Ozonation as a pre-treatment for anaerobic digestion of waste activated sludge: Effect of the ozone doses

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Abstract
The effect of different ozone doses was assessed in terms of biogas production, anaerobic digestion (AD) kinetics and concentration of amino acids (AA) and long chain fatty acids (LCFA) in the waste activated sludge (WAS). Four different ozone (O_3) doses were used: 0.043 gO_3/g_{TSS}, 0.063 gO_3/g_{TSS}, 0.080 gO_3/g_{TSS} and 0.100 gO_3/g_{TSS}. The lower doses resulted in biogas production increases and faster kinetics in the AD of SS, while the higher doses led to poorer process performance. Ozonation of WAS resulted in a non-linear reduction of the AA concentration. The concentration of LCFA was also reduced with linear correlation with the ozone dose. The reaction products of LCFA (aldehydes) might be the cause of inhibition observed in the anaerobic digestion of WAS treated with higher ozone doses.

Keywords
ozone; pre-treatment; WAS anaerobic digestion; amino acids; long chain fatty acids; aldehydes

INTRODUCTION

In recent years, optimisation of the anaerobic digestion (AD) of sewage sludge (SS) has aroused great interest due to the use of biogas as a renewable energy source for increasing the energy self-sustainability of waste water treatment plants (WWTPs). One of the strategies for AD optimisation is the pre-treatment of waste activated sludge (WAS) to increase biogas production, reduce volatile solids, improve SS dewatering and reduce pathogen content. Biological, mechanical, thermal and chemical sludge disintegration has been investigated (Carrère *et al.*, 2010).

Ozonation is the chemical method most widely used to solubilise WAS. While ozonation applied to reduce excess sludge has been widely investigated, only few studies are focused in the ozonation of WAS with the aim to increase the biogas production during the AD process. The effect of ozonation on WAS AD depends on the O_3 doses applied. Some controversy about the optimal O_3 dose is seen in the bibliography. Yeom *et al.* (2003) found that the optimal dose to enhance biogas production was 0.2 gO_3/g_{TSS} while Bougrier *et al.* (2006) suggested that mineralization of dissolved organic matter occurred at 0.15 gO_3/g_{TS}.

The aim of this work is to increase knowledge on the effect of the O_3 dose on the subsequent WAS AD. Biogas yield and kinetics were determined in batch AD of WAS pre-treated with four different O_3 doses and compared with SS without pre-treatment. The best and worse doses in terms of biogas yield and kinetics were selected to analyze and compare the effect of O_3 doses on the proteins and lipids present in WAS.

MATERIALS & METHODS

Substrates

Samples of WAS, primary sludge (PS) and inoculum for the experimental AD tests were taken from the flotation tank, the primary settler and the anaerobic digester of Castelló de la plana WWTP respectively.

Ozonation

The ozonation unit consists of a corona discharge type ozone generator with a production capacity of 2gO_3/h from oxygen. The inlet gas preparation system consists of an oxygen concentrator TOPAZ plus model provided by AIRSEP. O_3 concentration in the O_3 enriched gas produced by this system is measured by means of an O_3 analyser GM-PRO (Anseros®). The contact reactor consists of a 10 L transparent PVC reactor. WAS was pre-treated applying 4 different doses (0.043 gO_3/g_{TSS}, 0.063 gO_3/g_{TSS}, 0.080 gO_3/g_{TSS} and 0.100 gO_3/g_{TSS}). Before the ozonation pre-treatment, the WAS samples were bubbled with N_2 until the oxygen content was negligible.

Batch anaerobic digestion test

Two sets of batch AD tests were run using as a substrate 1) WAS (1 sample without pre-treatment and 4 ozonated samples) and 2) mixed sludge (60WAS:40PS vv) with the same pre-treatment scheme applied to the SS fraction. Experimental tests procedure was based on Verein Deutscher Ingenieure (VDI) Standard 4630 "Fermentation of organic materials". Glass bottles with a capacity of 2L were filled with inoculum and the substrate with an inoculum to substrate ratio (ISR) of 1 in terms of volatile solids. The vials were bubbled with N_2 and placed inside an oven at 33ºC. Biogas production was measured by Ritter Milligascounters® MGC-1 flow meter. Tests were run in triplicates.

Analytical methods

Total solids (TS), volatile solids (VS), total and volatile suspended solids (TSS and VSS) were determined according to Standard Methods (APHA, AWWA, WEF, 1998). AA were analyzed by HPLC-PDA and LCFA on the fat fraction were determined by GC-FID.

