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# Sequential ultrasound and low-temperature thermal pretreatment: Process optimization and influence on sewage sludge solubilization, enzyme activity and anaerobic digestion

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## HIGHLIGHTS

- Sequential ultrasound and thermal pretreatment of sewage sludge was assessed.
- Pretreatment led to solubilization and increased enzyme activity in sewage sludge.
- Optimal COD solubilization was obtained at 59.3 kg TS/L, 30,500 kJ/kg TS and 13 h.
- Methane yield and maximum production rate were significantly increased.
- Pretreatment increased electricity recovery from sludge up to 24%.

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## ABSTRACT

The influence of sequential ultrasound and low-temperature (55 °C) thermal pretreatment on sewage sludge solubilization, enzyme activity and anaerobic digestion was assessed. The pretreatment led to significant increases of 427–1030% and 230–674% in the soluble concentrations of carbohydrates and proteins, respectively, and 1.6–4.3 times higher enzymatic activities in the soluble phase of the sludge. Optimal conditions for chemical oxygen demand solubilization were determined at 59.3 kg/L total solids (TS) concentration, 30,500 kJ/kg TS specific energy and 13 h thermal treatment time using response surface methodology. The methane yield after pretreatment increased up to 50% compared with the raw sewage sludge, whereas the maximum methane production rate was 1.3–1.8 times higher. An energy assessment showed that the increased methane yield compensated for energy consumption only under conditions where 500 kJ/kg TS specific energy was used for ultrasound, with up to 24% higher electricity recovery.



## 1. Introduction

Concerns regarding increasing sludge generation in wastewater treatment plants (WWTPs) have increased. During 2012, the annual generation of sludge from sewage treatment facilities in Europe was approximately $10.0 \times 10^6$ tons (dry matter basis), whereas in China, sludge generation was over $6.0 \times 10^6$ tons (Eurostat, 2016; Zhang et al., 2016). The situation in Chile has not been different, with an estimated sludge generation of 300 ton/day during 2010 (Celis et al., 2008). In this scenario, sludge valorization through the recovery of energy and nutrients represents a fundamental step toward developing sustainable WWTPs.

Anaerobic digestion (AD) is an environmentally friendly alternative for sludge stabilization. AD processes significantly reduce odor, pathogens and organic matter (Appels et al., 2008a). Moreover, biogases with significant percentages of methane (60–70% $CH_4$) and nutrient-rich digestates are obtained during digestion, which can be utilized as energy sources and commercial fertilizers, respectively (Carballa et al., 2011).

Modern WWTPs have integrated the benefits of AD; however, a few noteworthy AD performance drawbacks exist. Low performance rates are typically observed during the hydrolysis of organic matter in sewage sludge, which includes solids, flocs, extracellular

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polymeric compounds, cell walls and recalcitrant proteins and lipids (Abelleira-Pereira et al., 2015). This inefficiency requires sludge retention times of over 20 d, making the implementation of the technology unfeasible for most small-sized WWTPs.

Therefore, efforts have been made toward improving hydrolysis efficiency and the overall AD process. One preferred strategy is the use of physical, chemical and/or biological pretreatments that hydrolyze sludge in a step prior to AD (Carrère et al., 2010; Neumann et al., 2016). While a wide array of pretreatment technologies has been proposed, only a few have been successfully implemented at full scale, mostly due to limitations caused by energy consumption (Cano et al., 2015).

To overcome this issue, the use of low-temperature thermal hydrolysis (55–90 °C) has been proposed as an alternative to other more intensive technologies (Carvajal et al., 2013; Dhar et al., 2012; Ferrer et al., 2008). These process conditions promote the physical disruption and release of endogenous enzymes present in biological sludge flocs, resulting in organic matter solubilization and biogas production improvements during AD (Carvajal et al., 2013). Pretreatments at 55 °C have been reported to increase waste-activated sludge methane yields up to 23% after 12 h of pretreatment, with 1.3- to 1.7-fold higher maximum methane productivity rates than non-pretreated sludge (Carvajal et al., 2013).

Ultrasound has also proposed as an economically feasible pretreatment alternative (Dhar et al., 2012; Xie et al., 2007). The effects of ultrasound on sludge includes particle size reduction, organic matter solubilization, enzyme release and stimulation of biological activity (Pilli et al., 2011; Song and Feng, 2011; Yan et al., 2010; Zhang et al., 2008). Ultrasound has been reported to increase biogas production by 4–83% and volatile solids removal by 6–47% during AD (Neumann et al., 2016). The implementation of ultrasound for full-scale AD could lead to increased energy recovery from sludge. Xie et al. (2007) reported an increase of 45% in methane production in a full-scale facility, with a 2.5–1 ratio between net energy gain and energy consumption.

