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Assessment of free nitrous acid pre-treatment on a mixture of primary sludge and waste activated sludge: Effect of exposure time and concentration

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HIGHLIGHTS

- FNA pre-treatment on mixed sludge increased the solubility of the organic compounds.
- FNA pre-treatment on mixed sludge reduced cell viability below 10%.
- Low FNA pre-treatment times are preferred to improve methane production.
- Optimal FNA pre-treatment resulted in an increase of 25% in methane production.

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ABSTRACT

Free nitrous acid (FNA) has been shown to enhance the biodegradability of waste activated sludge (WAS) but its effectiveness on the pre-treatment of mixed sludge is not known. This study explores the effectiveness of four different FNA concentrations (0, 2.49, 3.55, 4.62 mg N-HNO_2/L) and three exposure times (2, 5, 9 h) lower than the ones reported in literature (24 h) on WAS characteristics and specific methane production (SMP). FNA pre-treatment reduced sludge cell viability below 10% in all cases after an exposure time of 5 h, increasing the solubility of the organic matter. The treated mixed sludge was used as substrate for the biochemical methane production tests to assess its SMP. Results showed a significant increase (up to 25%) on SMP when the sludge was pretreated with the lowest FNA concentration (2.49 mg N-HNO_2/L) during 2 and 5 h but did not show any improvement at longer exposure times or higher FNA concentrations.

1. Introduction

Anaerobic digestion (AD) treatment from organic waste is developing rapidly around the world because it can avoid the environmental pollution resulting from untreated wastes and reduce reliance on fossil fuel (Ratanatamskul et al., 2014; Neumann et al., 2015). Furthermore effluent obtained after AD of sludge (stabilized effluent) is broadly recognized as a valuable substrate for agricultural soil amendment (Forster-Carneiro et al., 2010; Riau et al., 2012; Gianico et al., 2015). AD of biowastes, which are ultimately converted into methane (CH_4) and carbon dioxide (CO_2), includes two phases: hydrolytic-acidogenic phase (dark fermentation) and acetogenic-methanogenic phase and is performed by a microbial consortia comprising hydrolytic-acidogenic bacteria (fermentative bacteria), acetogenic bacteria and *Archaea* (Zahedi et al., 2014a). AD of waste activated sludge (WAS) is widely used to obtain methane from the organics present in the WAS. However, methane production in these systems is often limited by the slow fermentation rates of this substrate (hydrolysis and acidification) and its poor biochemical methane potential (Carrere et al., 2010; Liu et al., 2012; Wang et al., 2013, 2014; Lee et al., 2014; Zhao et al., 2015; Li et al., 2016; Ennouri et al., 2016). To overcome this limitation, research has been focusing on developing novel WAS pretreatment methods to improve sludge biodegradability and enhance biogas production (Carrere et al., 2010; Liu et al., 2012; Lee et al., 2014). These technologies aim at destroying cells and/or solubilize the extracellular polymeric substances (EPS) present in WAS, causing the release of intracellular and/or extracellular constituents to the aqueous phase (Carrere et al., 2010; Wang

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et al., 2013; Gianico et al., 2013). These are more easily biodegradable during anaerobic digestion, thereby enhancing specific methane production (mL of methane per SV added) (Wang et al., 2013). The most commonly used techniques for WAS treatment include thermal, mechanical, electrical and chemical treatments (Carrere et al., 2010; Alagoz et al., 2015; Zhang et al., 2015). However, most of the above mentioned pre-treatments are cost intensive due to high energy and/or chemical requirements. Free nitrous acid (FNA) has been demonstrated to be an attractive and economical pre-treatment for WAS (Law et al., 2015), causing a strong biocidal impact on microorganisms at mg/L levels (Pijuan et al., 2012). Also, it has been demonstrated to increase sludge biodegradability and specific methane production (SMP) at FNA concentrations in the range of 0.36–2.13 mg N-HNO_2/L with an exposure time of 24 h (Wang et al., 2013). However, a recent study conducted with primary sludge (PS) showed that the FNA pre-treatment compromised the MP from this sludge, also resulting in a limited release of readily biodegradable substances with FNA treatment in the range of 0.77–3.85 mg N-HNO_2/L under 24 h exposure times (Zhang et al., 2016).

In most domestic wastewater treatment plants, PS and WAS are mixed (mixed sludge) and digested together. This study aims at: i) assessing the feasibility of the FNA pre-treatment in mixed sludge; ii) exploring the effect of lower (<24 h) exposure times to FNA pre-treatment on mixed sludge characteristics (a reduced pretreatment time is preferred for real application since it reduces the volume of the pretreatment tanks); and iii) evaluating the effect of the different FNA-pretreatments on the sludge biochemical methane potential (BMP). The effect of the FNA pretreatment on the sludge characteristics was assessed at 4 different FNA concentrations (0, 2.49, 3.55 and 4.62 mg N-HNO_2/L) and 3 different exposure times (2, 5 and 9 h). BMP tests were also conducted in triplicate for each conditions tested. This is the first study reporting the effectiveness of the FNA pre-treatment in mixed sludge at low exposure times.

