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Enhancing sludge biodegradability through free nitrous acid pre-treatment at low exposure time

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HIGHLIGHTS

- Low FNA pre-treatment times (PTs) are effective to improve methane production.
- FNA on waste activated sludge (WAS) reduced cell viability to very low levels.
- Low FNA pre-treatment PTs on WAS increased the solubility of the organic compounds.
- Optimal FNA pre-treatment resulted in an increase of 20% in methane production.

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ABSTRACT

The effectiveness of low free nitrous acid (FNA) pre-treatment times (PTs) (<8 h) on waste activated sludge (WAS) is not known. This study explores the effectiveness of four different FNA concentrations (0, 2.49, 3.55 and 4.62 mg N-HNO_2/L) and three low PTs (2, 5 and 8 h) on WAS characteristics and methane generation. Increasing FNA concentrations and PTs resulted in an increase in the solubility of the organic matter (chemical oxygen demand, proteins and polysaccharides). Cell viability was below 15% in all cases at PTs higher than 2 h. Biochemical methane production tests (BMP) showed a significant increase (20–27%) on specific and total methane production (SMP and MP) when the sludge was pre-treated with 2.49- and 3.55 mg N-HNO_2/L during 5 h and 8 h. Increasing PT (>5 h) resulted in a decrease in MP due to a volatile solid reduction on WAS during the pretreatment. The highest FNA concentration tested (4.62 mg N-HNO_2/L) did not further improve MP and SMP. This study clearly shows the effectiveness of the FNA sludge pretreatment at low exposure times.

1. Introduction

It is well known that methane production (MP) from waste activated sludge (WAS) is often limited by the slow fermentation rates (hydrolysis and acidification) and its poor biochemical methane potential (BMP) [1–10]. To overcome this, recent research has been focusing on developing a novel, attractive and economic pre-treatment for WAS based on free nitrous acid (FNA) [6,7,11–14]. FNA destroy cells and solubilize the extracellular polymeric substances (EPS) (especially proteins and polysaccharides) present in WAS, causing the release of intracellular and/or extracellular constituents to the aqueous phase [4,6,7,11,15], which are more easily biodegradable during anaerobic digestion (AD), thereby enhancing specific methane production (mL of methane per volatile solid added) (SMP) [6]. FNA pre-treatment has been demonstrated to cause a strong biocidal impact on microorganisms, to increase sludge biodegradability and SMP at FNA concentrations in the range of 0.36–2.13 mg N-HNO_2/L [6,7,12,13]. FNA exists in equilibrium with nitrite and the mechanisms by which nitrite and FNA have been reported to act as cytotoxins include the following [16,17]: (i) FNA can lead to the formation of reactive nitrogen and oxygen species in the cytoplasm including nitric oxide (NO), nitrogen dioxide (NO_2), peroxynitrite ($ONOO^-$), hydroxide ion (OH^-) and hydrogen peroxide (H_2O_2), all of which exhibit toxicity towards bacterial cells, causing cell death; (ii) FNA has been suggested to act as an uncoupler acting to circumvent the ATP synthesis as a result of a short-circuit formed by FNA transporting protons across the inner membrane and back into the cell and so increasing the conductance of the cytoplasmic membrane; and (iii) FNA may be able to directly inhibit electron carriers. The disadvantage of the

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FNA pre-treatment is the long pretreatment times (PTs) suggested in the literature to date (24 h). This is an important aspect, because a reduced PT is preferred for real application since it reduces the volume of the pretreatment tank. With this study we aim at exploring the effect of pre-treatment times lower than the ones reported in literature (24 h) on WAS biodegradability and methane generation. The effect of the FNA pre-treatment 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 8 h). To evaluate the effect of the different FNA pre-treatment on the biochemical methane potential (BMP), BMP tests were conducted in triplicates for each conditions tested. This is the first study reporting the effectiveness of the FNA pre-treatment in WAS at low pre-treatment times and on MP (not only on the SMP). This is important, since for industrial application, the increase on the SMP have to be linked to an increase on the MP and not due to a volatile solid reduction on WAS during the pre-treatment. Until now the FNA biocidal effect on SMP of WAS was only associated with the FNA concentration but not with the PT.

2. Materials and methods

2.1. Lleida WWTP, WAS and inoculum

The Lleida WWTP (Catalonia, Spain) where the sludge and inoculum was taken serves 130,000 PE treating 60,000 m^3/d of domestic wastewater. The conventional treatment used in this plant consists of preliminary (fat and sand removal equipment with a hydraulic retention time (HRT) of 12 min), primary treatment (primary clarifier with HRT = 1.82 h), and then a secondary treatment where microorganisms are used to consume organic matter and nutrients from the wastewater in the activated sludge unit (HRT and solid RT (SRT) of 0.36 d and 9.55 d, respectively). Primary sludge (PS) is a result of capturing suspended solids and organics in the primary treatment process through gravitational sedimentation and WAS is obtained from the secondary clarifier (HRT = 4.88 h). PS and secondary WAS are thickened and mixed (sampling point) before undergoing mesophilic (37 °C) anaerobic digestion at 26 days of SRT in two anaerobic bioreactors with a total volume of 5000 m^3/d and biogas production around 2800 m^3/d. Finally, digested sludge is dewatered before its disposal.

