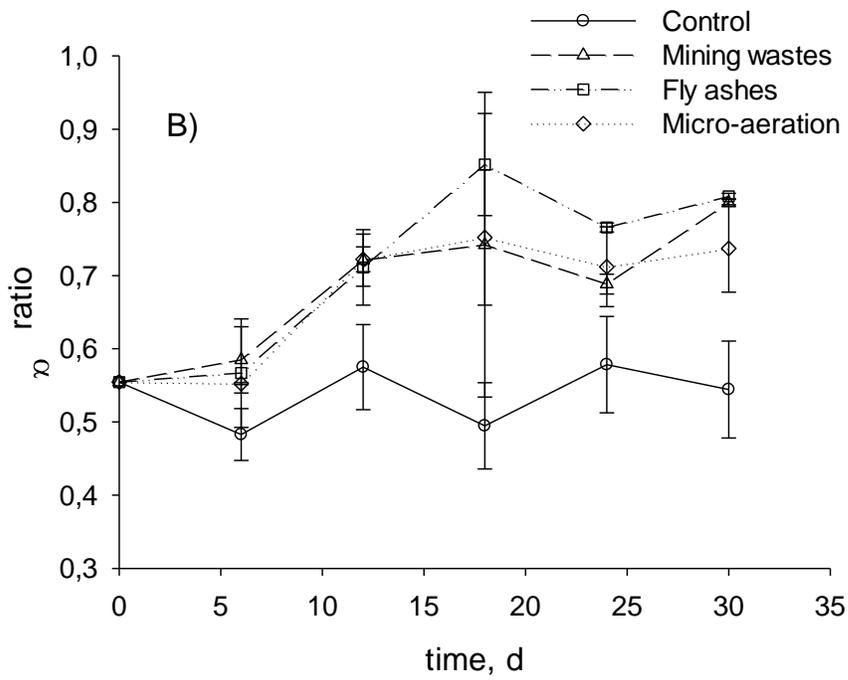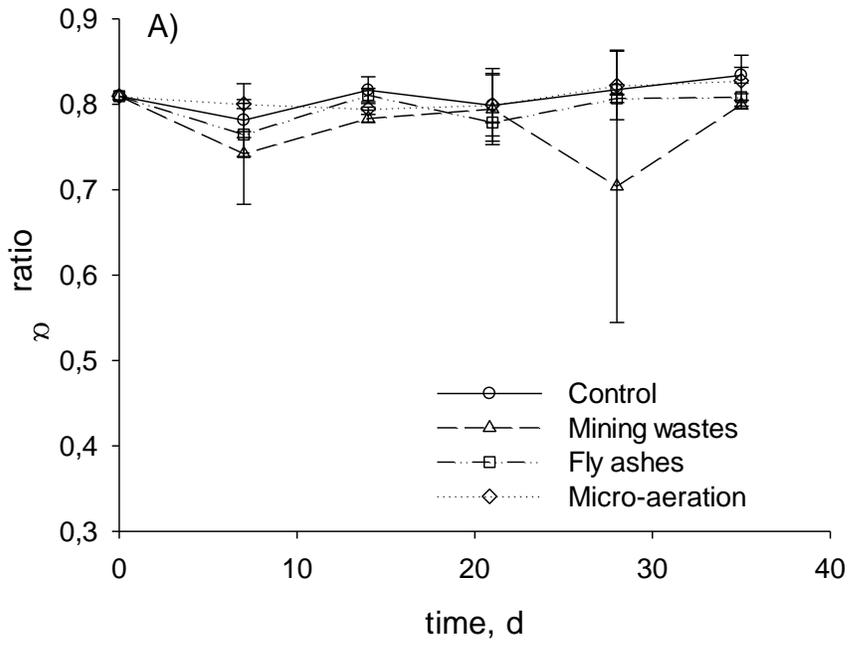
Fig. 1
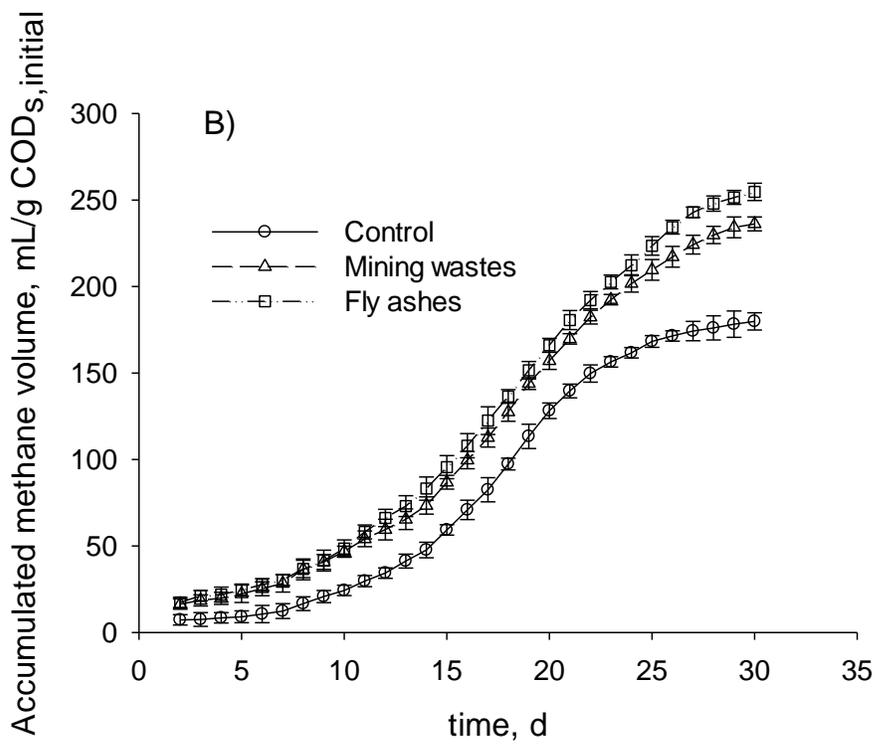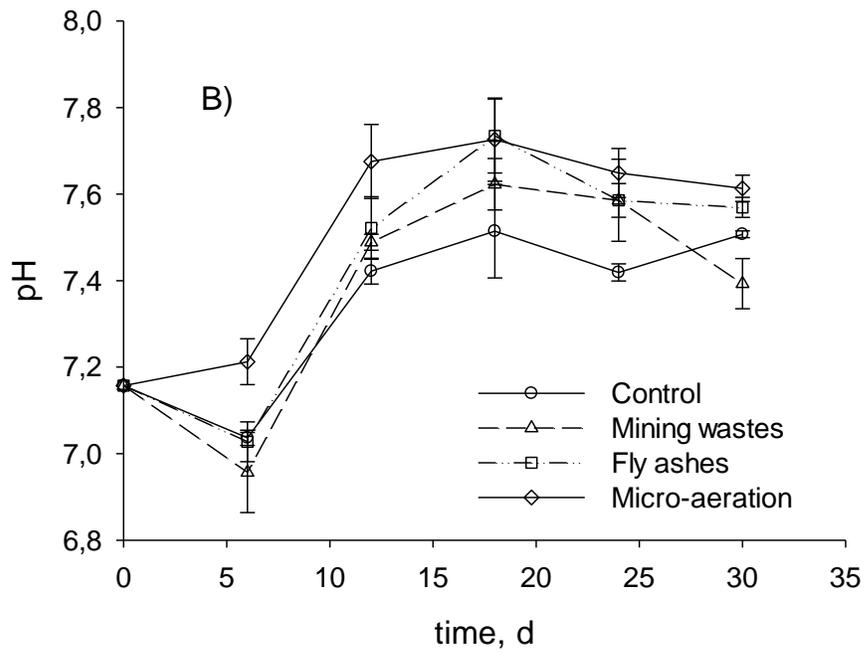
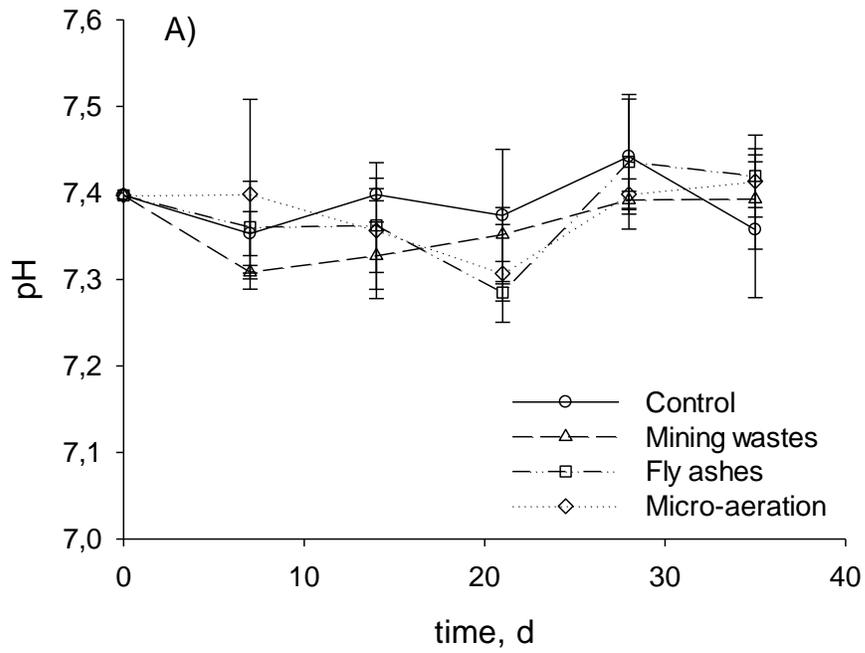Fig. 2
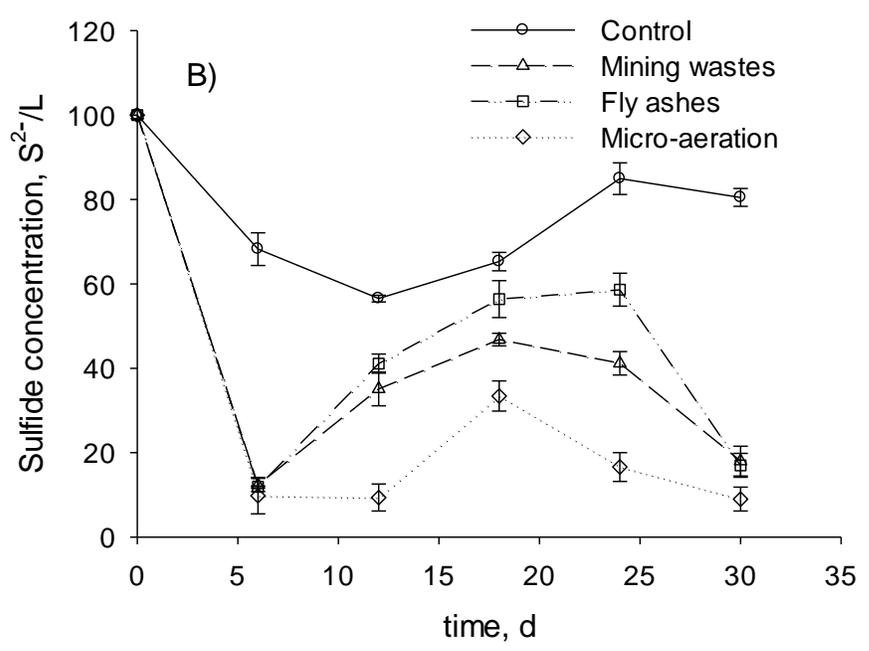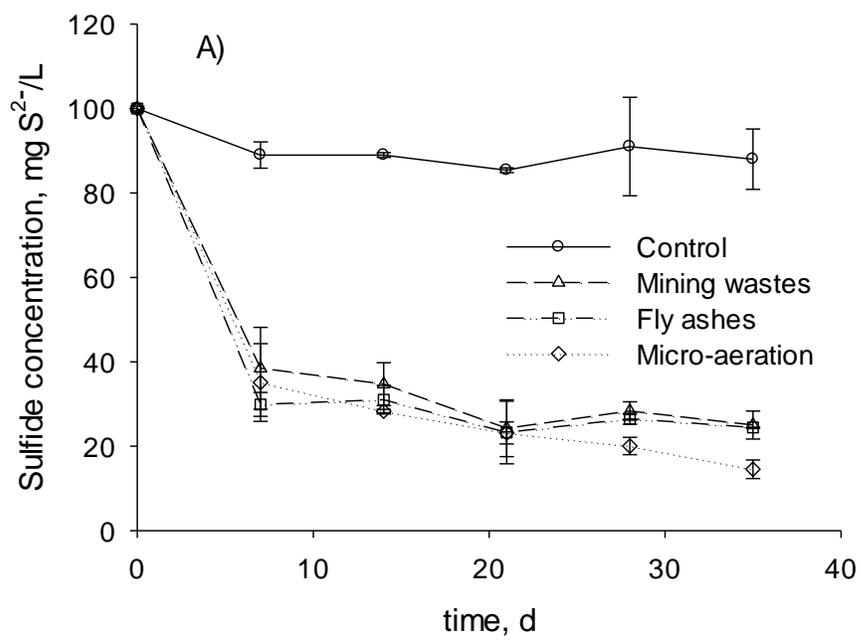
