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RESEARCH ARTICLE

Effects of low-dosage ozone pre-treatment on the anaerobic digestion of secondary and mixed sludge

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Abstract

The present study investigated the effects of ozonation pre-treatment at low-ozone dosage (below 100 mgO_3/gTS_0) with respect to previous studies, on the anaerobic digestion of waste-activated sludge alone and a mixture of activated sludge and primary sludge. Methane production and volatile suspended solids reduction efficiency were determined for different specific ozone dosages and compared with the values obtained in the absence of pre-treatment. Among the dosages tested in the study (from 4.8 to 73.2 mgO_3/gTS_0 for mixed sludge and from 3.5 to 53.6 mgO_3/gTS_0 for waste-activated sludge), the best results were obtained at the lowest ones: 4.8 and 3.5 mgO_3/gTS_0 for mixed sludge and waste-activated sludge, respectively. Indeed, at this dosage, an additional methane production of about 6% and 30% was achieved for mixed and waste-activated sludge, respectively; furthermore, the maximum CH_4 production rate increased of about 21% and 33% for mixed and waste-activated sludge, respectively. With respect to the Gompertz model, the modified logistic model provided the best agreement to the experimental data of the specific methane yield production. The present study demonstrated the importance of investigating the application of low dosages when ozonation is being evaluated as a pre-treatment to enhance anaerobic digestion performance.

Keywords Activated sludge · Anaerobic process · Methane · Ozonation · Volatile solids

Introduction

Application of the biological processes in the wastewater treatment plant (WWTP) generates excess sludge as a consequence of the bacterial synthesis process. This sludge must be removed from the plant and transferred to the sludge processing line of the WWTP for a proper treatment before its final disposal or reuse (Metcalf and Eddy 2003). If the primary settlement tank is included in the layout of the WWTP, also the primary sludge (PS) must be treated along with the waste-activated sludge (WAS). In view of the treatment, it must be taken into account that PS and WAS significantly differ as far as the composition and also suitability to biodegradation are concerned. Indeed, WAS is mainly composed of microbial flocs, containing microorganisms, extracellular polymeric substances (EPS), and inorganic matter, and is known to be a substrate with relatively low biodegradability. Primary sludge is composed of natural fibers, fats, and other solids which are removed from the raw wastewater by settling, along with soluble compounds; therefore, it is referred to be more biodegradable as compared to WAS (Parkin and Owen 1986).

Legislation (such as EU Directive 99/31) regarding the quality of the treated sludge (usually referred to as biosolids) has recently become more stringent in terms of compliance for final disposal or reuse. As a consequence, costs of sludge processing are raised progressively and are expected to increase further in the near future. Therefore, numerous researches have been started to investigate different treatments for improving biosolids quality as well as for reducing biological sludge production (Metcalf and Eddy 2003).

Anaerobic digestion (AD) can be considered as an attractive option for this purpose, as it is able to produce a final sludge which is biologically stable and of reduced volume;

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furthermore, the organic matter of the sludge is converted through the process into a form of energy represented by biogas which is mainly composed of methane. The anaerobic digestion takes place through a series of consecutive steps, the first of which is the hydrolysis of the bacterial cells into a more biodegradable form. Usually, this step occurs at the lowest rate as compared to the following stages; thus, the biodegradation rate of the overall AD process and the conversion of the organic matter into biogas depend upon the hydrolysis rate. Increases of the hydrolysis rate make the AD more efficient in terms of biogas production yield and solid reduction efficiency and consequently more attractive as compared to the other sludge treatment alternatives. In the last years, several pre-treatment techniques have been proposed to enhance the AD performance; most of them have been only tested at lab-scale, while only few experimentations have been also applied at full scale. Advantage and feasibility of the pre-treatment depend not only on the enhancement of the hydrolysis rate that can be achieved, and therefore of the biogas production yield and solid reduction efficiency, but also on the additional costs associated to the implementation and operation of this technique (Chiavola et al. 2013).

