Ozonation of primary sludge and digested sludge to increase methane production in a chemically enhanced primary treatment facility

Jaime Chacana[1*], Marc-André Labelle[1,2], Antoine Laporte[3], Alain Gadbois[4], Benoit Barbeau[1], Yves Comeau[1]

[1]Polytechnique Montreal, [2]WSP Canada Inc., [3]City of Repentigny, [4]Veolia

CONTACT Jaime Chacana, Department of Civil, Geological and Mining Engineering, Polytechnique Montreal, 2900, Edouard-Montpetit Boulevard, Montreal, Quebec, H3T 1J4, Canada. Email: jaime.chacana@polymtl.ca

ABSTRACT

The purpose of this research was the investigation of the ozonation of sludge as a method to improve anaerobic digestion performance in a chemically enhanced primary treatment facility. Batch tests were conducted to evaluate the effect of ozonation on the physicochemical characteristics of both primary and digested sludge. Then, the performance of semi-continuous anaerobic digesters in combination with ozone treatment was investigated (pre-ozonation and post-ozonation). Ozonation of primary sludge did not increase the soluble COD nor the biodegradable COD, but resulted in the mineralization of a fraction of the organic matter into CO_2. However, the ozonation of anaerobic digested sludge resulted in an increase in soluble COD and biodegradable COD and in a small level of mineralization at the dose of 90 mg O_3/g COD. Pre-ozonation of primary sludge was not effective in enhancing the performance of the anaerobic digester. The coupling of ozonation and anaerobic digestion by means of the post-ozonation of digested sludge was found to be effective in improving methane production (+16%), for COD removal efficiency and for the dewaterability of anaerobic digesters compared to the control digester.

Keywords: Ozone; anaerobic digestion; digested sludge; primary sludge; methane production

1 INTRODUCTION

Physicochemical and biological processes in wastewater treatment result in the generation of a large amount of sludge. Sludge treatment and disposal represent a major factor in the design and operation of water resource recovery facilities (WRRFs) (Erden, Demir, and Filibeli 2010). Increasing sludge production, costs of sludge treatment and disposal, and stringent regulations, have resulted in the development of new strategies to reduce sludge production (Wei et al. 2003). Anaerobic digestion is commonly used for sludge reduction and methane production; furthermore, its performance can be improved with mechanical, chemical, thermal and other biological methods (Weemaes et al. 2000).

Chemical oxidation with ozone is one of the preferred chemical treatments, which not only permits sludge reduction, but is also considered to be effective in enhancing methane production via the oxidation and solubilization of sludge (Weemaes et al. 2000). To enhance the methane production of a chemically enhanced primary treatment (CEPT) facility, ozonation can be applied to primary sludge upstream of the anaerobic digester (pre-ozonation) or in the recirculation loop of the anaerobic digester (post-ozonation). Ozone treatment targets the enhancement of anaerobic digestion processes by altering the physicochemical properties and biodegradability of sludge (Weemaes et al. 2000; Meng, Liu, and Frigon 2015). Past studies on the effect of ozone have mainly focused on activated sludge. Limited information about the effect of ozonation on primary sludge (PS) and anaerobic digested sludge (DS) is available. Some studies have investigated the effect of ozone on COD reduction, solubilization of nutrients, and the impact on methane production potential (Weemaes et al. 2000; Manterola, Uriarte, and Sancho 2008; Meng, Liu, and Frigon 2015), but the partial and total oxidation of organic matter as a mechanism of COD reduction and the impact on the biodegradability of COD fractions of sludge samples have been not studied. A better understanding of the effect of ozone on PS and DS will provide valuable information for the design, operation and optimization of pre- and post-ozonation systems for a CEPT facility.

The main objective of this study was the evaluation of the ozonation of sludge as a method to increase the methane production of anaerobic digestion in a CEPT facility. This study first analyzes the impact of ozonation on PS and DS, in terms of changes in sludge and supernatant physicochemical characteristics at varying ozone doses. Second, the coupling of ozonation with anaerobic digesters was evaluated in two process configurations, pre-ozonation of PS and post-ozonation of DS each combined with semi-continuous lab-scale anaerobic digesters. The effects of ozone dose on methane production, COD removal efficiency, sludge settling properties and dewatering conditions were evaluated.

2 MATERIAL AND METHODS

2.1 Sludge ozonation

Sludge samples were collected from the Repentigny WRRF in Quebec. The plant treats an average flow of 25 000 m^3/d by a CEPT process. The PS evacuated from the settling tanks are treated by mesophilic anaerobic digestion (35°C) with a hydraulic retention time of 19 days. PS and DS were collected from settling tanks and anaerobic digesters, respectively. Samples were sieved through a 5 mm sieve to remove large debris and stored at 4 °C until use.

Sludge ozonation was accomplished in a 3.8 L column operated in a closed-loop. Ozone gas was injected into the reactor by means of a venturi injector (Model 484X, Mazzei, USA), while the sludge was recirculated with a peristaltic pump at 6 L/min. Ozone was generated from pure oxygen by an ozone generator (Model Peak 2X, Pinnacle, USA) producing 6 L STP/min at 12% by weight. The ozone concentration in the feed gas was measured with an ultraviolet (UV) ozone meter (BMT 964, BMT Messtechnik GmbH, Germany), whereas the amount of ozone in the off-gas was measured with the standard iodometric method (Rakness 2005). The highest ozone doses required to operate the closed-loop system for a period of 16 and 8.4 min for PS and DS, respectively. Under these conditions, average ozone transfer efficiency was calculated as 68 and 73%, respectively.

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91 *2.2 Analytical methods*

92 Total solids (TS) and volatile solids (VS) were analysed according to Standard Methods
93 (APHA et al. 2012). Samples were analyzed for total Kjeldahl nitrogen (TKN),
94 orthophosphate (o-PO_4) and total phosphorus (TP) by the QuickChem Method 8500
95 (Lachat Instruments, USA). Ammonia was measured by the AmVer™ Salicylate Test 'N
96 Tube™ Method (Hach Method 10031). Nitrate and nitrite were analyzed by
97 Chromotropic Acid Test 'N Tube Method (Hach Method 10020) and USEPA
98 Diazotization Method (HACH Method 10207), respectively. Volatile fatty acids (VFAs)
99 and alkalinity were measured by a titration method (Lutzhoft et al. 2014). The ozonation
100 experiments were performed in triplicate for ozone doses between 0 to 220 mg O_3/g
101 COD.
102 Heavy metals in DS were measured using an inductively coupled plasma optical
103 emission spectrometer (Agilent 7700x, Agilent Technologies, Germany) with sludge and
104 filtered samples (S-Pak 0.45 µm filter, Millipore, USA) being acidified with a solution of
105 hydrochloric acid and nitric acid before measurement. Solubilization of heavy metals
106 (S_{HV}), was used to represent the release of heavy metal during ozonation (Wan et al.
107 2014). This was calculated by Eq. (1):

$$S_{HV} = (C_{sD0} - C_{sO3})/C_{T0} \quad (1)$$

108 where C_{T0} is the concentration of heavy metals in the sludge before ozonation, C_{sD0} is
109 the concentration of heavy metals in the filtered sample before ozonation and C_{sO3} is
110 the concentration of heavy metals in the filtered sample after ozonation. S_{HV} was
111 calculated for each measured heavy metal as well as for the total amount heavy metals.
112 The particle size distribution (PSD) was measured by laser granulometry (Mastersizer
113 3000, Malvern Instruments Ltd., U.K.). The type of particle was considered to be
114 opaque (Fraunhofer approximation) as is recommended for sludge samples (Govoreanu
115 2004). The particle distributions were expressed in volume equivalent particles in a
116 range of 0.01 to 3500 µm.

