Ozonation as a Pretreatment to Increase the Energy Recovery Potential of Sewage Sludge: A Bench Study with Biotrickling Filter Sludge

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The objective of this work was to assess the application of ozonation as a pretreatment to improve the thermal and electrical energy recovery potential of sewage sludge, based on a lab-scale study conducted with sewage sludge from a biotrickling filter (BTFS). Ozonation was carried out under the natural pH of BTFS, at applied ozone doses of 25, 150, and 275 mg O_3 . $g⁻¹ TS$. Batch anaerobic digestion (AD) tests were performed to assess the effects of ozone pretreatment on the methane production potential of BTFS. The impact of ozonation on the energy recovery potential was analyzed based on primary energy and electrical energy balance assessments. Ozone pretreatment increased the specific methane production potential (mL CH₄. g^{-1} VS_{BTFS}) by up to 75%, which means an additional primary energy production potential of about 2.4 MW.h. $t⁻¹$ of sludge.

Introduction

Anaerobic digestion (AD) is a consolidated technology which is commonly used to treat organicrich substrates, such as sewage sludge, manure and other wastes [1-2]. However, the presence of complex organic molecules can hinder the hydrolysis in the AD of some of these substrates [2].

In view of this, the potential of ozonation to improve AD of complex substrates has been widely studied [1-2], as it can promote the partial oxidation of organic compounds, leading to cell lysis, solubilization, and formation of molecules with increased biodegradability.

The knowledge about the effects of ozone pretreatment on the energy recovery potential of sewage sludge from biofilm reactors is still limited [2]. Given these facts, this work aimed at assessing the application of ozone pretreatment to improve the primary and electrical energy recovery potential of sewage sludge from a biotrickling filter (BTFS).

Material and Methods

Feedstock and inoculum

Fresh BTFS (feedstock) and anaerobic sludge (inoculum) were collected at a sewage treatment plant located in Itabira, Brazil. Inoculum (total solids $- TS = 2.5\%$, volatile solids $- VS = 1.7\%$ w/w) was obtained from a full-scale upflow anaerobic sludge blanket (UASB). Physicochemical analysis of BTFS and inoculum were done according to APHA [3].

Ozone pretreatment

Ozone pretreatment of BTFS was conducted using a bubble column reactor and an ambient air ozone generator (058011-Panozon XPM 300 SC, Brazil) (Graphical illustration), at a gas flow rate of 0.8 L.min-¹, an ozone production rate of 136.3 mg O_3 .h⁻¹, and a working volume of 0.7 L of BTFS. Ozonation was

carried out at the natural pH of BTFS ($pH = 5.0$). The applied ozone doses were 25, 125, 275 mg O_3 , q^{-1} TS. Ozone concentration in the off gas was determined by iodometric titration [3] to quantify the consumed ozone dose and assess the ozone mass transfer efficiency.

Anaerobic digestion

Biomethane potential (BMP) of raw (non-ozonated) and ozonated BTFS was assessed through batch AD tests. Experiments were performed in triplicate in 1 L serum bottles. Reactors were maintained at continuous mixing under mesophilic conditions (35 $^{\circ}$ C). Specific methane production (mL CH₄.g⁻¹) VS_{BTFS}) was measured using a gas flow meter (Anaero Technology, UK) and was normalized to standard temperature and pressure conditions. Specific methane production potential of digesters fed with raw or ozonated BTFS was compared by the Kruskal-Wallis test (α=0.05).

