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Effect of free nitrous acid pre-treatment on primary sludge at low exposure times

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HIGHLIGHTS

- pH control is not necessary during FNA pre-treatment on primary sludge (PS).
- FNA increases the solubility and reduces cell viability (<20%).
- At 1 h, FNA (with 650 mg N-NO_2^-) provided the highest methane production (MP).
- Similar enhancement on MP were obtained while subjecting the PS at mild at 2–5 h.
- FNA is not necessary to increase MP; mild agitations also improve MP (around 14–17%).

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ABSTRACT

The present study was undertaken to investigate the effect of different free nitrous acid (FNA) concentrations at low pre-treatment times (PTs) (1, 2 and 5 h) and without pH control with mild agitation on primary sludge (PS) biodegradability and methane production (MP). Increasing PTs resulted in an increase in the solubility of the organic matter (around 25%), but not on cell-mortality (>75% in all the cases with FNA) and neither on methane generation. FNA pre-treatment at low PTs improve MP (around 16% at PT of 1 h and 650 mg N-NO_2^-/L). However, a similar improvement was found with mild agitation of PS without FNA at 2 and 5 h. Taking into account the potential costs associated with the FNA pre-treatment, a mild agitation without FNA would be preferred to enhance MP in PS.

1. Introduction

Waste water treatment is a key process in our society to avoid pollution in our water bodies, as well as provide a source of water that can be directly used for irrigation. This last aspect is becoming more important due to climate change, with currently above 46% of cultivated areas in the world not receiving enough rain water for their agricultural needs (Yannopoulos et al., 2015; Valipour, 2015). Wastewater treatment is increasingly being applied worldwide, increasing as well sludge production. Sludge management is a serious issue since up to one-half of the costs of operating municipal Waste water treatment plants (WWTPs) is associated with sludge treatment and disposal (Lens, 2004; Peces et al., 2016). Anaerobic digestion (AD) is a sludge treatment process used in many WWTPs to stabilize primary sludge (PS) and waste activated sludge (WAS) from aerobic/anoxic biological treatment processes obtaining methane (CH_4) (Climent et al., 2007; Peces et al., 2016). PS is a result of the capture of suspended solids and organics in the primary treatment process through gravitational sedimentation, typically by a primary clarifier. The WAS is obtained from the secondary clarifier after the secondary treatment process whereby microorganisms are used to consume organic matter and nutrients from the wastewater. The different origin of PS and WAS make them to have different characteristics: WAS has a much higher content of microorganisms and proteins but lower fatty acids content and is less biodegradable having therefore a lower methane production potential than PS (Lens, 2004; Sato et al., 2001; Wilson and Novak, 2009; Zhang et al., 2016). On the other hand, PS has less microorganisms and more fatty acids (Cokgor et al., 2009; Peces et al., 2016; Zhang et al., 2016). In many WWTPs both sludge types are mixed before entering the anaerobic digester and also, in many cases, a pre-treatment of this sludge mixture is done

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to increase its biodegradability and enhance CH_4 production during the digestion process. Recent studies have demonstrated the efficacy of free nitrous acid (FNA) pre-treatment for WAS (Ganda et al., 2016; Ma et al., 2015; Wang et al., 2013, 2014; Wu et al., 2016). FNA, the protonated species of nitrite, can be produced in the same WWTP by the nitritation process of the anaerobic digestion liquor, making it economical and environmental more attractive than other pre-treatment methods. FNA destroy cells and solubilize the extracellular polymeric substances (EPS) (especially proteins and polysaccharides) present in sludge. This causes the release of intracellular and/or extracellular constituents to the aqueous phase (Carrère et al., 2010; Ma et al., 2015), which are more easily biodegradable during AD, thereby enhancing methane production (Wang et al., 2013).

On the other hand, the only study present in the literature where FNA pre-treatment is used in PS suggests that this pre-treatment compromises the methane production (MP) (Zhang et al., 2016). In that study PS was exposed to different concentrations of FNA (from 0.77 to 3.85 mg N-HNO_2/L) during 24 h. In all tests an increase on the soluble chemical oxygen demand (COD) concentration was detected. However, lower methane production rate and methane production potential was observed in the PS treated with FNA as compared with the non-treated control. Their results indicated that FNA pre-treatment at 24 h resulted in the methane potential reduction of 1–7%.

In another study, Zahedi et al. (2016) applied an FNA pre-treatment to a mixture of PS and WAS obtaining an improvement on the MP when the pre-treatment time was reduced to 5 h. If that improvement was linked only to WAS or to PS remained unclear.

In the present study, the effect of the FNA pre-treatment on PS characteristics was assessed at 4 different FNA ranges (0; 1.2–3.9; 1.7–5.6; and 2.6–7.3 mg N-HNO_2/L) and 3 different exposure times (1, 2 and 5 h). Also the effect of mild mixing was studied. To evaluate the effect of the different pre-treatments on the biochemical methane potential (BMP), BMP tests were also conducted in triplicates for each conditions tested.

