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Potential of high-frequency ultrasounds to improve sludge anaerobic conversion and surfactants removal at different food/inoculum ratio

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HIGHLIGHTS

- Novel application of high frequency ultrasounds as sludge pre-treatment is proposed.
- Effect of food/inoculum (F/I) ratio was assessed by batch anaerobic digestion tests.
- First order kinetic evidenced decreasing trend of hydrolysis rate by increasing F/I.
- Ultrasounds improved specific biogas production, particularly at low F/I.
- F/I affected the anionic surfactants removal and the homologues degradation pathway.

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ABSTRACT

High-frequency ultrasounds have recently gained interest as oxidative technique for sonochemical degradation of organic contaminants in water. In this study an innovative approach applying 200 kHz ultrasounds to improve both sludge anaerobic biodegradability and decontamination is proposed. Digestion tests were performed on batch reactors fed either with untreated or sonicated sludge, at different food/inoculum (F/I) ratio, in the range 0.3–0.9. First order kinetic highlighted a decreasing trend of the hydrolysis rate by increasing F/I, both for untreated and sonicated sludge. Positive effect of ultrasounds on specific biogas production was evident, but the conversion rate for pretreated sludge was strongly affected by F/I, and decreased by increasing F/I. Anionic surfactants anaerobic removal occurred in all tests, but the effect of ultrasounds was significant only at F/I = 0.3. By pretreating sludge with high frequency ultrasounds, low F/I was the ideal ratio improving both sludge anaerobic digestion and decontamination.

1. Introduction

Biosolids land application is nowadays considered the best environmental and economic option to reduce the sludge volume requiring disposal on landfill. In order to produce suitable biosolids, advanced sludge treatments have to (a) reduce sludge volume and mass, (b) remove putrescible and degradable materials, avoiding odour generation, and (c) eliminate pathogens. Among treatment options, anaerobic digestion represents a widely applied biological technology for stabilizing sludge, also because the biogas produced during the digestion process is a clean and environmentally friendly fuel.

One of the crucial factors affecting anaerobic digestion of organic solids is the selection of the food/inoculum ratio as well as the assessment of anaerobic biodegradability of sludge (Neves et al., 2004).

The food to inoculum ratio (F/I) is expressed as the amount of feedstock volatile solids (VS) added per the amount of inoculum VS (Liu et al., 2009). Although this ratio could theoretically affect only the kinetics, and not the ultimate methane yield (which depends only on the organic matter content), it is widely reported that too high F/I may be toxic while too low F/I could prevent enzyme induction for biodegradation (Neves et al., 2004; Prashanth et al., 2006). According to Neves et al. (2004) a substrate to inoculum (*S/I*) ratio ranging between 0.5 gVS/gVS and 2.3 gVS/gVS could prevent volatile fatty acids accumulation and instability of the anaerobic process. Further studies (Liu et al., 2009) showed that the biogas yield was inversely related to the *S/I* ratio in the range 1.6–5.0.

Nevertheless, the biogas yields for the anaerobic digestion of solid wastes, as sewage sludge, are generally low because of the

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biological hydrolysis, considered the rate-limiting step of the whole process due to the particulate nature of this feedstock (Pavlostathis and Gosset, 1986; Shimizu et al., 1993; Tomei et al., 2008).

During the hydrolysis phase, several processes take place, namely the disintegration of sludge matrix, the solubilisation of particulate matter and the biological decomposition of extracellular polymeric substances, primarily responsible of sludge floc structure and integrity. For this reason, in recent years, a great deal of attention has been focused on mechanical, thermal or chemical pre-treatments of waste activated sludge, which facilitate breakage of flocs, and cell walls, enhancing the hydrolysis of sludge volatile solids (Braguglia et al., 2011; Carlsson et al., 2012; Khanal et al., 2007; Pilli et al., 2011). Among mechanical methods, ultrasounds at low frequency (around 20–24 kHz) has been extensively used as sludge pretreatment for improving anaerobic digestion performances, both at lab scale (Bougrier et al., 2005; Perez-Elvira et al., 2009; Tiehm et al., 2001) and full-scale applications (Neis et al., 2008; Xie et al., 2007).

Furthermore, it was recently demonstrated by Gallipoli and Braguglia (2012) that also higher ultrasounds frequency, as 200 kHz, caused floc matrix disintegration and organic matter solubilisation. At the same time, high frequency ultrasounds gained interest for wastewater decontamination because of the oxidative degradation of organic contaminants by means of OH radicals, generated from water sonolysis. However, despite the high amount of persistent and ubiquitary organic contaminants present in sewage sludge, the application of ultrasounds to degrade pollutants via sonolysis before anaerobic degradation, was never reported in literature so far.