Among the different pre-treatments proposed for AD, thermal process, ultrasound oxidation, electro-oxidation, and chemical oxidation have been demonstrated to be the most promising (Bougrier et al. 2006; Carlsson et al. 2012; Feki et al. 2015; Pérez-Elvira et al. 2009; Vlyssides and Karlis 2004). More recently combinations of different pre-treatments have been also successfully applied, such as ultrasound with ozone oxidation, ultrasound oxidation with thermal treatment, hydrogen peroxide oxidation with microwave, and hydrogen peroxide oxidation with heat (Dhar et al. 2012; Özön and Erdinçler 2019; Xu et al. 2010; Tian et al. 2015; Yang et al. 2012; Wenjing et al. 2019).

The action of ozone as a strong oxidant is well known and widely applied for different purposes in the field of wastewater (such as for increasing biodegradability of organic matter) and water treatment processes (like disinfection) (Gao et al. 2019). Application of ozone in different sections of the wastewater treatment plants has proven to be also capable of significantly reducing biological sludge production (Fall et al. 2018; Yasui and Shibata 1994; Yasui et al. 1996). When sludge is subjected to ozonation, the bacterial cells undergo the lysis process with the release of intracellular compounds into the medium (Meng et al. 2015). Ozone can be dosed on a fraction of the return sludge from the secondary settlement tank or prior to the digestion tank. In the latter case, an enhancement of the bacterial cells biodegradability is obtained, which in turn determines an increase of the volatile solids reduction efficiency (Chiavola et al. 2013; Pei et al. 2015). Furthermore, in the case of anaerobic digestion, the higher biodegradability allows an increase of the biogas production rate (Chacana et al. 2017; Wenjing et al. 2019). Partial ozonation of sewage sludge from a domestic wastewater treatment plant could alter up to 67% of the organic matter: about 30% was solubilized, while about 40% was removed. Anaerobic degradability tests indicated that the pre-treatment step enhanced the subsequent anaerobic sludge digestion: at an ozone dose of 0.1 gO_3/gCOD, the methane production was increased by a factor of 1.8, while the methane production rate was 2.2 times higher as compared to the untreated sludge (Weemaes et al. 2000). The ozone pre-treatment solubilized around 37% of the solids at 0.05 gO_3/gTS ozone dose and resulted in improved solid reduction efficiencies (increase by 35–90%) depending on the applied ozone during the following anaerobic digestion; higher methane recovery was also obtained (Goel et al. 2003).

The past researches demonstrated that the effects of ozonation are strictly dependent upon the applied ozone dosage: increasing dosage usually provides higher benefits in terms of solid reduction and methane production enhancement. However, it is likely that energy consumption for ozone production also increases consequently and therefore cost of the pre-treatment. Particularly, previous reports suggested that the ozone-activated sludge process would be economically viable with doses between 25 and 45 mgO_3/gCOD approximately (Chu et al. 2009). However, in many studies, the O_3 quantities used were higher, ranging from 40 to 300 and in few cases up to 1400 mgO_3/g COD (Qiang et al. 2013). Ozone dose lower than 11 mgO_3/g mixed liquor suspended solids (MLSS) determined very low bacteria destruction and cell solubilization; in the range of 11–90 mgO_3/gMLSS, ozone had significant effect on cell permeabilization and disruption. Greater than 90 mgO_3/gMLSS, the number of live cells and dead cells were both stable, and the quantity of material in bulk liquid increased slowly (Meng et al. 2015).

Although the advantages of the increased methane yield and solids reduction have been proven by a number of researches, nevertheless the relative applicability of the ozone pre-treatment has not been fully assessed with respect to different types of sludge, either WAS or a mixture of WAS and PS (Carlsson et al. 2012). It is expected that the effects on WAS and on the mixture of PS and WAS can be different, owing to the specific characteristics and properties. For instance, since WAS is known to be less biodegradable, ozonation might be effective in increasing degradability of its bacterial cells. With respect to primary sludge, Carrère et al. (2010) reported that ozonation was unable to produce beneficial effects.

Due to the high energy consumption that may be associated with ozone generation, there is a need for a better understanding and for optimizing the performance of the ozonation process, with respect to the sludge type and the applied doses (Fall et al. 2018).