2.3 COD fractionation

Chemical oxygen demand (COD) characterization of ozonated samples and controls was performed by a physicochemical separation method and a biodegradability assay (Wentzel 1999; Lu, Zhang, and Zhang 2010). A control was tested to evaluate the effect of treatment without ozone injection. COD were measured by using HACH methods (HACH Reactor Digestion Method 8000). The physicochemical COD characterization of sludge was classified into three major components: soluble COD (S_{COD}), colloidal COD (C_{COD}) and particulate COD (X_{COD}). Likewise, each of these components was subdivided into biodegradable and non-biodegradable fractions.

Initially, the samples were centrifuged at 2000 g for 2 minutes to remove very large particles (>> 1.2 µm). After centrifugation, the remaining suspension was filtered using Whatman GF (1.2 µm) filters. Then, a portion of the filtered suspension was flocculated with 1 g/L $ZnSO_4$ solution and the suspension was filtered using 0.10 µm filters (Supor®-100 membrane filter, PALL Life Sciences, USA). S_{COD} was measured on the 0.1 filtered samples, the colloidal + soluble COD (CS_{COD}) was defined as the obtained from the 1.2 µm-filtered samples and the total COD was measured on the samples before the initial centrifugation. C_{COD} was determined from the difference between CS_{COD} and S_{COD}. X_{COD} was calculated from the difference between the total COD and CS_{COD}.

Anaerobic biodegradability was determined by batch biochemical methane potential (BMP) test (Saha, Eskicioglu, and Marin 2011; Raposo et al. 2011). The biodegradability of the resulting fractions was presented in terms of biodegradable COD and non-biodegradable COD. Batch tests were performed under mesophilic conditions (at 35 °C) in 160 mL glass bottles. The sludge from the mesophilic anaerobic digester from the Repentigny WRRF was used as inoculum for tests. Then, samples from flocculation + filtration, 1.2 µm-filtered sample and total samples were submitted to BMP assays. Biodegradable COD of samples was calculated indirectly from the theoretical methane yield of 350 mL STP CH_4/g COD, considering the conversion of CH_4 to COD. A gas

147 manometer (model DG25, Ashcroft, USA) was used to measure the biogas production.
148 The methane gas content was measured with a gas chromatograph (model GC-456,
149 Bruker, USA) equipped with a thermal conductivity detector (150 °C).

150 2.4 Mineralization and partial oxidation of COD

151 Total COD, total organic carbon (TOC), TS, and the CO_2 in the off gas of the ozone
152 reactor were analysed to monitor the effect of ozonation on sludge. Before ozonation of
153 sludge samples, the headspace of the ozone reactor was purged with nitrogen gas to
154 avoid any interference with the CO_2 present in the headspace of the reactor. TOC was
155 analyzed with a Total Organic Carbon Analyzer (Dohrmann DC 190, Rosemount
156 Analytical, USA), and the CO_2 in the gas was measured by gas chromatography (model
157 GC-456, Bruker, USA). The following equations were used to determine the percentage
158 of COD decrease triggered by partial oxidation ($\mu_{CODpartox}$, Eq. 3) and mineralization of
159 organic matter (μ_{CODmin}, Eq. 4) (Carbajo et al. 2007):
160

$$COD_{partox} = TOC_i \cdot (COD_0/TOC_0) - COD_i \quad (2)$$

$$\mu_{CODpartox} = 100 \cdot COD_{partox}/(COD_0 - COD_i) \quad (3)$$

$$\mu_{CODmin} = 100 - \mu_{CODpartox} \quad (4)$$

161

162 where COD_0 and TOC_0 are the total COD and TOC of sample before ozonation; COD_i
163 and TOC_i are the total COD and TOC of sample after ozone treatment.

164 2.5 Evaluation of foaming potential

165 The foaming potential of samples was determined based on the method of Kougias et
166 al. (2013). The foam formation tendency was evaluated by adding a 50 mL sample to a
167 cylinder that was aerated at an air flow rate of 100 mL/min during 5 min. After the
168 aeration period, the volume of the foam formed was recorded. The foam stability was
169 estimated by stopping the air supply and measuring the remaining foam after 30 min.
170 The foam tendency was defined as the foam volume after aeration (mL) per flow rate of
171 air (mL/min) and the foam stability was defined as the foam volume remaining in the

cylinder, 30 min after aeration (mL) per foam volume after aeration (mL). Measurements of foam potential were conducted in duplicate.

2.6 Coupling of sludge ozonation and anaerobic digestion

Coupling sludge ozonation with anaerobic digestion was performed in two process configurations. The first one was pre-ozonation of PS in combination with anaerobic digestion while the second configuration was post-ozonation of DS. For each configuration, an anaerobic digester was operated in parallel with a control digester not receiving ozonated sludge.

The lab-scale anaerobic digesters consisted of cylindrical PVC tanks (9.0 L) equipped with a magnetic stirrer. The digesters were operated in semi-batch mode, with manual sampling and feeding. The organic loading rate and the hydraulic retention time were controlled at 1.3 kg $VS \cdot m^{-3} \cdot d^{-1}$ and 19 days, respectively. The temperature and pH of digesters were maintained at 35 °C and 7.0, respectively. Biogas production was measured by a respirometry system operated in anaerobic mode (AER-200, Challenge Technology, USA). Biogas production was periodically collected and its methane content was measured by using a gas chromatograph (model GC-456, Bruker, USA). VS, pH and biogas production were monitored daily.

The start-up of anaerobic digesters was carried out using DS from the Repentigny WRRF. Throughout the course of the start-up and ozone experiments, the digesters were fed with PS. DS samples were collected every 1 to 2 weeks from Repentigny WRRF. The samples were adjusted to 40 g COD/L with distilled water and then stored at 4 °C until use. The reactors were fed with PS at an average flowrate of 420 mL/d.

After stabilization of VS in the sludge effluent, the digesters were operated in a pre-ozonation mode. For this configuration, the first digester was fed with ozonated PS at ozone doses of 5, 25 and 75 mg O_3/g COD, while the second digester was fed with PS without ozone treatment (control digester). Afterwards, both digesters were again stabilized with unozonated PS. Then, the digesters were operated in a post-ozonation configuration. Both digesters were fed with PS, but a fraction of DS was withdrawn as

the same sample was fed to the digester after the ozone treatment. The recycling rate ($mL \cdot d^{-1}/mL \cdot d^{-1}$) was defined as the ratio between the ozonated flow rate and the influent flow. For each scenario, the ozone dose was applied in the range needed to produce the maximum impact on increasing the biodegradability at recycling rates between 0 and 1.2. The ozonation of sludge was performed two to three times per week and the ozonated sludge was stored at 4°C.

For each experiment, the digesters were operated until VS stabilization, which took a minimum duration of 1 month, and then the samples of DS, biogas and PS were collected during three consecutive days for analysis. Dewatering and sludge settling properties were also evaluated by means of capillary suction time (CST) (304B CST-meter, Triton Electronics, UK) time to filter (TTF) and sludge volume index (SVI) (APHA et al. 2012).