For the present study, WAS was collected from the secondary sludge thickener. The pH, total solids (TS), volatile solids (VS) and soluble chemical oxygen demand (SCOD) concentrations were 6.4 ± 0.1, 40 ± 1 g TS/kg, 29 ± 0 g VS/kg and 51.6 ± 0.2 mg SCOD/g VS, respectively.

For the BMP tests, the inoculum was collected from one of 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 pH, TS, VS and SCOD concentrations in the inoculum were 7.8 ± 0.2; 25 ± 0 g TS/kg, 14 ± 0 g VS/kg and 24.9 ± 0.2 g SCOD/g VS, respectively.

2.2. FNA pre-treatment methodology

The FNA pre-treatment tests were carried out in four polyethylene batch reactors of 1.5 L of working volume. The batch reactors were covered during the pretreatment to avoid loss of organics. Four mechanical stirrers (FLUCOMATIC 6 system, SELECTA S.A) were used at a speed of 100 rpm to mix the pre-treatment reactors. 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 N-$HNO_2 = (S_{N\text{-}NO2})/(Ka * 10^{pH})$ with the Ka value found from $e^{-2300/(273+°C)}$ for a given temperature [18]. 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 concentration (Table 1). pH was controlled at 5.5 ± 0.1 by using 1.0 M HCl solution. For each FNA concentration test, sludge samples were withdrawn at different exposure times (2, 5 and 8 h) to evaluate both the effect of the exposure time and the FNA concentration in the WAS characteristics. The pre-treatment assays were carried out at room temperature (~25 °C).

2.3. Biochemical methane potential (BMP) tests

BMP tests were used to quantify 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). BMPs were set up with an inoculum to pre-treated WAS ratio of 2.4 on a dry VS basis. Each BMP test contained 80 mg of inoculum and 20 mg of WAS pretreated with FNA (0, 2.49, 3.55 and 4.62 mg N-HNO_2/L; see Table 1) according to Zahedi et al. [19]. Ratios inoculum/Substrate (I/S) between 2 and 4 are required to ensure the proper performance of BMP tests [20,21]. A control test (WAS without nitrite and pH control) was also conducted. 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.

Three sets of blanks (blanks I, II and III) were also conducted. Blank I contained inoculum and Milli-Q water without WAS. Blanks II and III were identical to blank I except with the addition of nitrite stock solution, which resulted in an initial nitrite level of around 70 and 130 mg N-NO_2^-/L, respectively, in blanks II and III. This was done to evaluate the effect of nitrite on the performance of the inoculum. The initial nitrite levels of 70 and 130 mg N-NO_2^-/L in blanks II and III were similar to the lowest and the highest initial nitrite levels found in the BMP tests conducted with pre-treated WAS.

All tests were done in triplicates. The BMP tests lasted for 40 days, when no biogas production was detected. The biogas production was monitored on a daily basis during the first 10 days and every 2–4 days afterwards. The biogas production from the WAS was obtained by subtracting the biogas production from the inoculum (Blank I). MP (milliliters of methane produced) and SMP (milliliters of methane produced per gram of VS added) have been expressed under normal pressure (P = 1 atm) and temperature conditions (T^a = 0 °C).

2.4. Analytical methods

TS, VS, soluble Kjeldahl nitrogen (SKN) and SCOD were determined according to standard methods [22] and Zahedi et al. [23,24]. NH_4^+ was analyzed via ion chromatography (ICS5000, DIONEX). Biopolymers (proteins and carbohydrates) were measured in the soluble phase before and after pretreatment. To separate solid particles from soluble phase, sludge was centrifuged during 10 min at 13000 rpm and the supernatant was filtered through a 0.20 μm pore size glass fiber filter. Proteins were measured with the Folin Phenol Reagent according to Lowry [25] and Peterson [26] and carbohydrates were measured using a colorimetric method (fenol plus sulfuric acid) according to Dubois [27].

The biogas volume was measured with a pressure sensor PM7097 (IFM electronic) at the start of each sampling event at the headspace of the BMP bottles. Cumulative gas production was calculated from the pressure increase in the headspace volume (150 mL). CH_4 concentration in the biogas was measured using an infrared specific CH_4 sensor: GasTech S-Guard (GIR-3000 Model). This sensor was calibrated using a commercial 100% CH_4 bottle (Abelló Linde S.A.).