RESULTS

Effect of ozone on biogas potential

Secondary sludge. Cumulative biogas production curves and daily biogas production of the 10 first days of batch AD test of the WAS are shown in figures 1a and 1b respectively. Dose 1 (0.043 gO_3/g_{TSS}) shows the faster kinetics, reaching the maximum daily biogas production by the second day of experiment (figure 1b). The biogas potential was increased by 5% with respect to the WAS without ozone pre-treatment. Dose 2 (0.063 gO_3/g_{TSS}) shows similar kinetics as the non pre-treated WAS sample, but the biogas potential is 21% higher. Doses 3 and 4 (0.080 & 0.100 gO_3/g_{TSS}) showed worse –and similar– initial kinetics and less biogas potential than the non pre-treated SS, but dose 4 had higher biogas potential than dose 3. The daily biogas production of SS treated with dose 4 increased by the sixth day of the experiment suggesting than some extra biodegradable organic matter was available. Biogas composition (CH_4, CO_2, H_2S, and H2) was similar in all samples (data not shown).

Mixed sludge. Cumulative biogas production curves and daily biogas production of the mixed sludge are shown in the figures 1c and 1d. In this case the mixtures of PS with the pre-treated WAS showed a similar increase in the biogas potential with respect to the mixture with WAS without pre-treatment, regardless of the O_3 dose applied. This fact suggested that the lower biogas potential of the WAS pre-treated with the higher doses 3 and 4 (figures 1a and 1b) is due to an inhibitory effect and not to a mineralization of the organic matter.

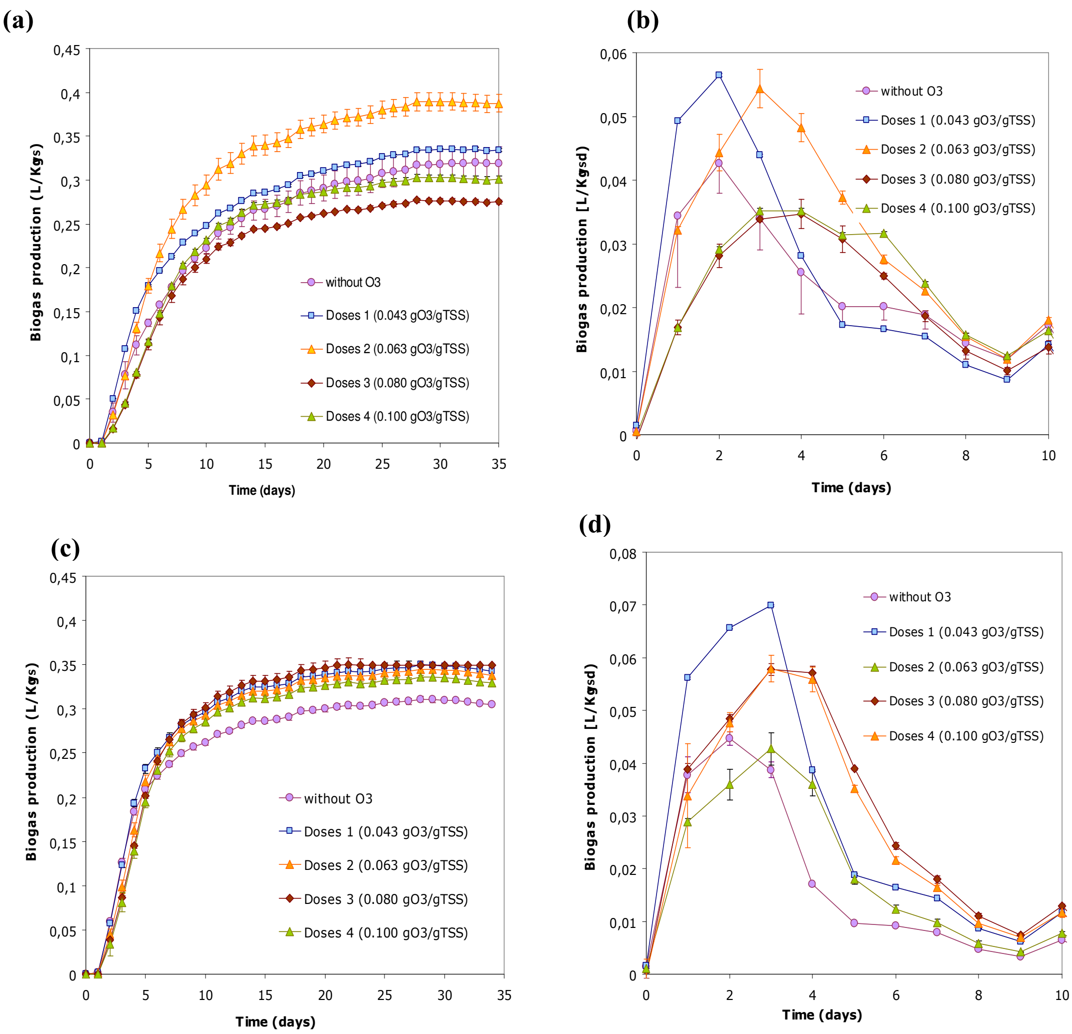

Figure 1. (a) Cumulative biogas production of WAS; (b) Daily biogas production of WAS; (c) Cumulative biogas production of mixed sludge; (d) Daily biogas production of mixed sludge.