Energy balance

The impact of ozonation on the energy recovery potential of BTFS was investigated based on two scenarios. In the first, it was considered that the methane produced is recovered to produce electrical energy in motor-generators, whereas in the second, the biogas produced is improved to produce primary energy which can be used as thermal energy. Both energy balance (EB) assessments were calculated based on the additional methane produced due to ozonation and on the energy required for ozone generation (7.5 \times 10⁻³ kW. h. g⁻¹ O₃ [1]), according to Equations 1-2:

$$
EB = Ep - Er
$$
 Eq. 1
Ep = $\eta \cdot NCV \cdot (CH_{4, OZ} \cdot CH_{4, N \cdot OZ})$ Eq. 2

where $Ep = energy$ produced due to ozonation; Er: energy required for ozone generation; η = energy conversion efficiency (100% for primary and 30% for electrical energy $[4]$); NCV = net calorific value of $CH_4(9.97 \times 10^{-3} \text{ kW.h. L}^{-1} [7])$; $CH_{4, OZ} = CH_4$ produced from ozonated BTFS; $CH_{4, N-0Z} = CH_4$ produced without ozone pretreatment.

Results and Discussion

Ozone pretreatment led to the removal of 29-50% of VS and TS content of BTFS (Table 1), which may represent significant decreases on sludge disposal costs [3]. In parallel, ozonation promoted increases of 30-100% of the soluble COD concentrations, potentially promoting the formation of more bioavailable molecules [6].

As a result, ozonation significantly (Kruskal-Wallis pvalue=0.01) increased the SMP of BTFS by up to 75% (275 mg O₃. g⁻¹ TS) (Figure 1), which is equivalent to an additional thermal energy potential of up to 3.2 MW.h. t^1 VS $_{\text{BTFS}}$ (Figure 2). In terms of electrical energy recovery potential, a positive energy balance was only achieved for the lowest ozone dose (25 mg O_3 . g^{-1} TS). This occurrs due to the reduced conversion efficiency of electrical energy production [4].

It is also important to consider that the acidic pH of BTFS can favor a direct reaction mechanism between ozone and the organic content of sludge. On the other hand, increasing the reaction pH can induce the formation of radicals (*e. g.*, HO●) with a reducing potential higher than ozone. In comparison to ozone, these radicals tend to react preferably and non-seletively with organic matter and form more oxidized (or completely oxidized) products [6]. Thus, due to the influence of the pH on the reaction kinetics and mechanisms during ozonation, further studies can investigate the impact of pH change on energy recovery potential of BTFS.

Figure 1. Specific methane production (SMP – L CH₄. q^{-1}) VSBTFS) of inoculum and raw and ozonated BTFS.

The consumed ozone dose were determined experimentally as 24, 122 and 166 mgO₃. g^{-1} VS. Since ozonation has its own energy requirement, using reactors that promote better ozone mass transfer [7] can improve the energy recovery potential and increase the potential revenues from BTFS treatment.

Figure 2. Energy balance (MW.h. t^{-1} VS_{BTFS}). **a)** Electrical **b)** Primary.

Applied O ₃ dose	ΤS (g.L ^{.1})	٧S (g.L ^{.1})	VS/TS ratio	COD _f $(g.L^{-1})$	pH	O ₃ mass transfer efficiency (%)
0 mg O_3 g ⁻¹ TS _{BTFS}	4.5	3.4	0.75	0.3	5.0	-
25 mg O_3 g ⁻¹ TS _{BTFS}	3.2	2.4	0.76	0.4	5.0	94.3
150 mg O_3 g ⁻¹ TS _{BTFS}	3.0	2.3	0.76	0.3	5.0	81.1
275 mg O_3 g ⁻¹ TS _{BTFS}	2.2		0.76	0.6	5.0	60.5

Table 1. Characteristics of raw and ozonated sewage sludge from biotrickling filter (BTFS).

TS: total solids; VS: volatile solids; COD: chemical oxygen demand; CODf: filtered chemical oxygen demand.

Conclusions

Results evidenced that ozonation can substantially reduce sludge disposal costs, in parallel to significantly increasing the potential revenues in sludge management, especially through primary energy recovery. We are delving into studies on alternatives for recovering sewage sludge as an energy source, considering the potential of ozone to improve substract AD and taking into account costs and reduction of carbon emissions.

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