3 RESULTS AND DISCUSSIONS

3.1 Effect of ozonation on primary sludge and anaerobic digested sludge

3.1.1 COD fractionation

The effect of ozonation was evaluated based on the physicochemical and biodegradable characterization of COD. COD fractionation of PS and DS is presented in Figure 1a and 1b, respectively. More detailed information is presented in Table S1 and S2 (Supplementary Information). Prior to ozonation, the predominant COD fractions in the PS and DS were particulate COD (95 and 88%, respectively), whereas the colloidal and soluble fractions were very small. The non-biodegradable fraction of the PS and DS were 38 and 83%, respectively. This large difference of biodegradability between these the two sludges is attributed to the effect of anaerobic digestion degrading a large part of the biodegradable fraction. Ozonation of PS did not significantly increase the soluble COD, and the impact on its biodegradable and non-biodegradable soluble fractions was low. However, ozonation of DS resulted in an increase in sludge solubilisation. The observed solubilization was lower than in previous studies reporting ozonation of activated sludge (Bougrier et al. 2007), which could be caused by the difference in the nature and composition of the organic matter of these samples. The mechanical effect

of pumping, evaluated by means of control, showed no significant impact on the solubilization of organic matter.

Ozonation is expected to generate soluble organic matter by the oxidation of organic polymers and the release of intracellular compounds due to the damage and lysis of bacteria (Manterola, Uriarte, and Sancho 2008; Meng, Liu, and Frigon 2015). The higher release of soluble COD resulting from the ozonation of DS rather than PS can be caused to the higher content of microorganisms in the DS. High biodegradable colloidal COD was also obtained by increasing the ozone dose of PS and DS (Figure 1a and 1b). However, particulate COD decreased.

The biodegradable COD of DS increased from 2.5 to 3.9 g COD/L for an ozone dose of 90 mg O_3/g COD, representing an increase of methane production of 55% (Figure 1b). A similar effect was observed at 140 mg O_3/g COD, but the methane production was not significantly increased compared with the ozone dose of 90 mg O_3/g COD ($p < 0.01$). Its non-biodegradable fraction, however, was reduced from 12.4 to 8.9 g/L at 140 mg O_3/g COD ($p < 0.01$). The increase of biodegradable COD was lower than the decrease of non-biodegradable COD, which could be ascribed to the mineralization to CO_2 of a fraction of the organic matter, as further discussed below.

3.1.2 Mineralization and partial oxidation

Total COD, TOC, $CO_{2(g)}$ and total solids were determined during the ozonation of PS and DS to clarify the impact of ozone oxidation on sludge organic matter (Table 1). An increase in ozone dose resulted in a decrease in COD and TOC concentration. The treatment of PS with an ozone dose of 220 mg O_3/g COD achieved a COD decrease of 14% and a TOC decrease of 10%. Similarly, for the treatment of DS at an ozone dose of 210 mg O_3/g COD, the COD and TOC decreased by 22% and 14%, respectively.

The partial oxidation and mineralization efficacy was evaluated at different ozone doses (Figure 2a). A high partial oxidation efficiency was achieved for ozone doses below 30 mg O_3/g COD and 90 mg O_3/g COD for PS and DS, respectively. This indicates that for low ozone doses, the COD decrease is not only caused by the mineralization of organic matter but also by the partial oxidation of organic matter into intermediate products. The partial oxidation efficiency was lower for high ozone doses, indicating that a higher

fraction of COD decrease is due to the complete oxidation of organic matter into carbon dioxide and water. For the highest ozone doses, the percentage of COD decrease triggered by mineralization was 74 and 67% for PS and DS, respectively.

For the ozonation of DS, the maximum biodegradability coincides with a low mineralization of organic matter. The biodegradability of samples was reduced for higher ozone doses (90 mg O_3/g COD), probably caused by the increased mineralization of organic matter. The low performance of ozone to increase the biodegradability of PS may be related to the high mineralization observed with low ozone doses.

High ozone doses decreased significantly the concentration of TOC confirming that the decrease of COD during ozonation is caused in part by the mineralization of organic matter. Furthermore, the increase of CO_2 in the off gas of the ozone reactor and the carbon mass balances further supports this conclusion (Table 1). The decrease in TOC during ozonation is consistent with previous studies on the ozonation of activated sludge which suggests that mineralization was the main mechanism of COD decrease (Déléris et al. 2000; Weemaes et al. 2000). However, our study indicates that the COD decrease not only results from mineralization but also from partial organic matter oxidation, especially for low ozone doses.

The sludge evaluation based on TS has shown a slight decrease reaching up to 6 and 8% for ozonation of PS and DS, respectively (Table 1). TS and TOC concentrations are strongly correlated following ozonation (Figure 2b), indicating that the mineralization of organic matter is the main mechanism of sludge mass reduction during ozone treatment. It has been reported that the ozone is able to oxidize most of the organic matter contained in a sludge, but the complete mineralization of sludge requires unrealistically high ozone doses (Déléris et al. 2000).

During ozonation, the effect of solubilization of organic matter appears to be most important at medium ozone doses, whereas mineralization of organic matter requires high ozone doses. The main impact of ozonation on DS was the increase of biodegradable COD and soluble COD, as well as the mineralization of organic matter. These parameters could allow the increase in performance and/or capacity of anaerobic

digesters, due to the improved degradation of organic matter and the increased methane production.

3.1.3 Particle size distribution

The effect of ozone treatment on the particle size of PS and DS is shown in Figures 3, S1 and S2 (Supplementary Information). The particle size distribution (PSD) indicated that ozone treatment causes the formation of smaller particles, as confirmed by the decrease in the mean particle sizes (D_v50) for both sludge samples (Figure 3a and b). The ozone treatment of PS resulted in a decrease of D_v50 up to 59% while its control was reduced up to 47%. A similar behavior was observed for ozonated DS and its control with a reduction of D_v50 up to 49 and 39%, respectively.

During ozone treatment, the samples were subjected to the oxidizing effect of ozone (and free radicals) and the mechanical effect of pumping due to sludge recirculation. Therefore, these results indicate that the reduction of particle sizes during the treatment was greatly influenced by the pumping of sludge and, to a lesser extent, by the action of ozone. The mechanical friction exerted by pumping and recirculation of samples in the ozone reactor likely caused the disaggregation of sludge, a process that has been reported in several mechanical methods using a relatively low energy input (Müller 2000). It has not been possible to verify the effect of ozone on soluble molecules using the laser granulometer due to the limitations of the device for measurement as well as the inaccuracies related to the use of Fraunhofer diffraction theory for very small colloids (Govoreanu 2004). However, as discussed previously, the soluble COD was not increased through the pumping and recirculation of sludge samples (controls); thus, these results suggest that the disaggregation of particles mainly affected the size distribution of larger particles. The solubilization by cell disintegration requires a large amount of mechanical energy (Müller 2000). Ozone oxidation causes cell disintegration, releasing intracellular compounds from the microorganisms present in digested sludge, thus, increasing the soluble matter, such as the COD fractionation assays that have been shown for DS.

3.2 Effect of ozone on solubilization of nitrogen and phosphorus

The effect of different ozone doses on nitrogen and phosphorus compounds was evaluated in terms of filterable TKN (CS_{TKN}), ammonia, nitrite, nitrate, filterable phosphorus (CS_P), and orthophosphates.

During ozonation, CS_{TKN} of PS and DS increased significantly from 180 to 200 mg N/L (11%) and from 430 to 570 mg/L (33%), respectively (>200 mg O_3/g COD) (Figure 4a). Ozone doses above 50 mg O_3/COD reduced significantly the concentration of ammonia in the PS, reaching a maximum decrease of 40% at 140 mg O_3/g COD, but it was slightly increased at higher ozone doses. Although the ozonation of DS showed an initial decrease in ammonia, its concentration was increased up to 19% ($p = 0.04$) at 210 mg O_3/g COD (Figure 4b). The increase in ammonia during the ozonation of DS can be related to the hydrolysis of proteins from the solubilized organic matter (Bougrier et al. 2007; Manterola, Uriarte, and Sancho 2008). Nitrate concentration increased during ozonation (Figure 4c) but nitrite was initially oxidised (Figure 4d).