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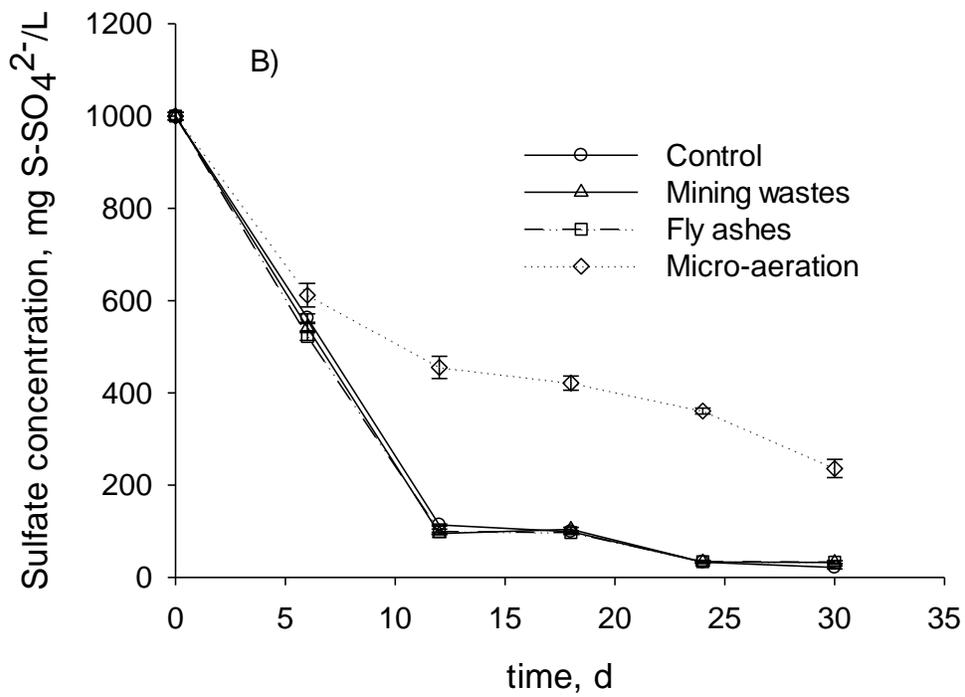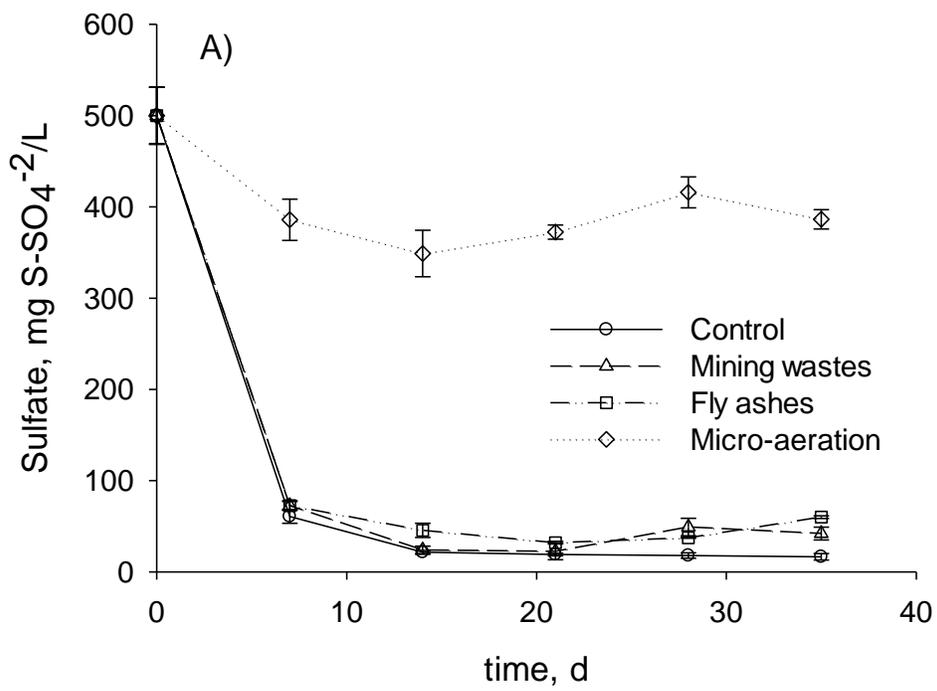
Fig. 4

Fig. 5

Fig. 6

Table 1. Chemical characterization of the mining wastes and fly ash used in the experiments, mg/kg.

Element	Mining Wastes	Fly ashes
Mg	67.32	< DL
Cr	8.24	2.92
Cd	0.02	< DL
Fe	306.61	3083.58
Ni	12.44	6.17
Cu	0.12	2.21
Co	1.63	< DL
Al	0.03	1315.42
V	< DL	13.36
Ba	< DL	44.36
B	<DL	35.03
Mn	0.02	21.05
Zn	0.73	5.4

DL: Detection limit

Table 2: Substrate concentrations used for the conditions "low load" and "high load".

Component	Concentration Low Load, mg/L	Concentration High Load, mg/L
SO_4^{-2}-S	519	1,135
S^{-2}-S	123	125
N	23	187
P	4.6	37
Glucose	5,378	11,203
CODs	5,754	10,988
$(NH_4)_2SO_4$	86.1	972.9
H_3PO_4	11.6	130.5
Na_2S	299.4	304.3
$NaHCO_3$	6.25	6.25