Among the organic contaminants accumulating into sludge, an important group is constituted by linear alkylbenzene sulphonates (LAS), a class of anionic surfactants, components of synthetic detergent formulations for both domestic and industrial purposes. Many studies about the biodegradation of LAS have demonstrated that anionic surfactants are readily biodegradable under aerobic conditions, while studies on LAS removal in anaerobic conditions showed a negligible surfactants biodegradation. In fact, according to the findings of Berna et al. (1989), high concentrations of LAS (5–10 g LAS/kg) have been found in anaerobically digested sludge. For this reason recent research was addressed to improve LAS anaerobic biodegradation potential (Angelidaki et al., 2004; Mogensen et al., 2003) since LAS are strongly adsorbed onto sludge.

On the basis of these considerations, main objective of this work was to assess the potential of high frequency ultrasounds as sludge pre-treatment, in order to combine the enhancement of the anaerobic sludge digestibility with the sludge decontamination via pollutants oxidation. The ultrasounds potential was evaluated by performing anaerobic digestion tests carried out with untreated and sonicated sludge, by monitoring organics solubilisation and removal, biogas production and linear alkyl benzenes sulphonates (LAS) fate during the anaerobic process.

The impact of the initial food/inoculum ratio on the digestion performances was assessed, too.

2. Methods

2.1. Sludge

The anaerobic digestion experiments were performed on waste activated sludge (WAS), untreated and sonicated at 200 kHz. The sludge was obtained from the municipal "Roma Nord" wastewater treatment plant, serving about 700,000 P.E. The treatment plant is a conventional one including screening, primary clarification and secondary treatment by activated sludge, operating with a quite high sludge age (20 d).

Secondary sludge was sampled from the recycle stream before secondary clarifier and gravity thickened for 24 h at 4 °C up to total solids concentration of 21–24 g/L, before feeding the bench scale anaerobic reactors.

The anaerobic inoculum was sampled from the full scale digester of the plant fed with mixed sludge. Microbial composition analysis of the inoculum was carried out with Fluorescence in situ Hybridization (FISH), using specific probes for Bacteria (EUB338mix) and Archaea (arc915) domains. FISH procedure is reported elsewhere (Braguglia et al., 2012). Bacteria relative abundances was 40% out of total cells (estimated with DAPI staining), while archaeal population was 5% out of total cells. Two predominant archaeal morphotypes were identified: long Methanosaeta filaments, and cocci organised in sarcine, identified as *Methanosarcina* spp.

The principal characteristics of secondary raw and sonicated sludge and inoculum used in the digestion tests are summarised in Table 1.

Total and volatile solids (TS and VS) were determined according to standard methods (APHA, 1998). To analyse the soluble phase, the particulate sludge matter was removed by centrifugation (10 min at 4000 rpm) and resulting centrate was filtrated through 0.45 μm pore size membrane filters. Soluble COD (Chemical Oxygen Demand), measured in duplicates, was determined by photometric determination of chromate consumption by the organic compounds, subsequent to digestion in concentrated sulphuric acid solution for 2 h at 148 °C by means of COD Cell Test by Spectroquant Merck (EPA method 410.4).

2.2. Ultrasound pretreatment

The ultrasound apparatus is constituted of flat-plate type stainless-steel ultrasonic reactor (model USW 51-051) supplied by Elac Nautik Incorporated, Kiel, Germany, operating at 200 kHz and an average power of 90–100 W. Both frequency and power were adjusted with the AG 1006 LF generator/amplifier (T&C power Conversion), connected to the transducer. The delivered ultrasound power, measured by calorimetric method, was in the range 10–20 W, and the average energy efficiency of this transducer was therefore ~15%. The plate type transducer is made up of a piezo-ceramic element and the active acoustic vibration surface area is approximately 25 cm^2. The reactions were performed in a 500 mL glass reaction chamber, double-walled (cooling jacket) and covered. Ultrasonic irradiation at 200 kHz was performed for 40 min on 400 mL of real waste activated sludge. The ultrasound treatment was carried out immediately before starting the anaerobic digestion experiments.

The effectiveness of the disintegration pretreatment was evaluated by measuring the "disintegration degree" (DD_{COD} %), namely the ratio of the soluble COD increase due to pretreatment to the maximum possible soluble COD increase (Braguglia et al., 2006). The degree of disintegration is dependent on the specific energy supplied (E_{spec}) which can be calculated by the Eq. (1):

$$E_{spec} = \frac{P \times t_t}{V \times TS} \tag{1}$$

where P is the power of the ultrasonic processor, t_t the sonication time, V the sludge treated volume and TS the sludge total solids

Table 1
Feed sludge and inoculum characterization.

	Raw sludge	Sonicated sludge	Inoculum
TS (g/L)	21.3–24.1	21.8–23.2	20.9–31.7
VS (g/L)	12.5–14.4	13–14.4	11.9–20.2
VS/TS (%)	57–65	58–66	55–64
Soluble COD (mg/L)	15–50	1125–1560	271–373
LAS (mg/kg d m)	50–60	40–70	400–670