Phosphorus was also solubilized by ozonation. An increase in orthophosphate and total phosphorus in the soluble phase was observed for both sludge samples (Figure 4e and f). This increase in organics and nutrients in the soluble phase can be attributed to the lysis of extracellular polymeric substance of sludge flocs and of sludge cells (Meng, Liu, and Frigon 2015). Ozonation of DS resulted in a rapid increase of organic carbon (soluble COD) and nutrients (nitrogen and phosphorus) in solution.

3.3 Effect of ozone on alkalinity, VFAs and pH

The alkalinity of the ozonated PS was reduced from 850 to 460 mg $CaCO_3$/L at an ozone dose of 220 mg O_3/g COD, while the alkalinity of the DS was reduced from 1670 to 660 mg $CaCO_3$/L at an ozone dose of 210 mg O_3/g COD (Figure 5a). While the concentration of VFAs of the DS gradually increased during ozonation, the concentration of VFAs of PS decreased, which is consistent with its low solubilization and high mineralization (Figure 5b).

The pH of PS was decreased from 7.1 to 5.2 as ozone doses increased from 0 to 220 mg O_3/g COD as illustrated in Figure 5C. The pH of the DS, however, was decreased from 7.4 to 6.9 at ozone doses from 0 to 210 mg O_3/g COD (Figure 5c). The decrease

in sludge pH and alkalinity may be due to the production acids compounds, such as carboxylic acids and VFAs, caused by the oxidation of organic matter (Bougrier 2005; Weemaes et al. 2000).

3.4 Heavy metals solubilization

The changes in heavy metal concentrations during sludge ozonation of DS are presented in Table 2. Sludge showed a high content of Fe due to the use of $Fe_2(SO_4)_3$ as a coagulant for the CEPT process of the Repentigny WRRF. The results showed that heavy metals in sludge were released into solution at an ozone dose of 210 mg O_3/g COD. At this dose, the solubilization of COD increased to 8.1%, while the solubilization of total heavy metals only increased 1.0%. Molybdenum and nickel were the heavy metals that were released the most, reaching a solubilization up to 67 and 22%, respectively. Although the content of iron was high in the sludge, its solubilization was very low (<1.0%). Iron solubilization might have been inhibited by the precipitation of $Fe(OH)_3$ caused by the ozone oxidation of dissolved iron (Fe^{+2}).

It has been reported that ozonation can release heavy metals from activated sludge due to the decrease in pH which facilitates its mobilization from the particulate matter to the supernatant (Park et al. 2008). Therefore, a possible reason for the low observed impact on the solubilization of heavy metals during this study could be the low impact of ozone on the pH of DS.

3.5 Foaming potential for ozonated samples

The foaming properties of PS and DS at different ozone doses are presented in Figure 6. Ozonation did not significantly increase the foaming tendency of PS. Otherwise, the foaming tendency of DS before ozonation was approximately 0.1 mL foam·mL air^{-1}·min^{-1}, but after ozonation, it increased significantly to 7.7 mL foam·mL air^{-1}·min^{-1}, thus, representing an increase of 77 times in foam volume. The foams produced by ozonated PS or DS were not stable and collapsed in less than 10 min once the air supply was stopped. These results are in agreement with the experimental observations that during the ozonation of DS, the foam increased as the operation time increased, consuming the reactor space, but that no significant loss of foam was detected. During ozonation of

PS, there was no observed foam accumulation. Apparently, the internal recycle loop of sludge used during ozonation allowed the foaming to be reduced by the mechanical breaking of foam.

The impact of ozonation on foam development has been attributed to the increase of concentrations of surface active agents in sludge supernatant, such as VFAs, proteins, and lipids, which have been recognized as foam-forming agents (Ganidi, Tyrrel, and Cartmell 2009).

The excessive accumulation of foam can complicate the control of a process by consuming reactor space and making inoperative the whole ozonation process (Janknecht et al. 2001). Strategies for enhancing foam reduction could include the dosing of a foam inhibitor (Ganidi, Tyrrel, and Cartmell 2009).

3.6 Ozone treatment combined with anaerobic digestion

The evaluation of the performance of pre-ozonation showed that the effect of ozonation does not significantly improve the methane production of PS for ozone doses between 0 to 75 mg O_3/g COD (Figure 7a). This coincides with the previous results from the COD fractionation of ozonated PS, which showed a limited effect on biodegradability and solubilization. Higher ozone doses were not evaluated considering the results obtained during the semi-continuous assays, as well as the previous COD fractionation assays that showed an increased mineralization of sludge at higher doses of ozone, and therefore, a probable decrease of anaerobic digester performance.

In terms of the combination of ozonation with an anaerobic digester by means of post-ozonation of DS, ozonation was found to be effective in increasing COD removal leading to subsequent improvements in methane production (Figure 7b). The highest methane production was achieved for an ozonated recycling rate of 1.2. The specific methane production increased from 189 to 218 mL N CH_4/g COD fed (+16%, $p < 0.01$) and the COD removal efficiency was increased from 51 to 59% ($p < 0.01$) with respect to the control digester. A higher recycling rate reduced the enhancement of anaerobic digestion performance, probably due to the increased biomass lysis caused by ozone compared to the growth rate of anaerobic biomass.

The post-ozonation of DS was the most effective configuration to operate with the anaerobic digesters, while the changes due to the pre-ozonation of PS were low. These results are consistent with anaerobic biodegradability tests performed in batch, in which the ozonation of DS produced a more pronounced increase of biodegradability than ozonation of PS. The increase in methane production depends on the initial biodegradability of the sludge with a greater effect on sludge containing a high fraction of non-biodegradable organic matter (Carrère et al. 2010).

A technico-economical evaluation has shown that the sludge ozonation requires greater operating and maintenance costs than the additional benefits from enhanced methane production; the post-ozonation requires approximately 0.15 USD/ kg COD, but these costs are reduced by 30 % due to the additional methane production and sludge reduction (Supplementary information). Full-scale application of ozone is an expensive alternative for improving anaerobic digester performance. However, a WRRF with available ozone for effluent disinfection could use the excess ozone capacity to improve anaerobic digester performance during winter, considering that the ozonation systems are expected only to operate at 100% capacity under the max flow and the disinfection requirements during this season are lower. This approach minimizes the capital expenditures, makes ozonation add flexibility for plant operation, as well as enhances the digester performance during this period of year. This alternative could be of interest for chemically enhanced primary treatment plants.

3.7 Evaluation of digested sludge dewaterability

The effect of ozone treatment combined with anaerobic digestion on sludge filterability and settleability is presented in Figure 7c and d. The pre-ozonation configuration has no significant effect on sludge filterability, in terms of CST and TTF compared with the control digester ($p > 0.18$). Likewise, for this configuration, settleability, measured as SVI, did not significantly change ($p > 0.07$).

Several studies have shown that ozonation deteriorates sludge filterability, which is heavily influenced by the increase of soluble COD (Scheminski, Krull, and Hempel 2000; Weemaes et al. 2000). Therefore, the low solubilization of COD caused by the ozonation of PS could explain the low impact of pre-ozonation on sludge dewaterability.