Another strategy that has gained relevance for improving the energetic performance of pretreatments is the use of combined processes. Combined pretreatment processes have been reported to promote hydrolysis mechanisms that result in improved effects over organic matter solubilization and biogas production (Tyagi et al., 2014). Because ultrasound and low-temperature thermal hydrolysis cause physical disruption and increased endogenous enzyme activity in sludge (Carvajal et al., 2013; Yan et al., 2010), their sequential combination is expected to improve organic matter hydrolysis through the integration of physical and biological phenomena. Therefore, the objective of this study was to assess the influence of this sequential process on sludge solubilization, enzyme activity and anaerobic digestion. Additionally, the operating conditions of the pretreatment were optimized. Finally, the energy balance of the process was estimated to preliminarily assess its feasibility at full-scale facilities.

## 2. Materials and methods

### 2.1. Sludge samples

Thickened mixed-sewage sludge (MSS) samples were obtained from the Biobío WWTP, Concepción, Chile (36° 48′ S, 73° 08′ W). The plant treats wastewaters generated in the metropolitan area of Concepción, serving approximately 500,000 inhabitants. The primary to secondary sludge ratio of the MSS was approximately 40/60% in volume and 65/35% in total solids (TS). Anaerobic inoculum for the AD assays was obtained from one of the two 8000 $m^3$ digesters used to stabilize the MSS in the WWTP.

### 2.2. Pretreatment assays

Configurations for single ultrasound, single low-temperature thermal hydrolysis and the sequential application of both processes were studied. Ultrasound was applied using a UP200ST ultrasonic homogenizer (Hielscher Ultrasonics GmbH, Germany) operating at 26 kHz. Samples of 500 mL were placed inside a beaker and continually agitated with a magnetic stirrer during sonication. Low-temperature thermal hydrolysis was performed in a Gerdhardt Thermoshake incubator at 55 °C temperature and under 70 rpm continuous agitation. Sludge samples were placed inside 500-mL beakers and covered with perforated tops to prevent water evaporation and promote microaerobic conditions (Carvajal et al., 2013). Plastic hoses were placed inside the sample to enhance $O_2$ diffusion into the sludge. Ultrasound was tested at specific energies (SE) of 500, 15,500 and 30,500 kJ/kg TS. Low-temperature thermal hydrolysis was performed with retention times (T) of 3, 8 and 13 h. All assays were performed in triplicate.

Solubilization was studied in terms of increases in soluble proteins, carbohydrates and chemical oxygen demand (COD). In addition to solubilization, the influence of the pretreatment over volatile fatty acids (VFA) concentration and the activity of protease and amylase enzymes in the soluble phase of the sludge were assessed. Acetic, propionic, butyric and valeric VFA concentrations were determined through gas chromatography and expressed as COD according to their stoichiometric oxygen demand.

Optimizations of three operational conditions (i.e., sludge concentration (SC), SE and T) over the solubilization of COD during ultrasound and sequential ultrasound/low-temperature thermal hydrolysis pretreatment were performed using response surface methodology (RSM). RSM is a statistical technique that can be used to simultaneously explore the relationship between several independent variables and selected responses and determine optimal conditions. The solubilization factor $f$ (%) of the COD was defined as the response for this assay and corresponds to the ratio between the increase in soluble COD due to pretreatment and the initial particulate COD. The soluble COD increase corresponds to differences between the COD determined in the soluble phase of the MSS after pretreatment (CODs) and the COD determined in the soluble phase of the raw MSS ($CODs_R$). The particulate COD is estimated as the difference between the total COD of the raw MSS ($CODt_R$) and the $CODs_R$, as shown in Eq. (1) (Bougrier et al., 2006).

$$f\ (\%) = (\mathrm{CODs} - \mathrm{CODs_R})/(\mathrm{CODt_R} - \mathrm{CODs_R}) * 100 \quad (1)$$

A $3^2$ full-factorial design with three levels (−1, 0, 1) according with Yeber et al. (2009) was utilized to assess the relationship between the variables SC and SE and the response $f$ during ultrasound application. SC was fixed at 18.3, 40.7 and 63.1 kg TS/L, whereas the SE levels were fixed at 500, 15,500 and 30,500 kJ/kg TS. The total number of observations required was 9, and the central point was replicated three times. On the other hand, a Box-Behnken design with three levels (−1, 0, 1) was utilized to study the relationship between SC, SE and T with $f$ after sequential ultrasound and low-temperature thermal hydrolysis pretreatment. Values for the three levels of SC and SE were the same as in the ultrasound experimental design. T was fixed at 3, 8 and 13 h. The total number of observations required was 13, and the central point was replicated three times. All experimental points were tested in duplicate.

Table 1 summarizes the experimental conditions tested during the pretreatment assays.

### 2.3. Anaerobic digestion tests

The AD tests were performed in batch conditions (biomethane productivity potential tests; BMP) using sealed vials of 120 mL