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# Increase in biogas production in anaerobic sludge digestion by combining aerobic hydrolysis and addition of metallic wastes

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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 metallic wastes. The aerobic pretreatment was performed during 48 h at 35 °C with an aeration flow of 0.35 vvm. 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 metallic 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.



## 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]. These sludges have a great amount of organic matter that must be stabilized before its final disposal [2]. Anaerobic digestion is widely applied for effective sludge stabilization and biogas production and it involves four steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis [3].

The hydrolysis step (particulate organic matter conversion into soluble substances) and the methanogenesis step (conversion of acetic acid, $CO_2$, $H_2$, and others to methane) are believed to be the rate-limiting steps of anaerobic digestion [4].

Several physical and chemical methods, individually or in combination, have been applied as hydrolytic pre-treatments such as ultrasonication, alkaline hydrolysis, high pressure extruding, ozonization, enzymatic hydrolysis and thermal hydrolysis [5–7]. 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 [8]. 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 de-waterability [9]. 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 [10]. 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

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150–180 °C and pressures of 0.37–0.95 MPa [11,12]. 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 [13], 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 [14].

Biological hydrolysis has also been studied [15,16]. The biological process that has given better results is micro aerobic hydrolysis [17,18]. Lim and Wang [19] 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. [20,21] 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 [22]. It has also been found that the absence of these micronutrients has caused problems in anaerobic processes [23,24]. On the other hand, it has been proven that the use of metallic compounds improves anaerobic biodegradability and biogas production [25]. Zhang et al. [26] 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. [27] 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 [28]. 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 [29].

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 [30–32]. 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 [33]. These disposal strategies not only increase the burden on landfills, but they also have a significant impact on the surrounding habitats and ecosystems [34]. But fly ash has an important content in several metals which are necessary for methanogenic archaea [35]. 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 metallic 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 metallic 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 g $CH_4$-COD·g $VSS^{-1}·L^{-1}$; VSS of 95–105 g $L^{-1}$, and pH of 7.4. In the micro-aeration tests no inoculum