The post-ozonation configuration improved dewatering characteristics of sludge compared to the control digester: for a recycling rate of 1.2, the CST and SVI were decreased by 20% ($p < 0.01$), and 17% ($p < 0.01$) respectively, while the decrease of TTF was not significant ($p = 0.30$). The discrepancy between the TFF and the other indicators can be explained by the high imprecision of measurement methods; however, the trends show an improvement in dewaterability. These results agree in part with those reported in the literature, in which anaerobic digestion was shown to neutralize the negative effect of ozonation on sludge dewaterability (Foladori, Andreottola, Ziglio 2010; Weemaes et al. 2000). However, these results showed a larger effect than expected, possibly due to the high COD solubilization observed during DS ozonation, and the high biodegradation of solubilized COD during the anaerobic digestion. These results suggest that the post-ozonation configuration could effectively reduce the energy and reagents consumption required for the dewatering process.

4 CONCLUSIONS

Based on the results of this study, the following conclusions can be drawn:

- Ozonation of primary sludge did not result in an increase in soluble COD while the ozonation of anaerobic digested sludge did, resulting in an increase from 1.1 to 2.9 g COD/L at an ozone dose of 140 mg O_3/g COD.
- Biodegradable COD of primary sludge did not increase following ozonation. However, biodegradable COD of anaerobic digested sludge was increased from 2.5 to 3.9 g COD/L for ozone doses up to 90 mg O_3/g COD, representing an increase in methane production of 55%.
- Ozonation caused the TOC mineralization of primary sludge and anaerobic digested sludge by 10 and 15%, respectively.
- Post-ozonation of digested sludge was found to be effective for improving methane production (+16%), COD removal efficiencies, and dewaterability of anaerobic digesters compared to the control digester. However, the pre-ozonation of primary sludge was not effective in enhancing the performance of the anaerobic digester.

The above findings provide a better understanding of the impact of ozone treatment in the anaerobic digestion of a chemically enhanced primary treatment.

Acknowledgements

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558 characterisation of the carbonaceous materials in municipal wastewaters." *Water*
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560

561 Tables and figures

562 Table 1: Sludge characteristics before and after ozonation.

Sample	Dose	COD	TOC	TS	Carbon mass balance		
					TOC loss	CO_2 gas	Balance
	mg O_3/g COD	g COD/L	g C/L	g/L	mg C	mg C	%
PS	0	43.5	10.0	42.9	0	0	
	10	42.3	10.0	42.8	49	57	118
	30	41.4	9.9	42.5	228	164	72
	50	39.8	9.6	42.0	551	303	55
	140	38.9	9.3	41.2	401	340	85
	220	37.3	9.0	40.2	521	427	82
DS	0	14.9	4.2	18.3	0	0	
	50	14.4	4.2	18.2	32	33	102
	90	13.8	4.2	18.1	76	76	99
	140	13.4	4.0	17.7	283	171	60
	170	12.4	3.9	17.3	245	211	86
	210	11.6	3.6	16.8	357	271	76

563

564 Table 2. Heavy metal solubilization after sludge ozonation (DS; 210 mg O_3/g COD).

Metals	Sludge (µg/L)	Supernatant (µg/L)		Solubilization (%)
		Control	Ozonated	
As	32	5.0	5.2	0.63
Cd	5.4	<0.20	0.23	0.6-4.3
Co	95	7.3	13	6.0
Cr	250	2.7	3.2	0.20
Cu	2300	13	34	0.91
Fe	1 900 000	3500	21 000	0.92
Mo	37	8.3	33	67
Ni	260	34	91	22
Pb	130	4	6.8	2.2
Se	<24	2	4.3	10-54
Zn	3800	16	38	0.58

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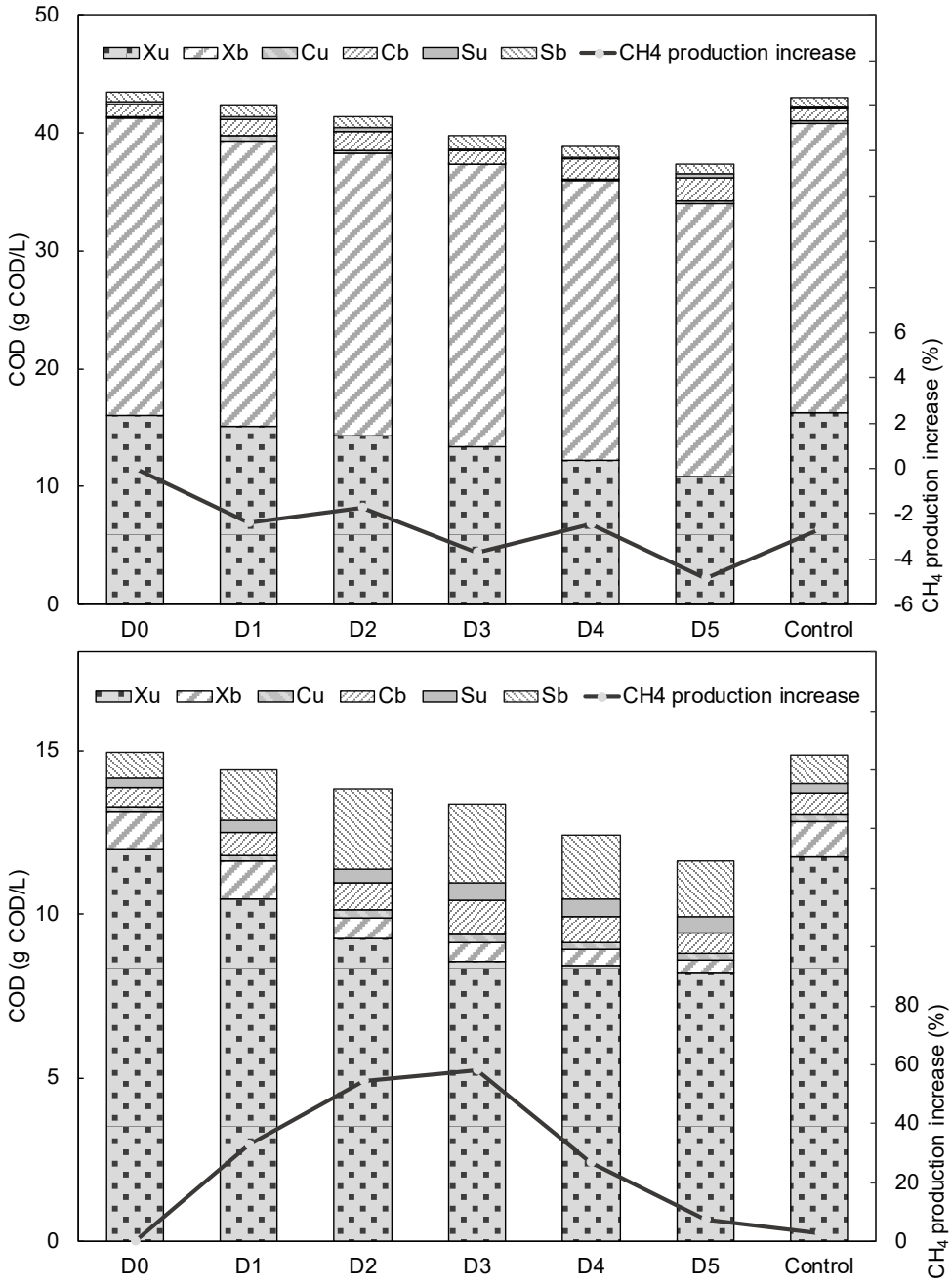