Effect of ozone on the amino acids and long chain fatty acids profiles

Amino acids. Figures 2a and 2b show respectively the total AA concentration and the LCFA concentration in the WAS non pre-treated and ozonated with dose 2 (0.063 gO_3/g_{TSS}) and 4 (0.100 gO_3/g_{TSS}). The total and soluble AA concentrations were 19 mg/L and 3 mg/L (no pre-treatment), 10 mg/L and 1 mg/L (dose 2, 0.063 gO_3/g_{TSS}) and 12 mg/L and 1 mg/L (dose 4, 0.100 gO_3/g_{TSS}). These results show that O_3 has an effect on the total and soluble AA. O_3 might introduce changes in their secondary and tertiary structure and it is possible that these changes are connected with the partial oxidation of the aromatic monomeric units of the proteins (Cataldo, 2003). The results suggested than the O_3 doses have not a linear relation with the AA profile.

Long chain fatty acids. The total lipids concentration in the WAS were 2275 mg/L (no pre-treatment), 1450 mg/L (dose 2, 0.063 gO_3/g_{TSS}) and 959 mg/L (dose 4, 0.10 gO_3/g_{TSS}). O_3 reacts with the unsaturated LCFA and the results suggested that a linear correlation exists between the LCFA concentration and the O_3 doses in the range studied in this work. In the presence of water, the products obtained from the LCFA oxidation with O_3 are aldehydes and hydroxyhydroperoxide (Pryor *et al.*, 1995). Aldehydes are inhibitors for the AD (Chen *et al.*, 2008). These results could explain the results observed in the batch AD experiments; at high O_3 doses (dose 3 and 4) the inhibitor concentration would be higher in the AD of SS only, thus causing a decrease on the biogas production, while in the AD of mixed sludge, the inhibitor would be diluted and therefore no such effects are observed. Moreover, if the O_3 dose is high enough, the aldehydes might be further oxidized and therefore their inhibitory effect would be reduced (dose 4).

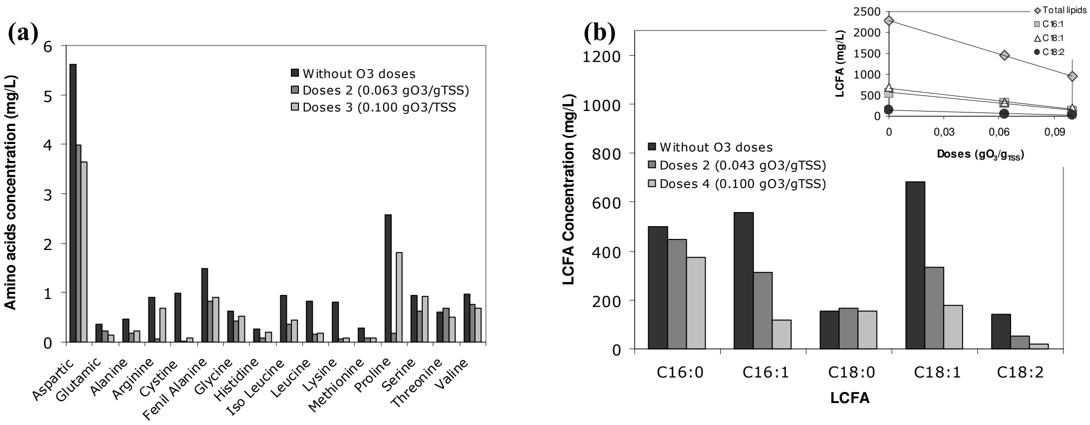

Figure 2. (a) AA concentration in the WAS with and without pre-treatment (dose 2 and 4); (b) LCFA concentration in the WAS with and without pre-treatment (dose 2 and 4).

CONCLUSIONS

The effect of ozonation on the biogas production and anaerobic digestion kinetics of waste activated sludge is different according to the ozone dose applied. The lower doses applied in this work led to improvements of the biogas production and faster kinetics, but poorer performance was observed with higher ozone doses. This effect is not observed in the anaerobic digestion of mixed sludge with ozonated waste activated sludge.

Ozone reduces the concentration of total AA and LCFA in the waste activated sludge. The LCFA oxidation produces aldehydes, which are inhibitory of the AD. This could explain the results of AD tests. Further research will be done to confirm this hypothesis.

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