2. Materials and methods

2.1. Sludge sources

The sludge subject to the pre-treatment with FNA was mixed sludge, a mixture of primary sludge and WAS (50% v/v). The mixed sludge was collected directly from the feed pipe of the industrial digesters from a local wastewater treatment plant (Lleida WWTP, Catalonia, Spain).

For the BMP tests, the inoculum was collected from the mesophilic anaerobic digester present at the same WWTP. This digester has a capacity of 2480 m^3 and treats mixed sludge produced in the WWTP. The total solids (TS), volatile solids (VS) and total chemical oxygen demand (TCOD) concentrations in the inoculum were 26.0 ± 1.7 g TS/kg, 14.8 ± 0.1 g VS/kg and 1.8 ± 0.2 g COD/g VS, respectively.

2.2. FNA pre-treatment methodology

Four batch tests were conducted in a 6 L laboratory scale reactor to expose the sludge to the 4 different FNA concentrations plus a control (without nitrite and without pH control). The batch reactor was connected to a programmable logic controller (PLC) for pH and stirring control. The concentrations of FNA tested were 0, 2.49, 3.55 and 4.62 mg N-HNO_2/L corresponding to 0, 350, 500 and 650 mg N-NO_2^-/L at pH 5.5 (Table 1). The FNA concentration was calculated using the formula $S_N - NO_2^- = Ka * 10^{pH}$ with the Ka value determined using the formula $Ka = e^{-2300/(273+T)}$ for a given temperature T (°C) (Anthonisen et al., 1976). A certain volume of a nitrite stock solution (118.3 g $NaNO_2$/L) was added at the beginning of each batch test to achieve the desired nitrite concentrations (Table 1). pH was controlled at 5.5 ± 0.1 by using 1.0 M HCl and 1.0 M NaOH solutions. For each FNA concentration test, sludge samples were withdrawn at different exposure times (2, 5 and 9 h) to evaluate both the effect of the exposure time and the FNA concentration in the characteristics of the mixed sludge.

Table 1
Experimental conditions applied in the pre-treatment, with the FNA concentration varied by adjusting the nitrite concentration and the pH level.

25 °C	Test 1	Test 2	Test 3	Test 4
FNA (mg N-HNO_2/L)	0	2.49	3.55	4.62
Nitrite (mg N-NO_2^-/L)	0	350	500	650
pH	5.5	5.5	5.5	5.5
Time of exposure (h)				
2	X	X	X	X
5	X	X	X	X
9	X	X	X	X

2.3. Biochemical methane potential (BMP) tests

BMP tests were used to quantify specific methane production from FNA pre-treated and non pre-treated sludge. The BMP tests were conducted in 250 mL serum bottles (with a working volume of 100 mL). Each BMP tests contained 80 mL of inoculum and 20 mL of mixed sludge. The bottles were sealed and stored in a temperature controlled incubator at 37 °C. All the bottles were continuously shaking at 150 rpm to ensure sufficient mixing.

Four blank tests (Blank I, II, III and IV) were conducted to assess the methane production from the inoculum and the effect that nitrite could potentially have on the activity of the inoculum. Blank I contained inoculum and Milli-Q water without pretreated sludge. Blanks II, III and IV were identical to Blank I but with the addition of nitrite stock solution, which resulted in an initial nitrite level of around 70, 100 and 130 mg N-NO_2^-/L, respectively, mimicking the nitrite concentrations present in the BMP tests when FNA pre-treated sludge was added.

All tests were conducted in triplicates (except for the blanks that were done in duplicates). The BMP tests lasted for 40 days, when no biogas production was detected. The biogas production was monitored on a daily basis over the first 10 days and every 2–4 days afterwards. The biogas production from the mixed sludge was obtained by subtracting biogas production from the inoculum (Blank I). Specific methane production was reported as milliliters of methane produced per gram of VS added (mL CH_4/g VS) under normal pressure (P = 1 atm) and temperature conditions (T^a = 0 °C).

2.4. Analytical methods

2.4.1. Physico-chemical analysis

TS, VS, soluble Kjeldahl nitrogen (SKN) and chemical oxygen demand (COD, total and soluble) were determined according to standard methods (APHA, 1995). VFA (acetic, propionic, isobutyric, butyric, isovaleric, valeric, isocaproic, caproic and heptanoic) were determined by gas chromatography, using a gas chromatograph (Shimadzu GC-2010) equipped with a flame ionisation detector (FID) and capillary column filled with Nukol. The NH_4^+ concentrations were analyzed via ion chromatography (ICS5000, DIONEX).

The biogas volume was measured with a pressure sensor PM7097 (IFM electronic) at the start of each sampling event at headspace of the BMP bottles. Cumulative gas production was calculated from the pressure increase in the headspace volume (150 mL) and expressed under normal conditions (0 °C, 1 atm). CH_4 concentration in the biogas was measured using an infrared