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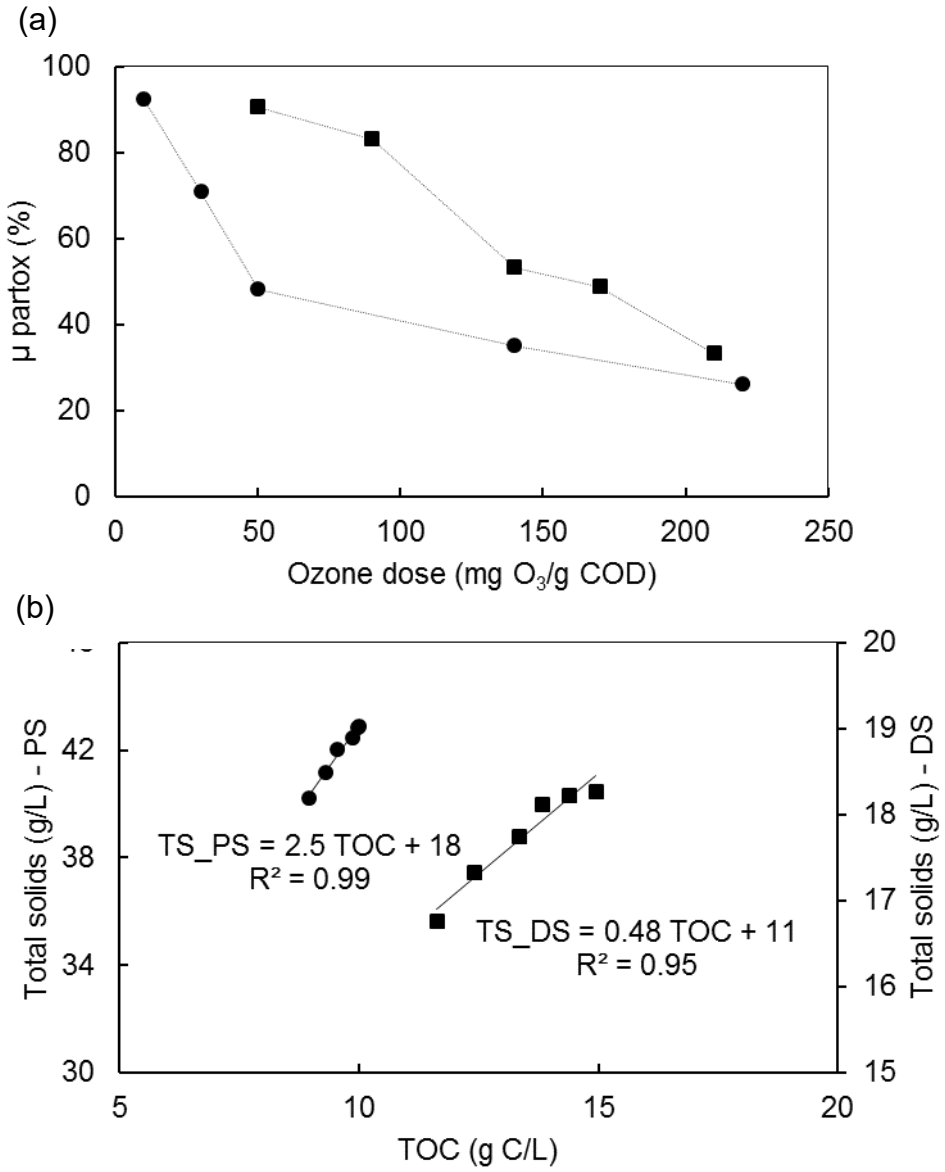
567 Figure 1: Effect of ozonation on COD fractionation of (a) primary sludge (D0 = 0; D1 =
568 10; D2 = 30; D3 = 50; D4 = 140; D5 = 220 mg O_3/g COD) and (b) anaerobic digested
569 sludge (D0 = 0; D1 = 50; D2 = 90; D3 = 140; D4 = 1740; D5 = 210 mg O_3/g COD).
570 Particulate unbiodegradable COD (X_u); particulate biodegradable COD (X_b); colloidal
571 unbiodegradable COD (C_u); colloidal biodegradable COD (C_b); Soluble
572 unbiodegradable COD (S_u); Soluble biodegradable COD (S_b).



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575 Figure 2: (a) Effect of ozone dose on the partial oxidation efficiency. (b) Correlation

576 between total solids and TOC. (●) Primary sludge; (■) Anaerobic digested sludge.

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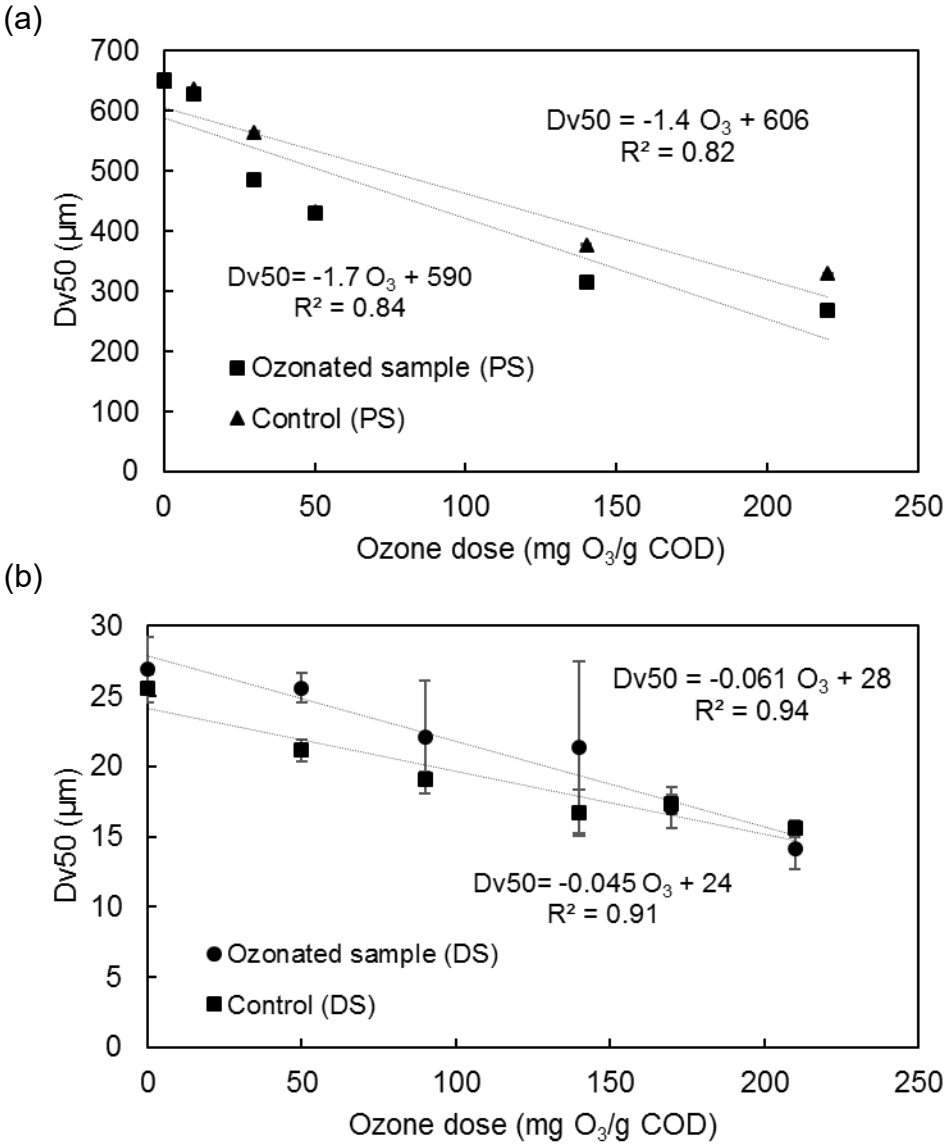

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581 Figure 3: Effect of ozone dose on particle size (median Dv50) of (a) primary sludge and
582 (b) anaerobic digested sludge.