This is the first study reporting the effect of the FNA pre-treatment in PS to enhance MP at low pre-treatment times and without pH control. Former studies have focused on long pre-treatment times (24 h) and addition of acid to have a fixed control of the pH values. These aspects are important, since low pre-treatment times are preferred for real application, reducing the volume of the pretreatment tank needed. Also, no pH control means substantial savings and lower risk from handling acids during the FNA pre-treatment process.

2. Materials and methods

2.1. Substrate and inoculum

The substrates that were used in batch tests are PS that withdrawn from the primary sludge clarifier from a WWTP (Lleida WWTP, Catalonia, Spain). The pH, total solids (TS), volatile solids (VS) and soluble chemical oxygen demand (SCOD) concentrations in the PS were 5.2 ± 0.1, 42 ± 1 g TS/kg, 32 ± 1 g VS/kg and 157 ± 2 mg SCOD/g VS, respectively.

For the methanogenic studies (BMP tests), inoculum from the mesophilic anaerobic digester present at the same WWTP was collected. The pH, TS, VS and SCOD concentrations in the inoculum were 7.4 ± 0.1; 23 ± 0 g TS/kg, 14 ± 0 g VS/kg and 29 ± 0 g SCOD/g VS, respectively.

2.2. FNA pre-treatment methodology

Four laboratory-scale continuously stirred polyethylene reactors were used in these studies. The pre-treatment reactors had a working volume of 1 L and were mixed at a speed of 100 rpm with four mechanical stirrers (FLUCOMATIC 6 system, SELECTA S.A). The concentrations of nitrite used were the same as those used by Zahedi et al. (2016), corresponding to 0 (Test 1), 350 (Test 2), 500 (Test 3) and 650 mg N-NO_2^-/L (Test 4). The FNA concentration slightly varied throughout each of the tests due to the fact that pH was not controlled and raised from 5.3 to 5.8 in the tests where nitrite was added. The FNA concentration was calculated using the formula $S_{N-NO_2^-}/K_a \times 10^{pH}$ with the Ka value determined using the formula $K_a = e^{-2,300}/_{(273+T)}$ for a given temperature T (°C) (Anthonisen et al., 1976). Different volumes of a nitrite stock solution (118.3 g $NaNO_2$/L) were supplemented in each reactor at the beginning of the experiment in order to achieve the targeted nitrite concentrations (Table 1). To unravel both the effect of the pre-treatment time and the effect of the FNA concentration in the characteristics of the primary sludge, sludge samples were taken at different exposure times (1, 2 and 5 h). The pre-treatment assays were carried out at room temperature (~25 °C).

2.3. Methane generation studies

To investigate the effect of FNA pre-treatment on the methane production potential of PS, BMP tests were used. The BMP tests were carried out in 250 mL serum bottles (with a working volume of 100 mL). Each BMP test contained 82 mg of inoculum and 18 mg of PS to maintain an inoculum to PS ratio of 2 on a dry VS basis. All the bottles were closed and maintained in a mesophilic temperature controlled (at 37 °C) employing a ST 700 incubator (POL-EKO). To ensure sufficient mixing, the bottles were continuously shacked at 150 rpm using a KS 260 basic orbital shaker (IKA).

To assess the methane generation of inoculums, as well as to evaluate the effect that nitrite could potentially have on the activity of the inoculums four blanks were conducted (Blank I, II, III and IV). Blank I contained inoculum and Milli-Q water without pre-treated 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 concentrations of around 63, 90 and 117 mg N-NO_2^-/L, respectively, mimicking the nitrite concentrations present in the BMP tests when FNA pretreated sludge was added. Methane production (MP, milliliters of methane produced) from the PS was obtained by subtracting the MP from the inoculum (Blank 1) according to the same methodology used in Zahedi et al. (2016). MP and specific MP (SMP, milliliters of methane produced per gram of VS added) have been expressed under normal conditions (P = 1 atm and T = 0 °C). The BMP tests were carried out in triplicates and lasted for 45 days.

2.4. Chemical and microbial analyses

TS, VS, soluble Kjeldahl nitrogen (SKN) and SCOD were determined according to standard methods (APHA, 1995). NH_4^+ was analyzed via ion chromatography (ICS5000, DIONEX). Proteins were measured with the Folin Phenol Reagent according to Lowry et al. (1951) and Peterson et al. (1977) and carbohydrates were measured using a colorimetric method (fenol plus sulfhidric acid) according to Dubois et al. (1956).

Biogas was monitored on a daily basis during the first 10 days and every 2–4 days afterwards. A pressure sensor PM7097 (IFM electronic) was used to determine the pressure increase in the headspace volume (150 mL) and cumulative gas production was calculated from these pressure increase. An infrared specific CH_4 sensor: GasTech S-Guard (GIR-3000 Model), that was calibrated using a commercial 100% CH_4 bottle (Abelló Linde S.A.), was used to determine of CH_4 in the biogas.