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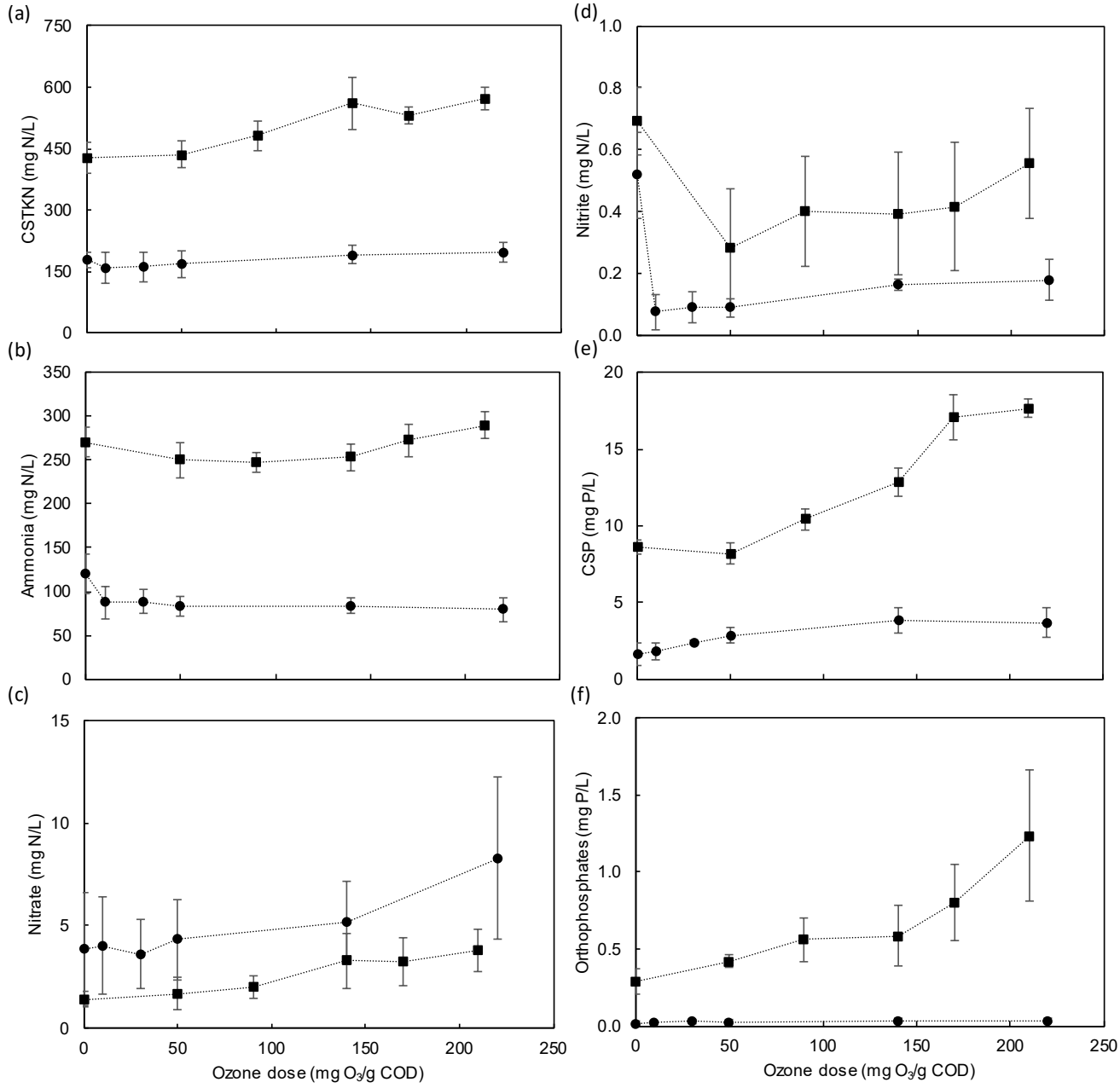

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586 Figure 4: Effect of sludge ozonation on nitrogen and phosphorus compounds: (a)
587 filterable TKN, (b) ammonia, (c) nitrate, (d) nitrite, (e) filterable phosphorus and
588 (f) orthophosphates. (●) Primary sludge; (■) Anaerobic digested sludge.

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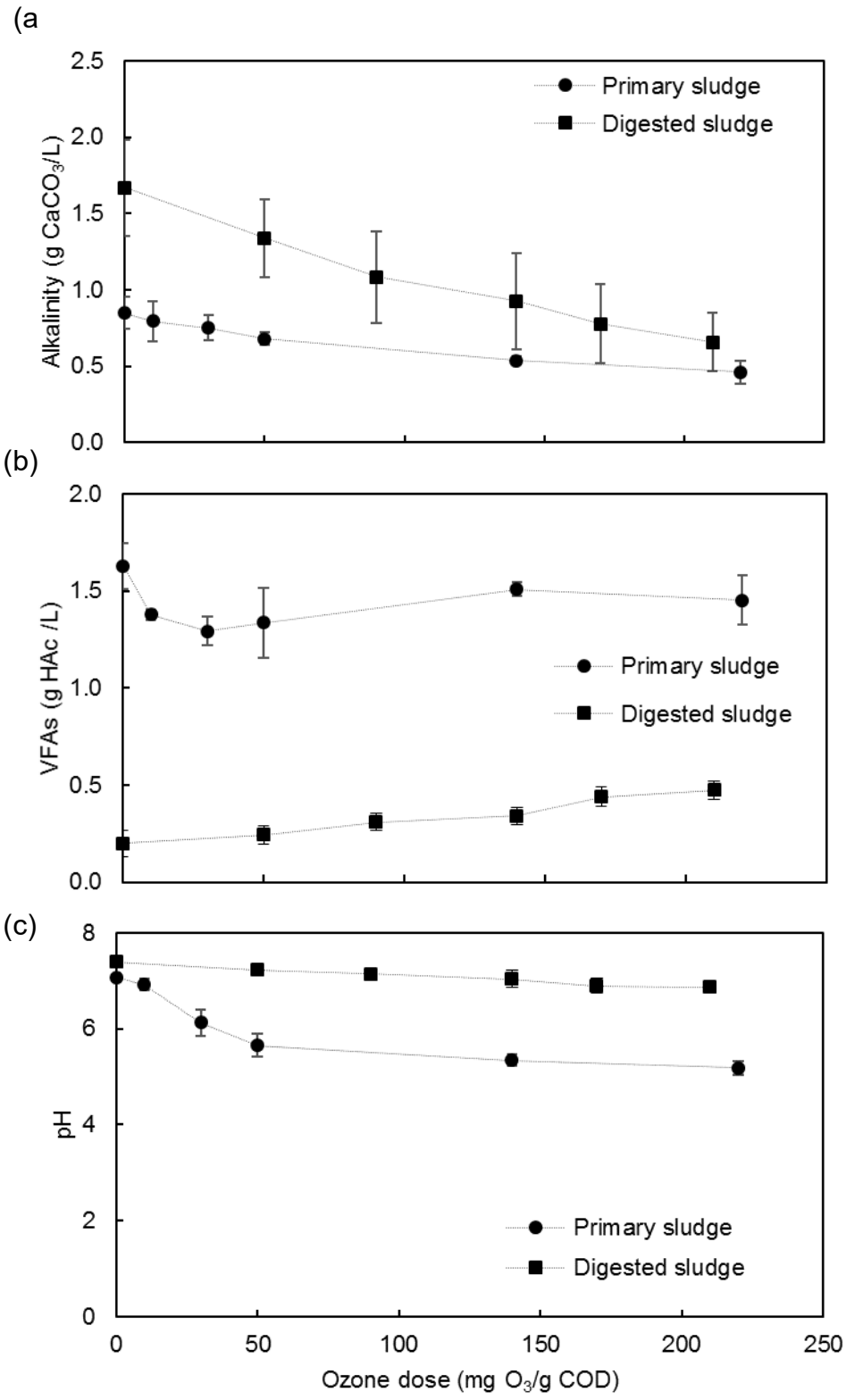

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595 Figure 5: Effect of ozonation on (a) alkalinity, (b) VFAs and (c) pH.

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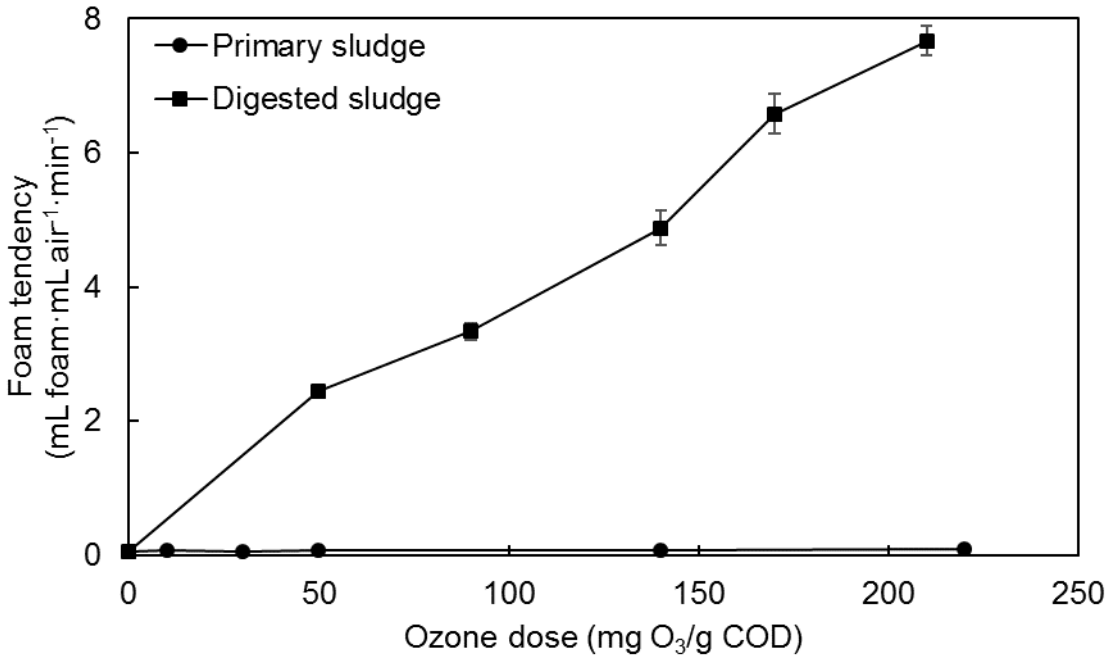

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598 Figure 6: Evaluation of foam tendency during ozonation of sludge samples.

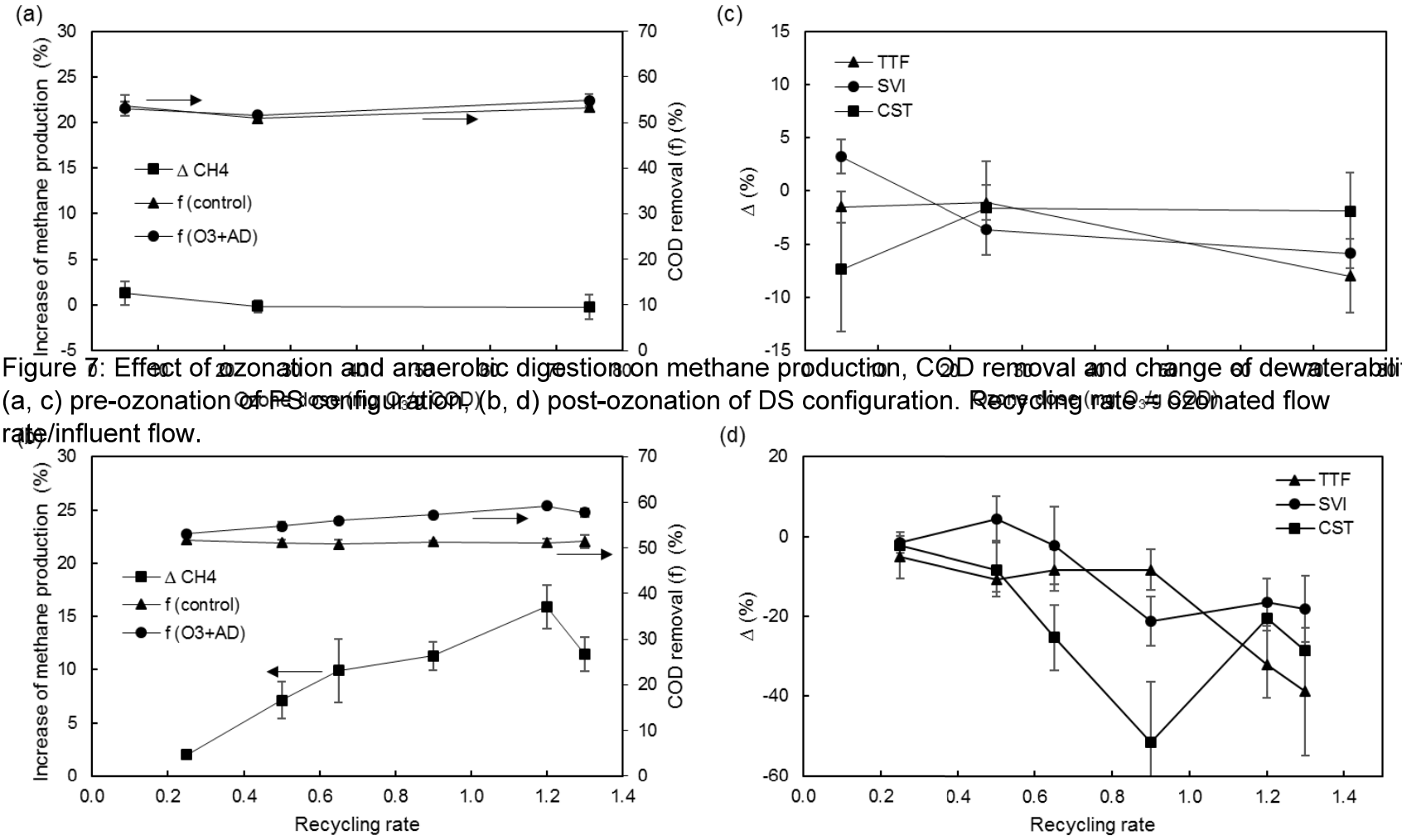

Figure 7: Effect of ozonation and anaerobic digestion on methane production, COD removal and change of dewaterability (a, c) pre-ozonation of RS configuration, (b, d) post-ozonation of DS configuration. Recycling rate = ozonated flow rate/influent flow.