The objective of the present experimental work was to evaluate the effects on methane production and volatile solids reduction of low-ozone oxidation as a pre-treatment to the anaerobic digestion process of only WAS and a mixture of WAS and PS. The main novelty of the study is represented by the application of ozone dosages below 100 mgO_3/gTS_0, which are far below the values applied in most of the past researches (Park et al. 2008; Qiang et al. 2013; Pei et al. 2015; Qiang et al. 2015; Yan et al. 2009). The hypothesis is that, if low ozone dosages are still capable of improving AD performance of WAS or PS + WAS, then cost of ozonation can be limited and energy and economic saving is achieved in the WWTP. As a consequence, ozonation would result more competitive with respect to other pre-treatments.

Material and methods

Activated sludge

Sludge samples were collected at two full-scale WWTPs (WWTP1 and WWTP2) both treating domestic sewage and having a capacity of 30,000 population equivalent (PE). The layout of the treatment plants was the same except for the presence of the primary settler in WWTP1 only. The water processing line in the plants consisted of the following main stages: screening, degritting, denitrification-nitrification-carbon oxidation, secondary settling, and disinfection. The waste-activated sludge, and the primary sludge when present, was treated through the following sequence of processes: thickening, biological digestion, and dewatering. Sludge characteristics before application of the ozone pre-treatment are reported in Table 1 (specific ozone dosage SD_{O3} = 0 mgO_3/gTS_0).

Ozone treatment tests

Sludge was ozonated in a 5 L contact column (2000 mm height). All the experiments were conducted at room temperature, in a semi-batch mode by ozone bubbling into the sludge sample. Particularly, ozone was supplied to the reactor by a Modular 4hc (Wedeco ITT Industries), using a porous ceramic diffuser placed on the bottom which released fine bubbles. The residual dissolved O_3 was found to be negligible, in accordance with other authors, likely due to the low ozone dosages applied in the experiments and the fast reactions with the organic matter present in excess (Fall et al. 2018). The ozone flow rate, Q_{O3}, was fixed at 4 g/h. All the ozone treatment tests were conducted in duplicate and the results obtained averaged. The ozone dosage was varied by changing the contact time (CT) between the gas stream and the sludge. The time needed to add the exact amount of ozone was preliminary calculated for each experiment based on the initial total solid (TS_0) content of the sludge. The SD_{O3} was obtained using the following equation:

$$SD_{O_3} = \frac{Q_{O_3} \cdot CT}{V_{sludge} \cdot TS_0} \quad (1)$$

where V_{sludge} represents the sludge volume subjected to ozonation.

The effect of ozone on the TS and VS percentage reduction (ΔTS_{ch} and ΔVS_{ch}, respectively) was calculated according to the following equations:

$$\Delta TS_{ch} = \frac{TS_0 - TS^{O_3}}{TS_0} \cdot 100 \quad (2)$$

$$\Delta VS_{ch} = \frac{VS_0 - VS^{O_3}}{VS_0} \cdot 100 \quad (3)$$

where VS_0 and VS^{O3} stand for the VS concentration before and after the ozone treatment, respectively; similarly, TS^{O3} indicates the TS concentration in the ozonated sludge.

COD solubilization due to ozone is commonly represented in terms of disintegration degree (DD). According to Zhang et al. (2009), the DD values were calculated as the difference between the soluble COD concentrations in the outlet ($sCOD^{O3}$) and in the inlet ($sCOD_0$) of the ozonation unit, divided by the particulate COD concentration in the sludge before the ozone treatment ($pCOD_0$ = $tCOD_0$–$sCOD_0$). The following equation was therefore applied:

Table 1 Sludge characteristics before and after ozonation

Type of sludge	SD_{O3} (mgO_3/gTS_0)	CT (min)	pH	TS (g/L)	VS (g/L)	tCOD (g/L)	sCOD (g/L)	DD (%)	ΔTS_{ch} (%)	ΔVS_{ch} (%)
PS + WAS	0	–	6.2	26.66	23.18	33.199	2.066	–	–	–
	4.8	7.7	6.7	26.30	22.84	31.393	2.153	0.28	1.36	1.47
	9.5	15.2	6.9	26.04	22.19	29.761	2.883	2.63	2.34	4.31
	73.2	117.1	7.1	25.25	20.98	26.174	4.060	6.40	5.31	9.52
WAS	0	–	6.7	11.47	10.29	12.089	0.868	–	–	–
	3.5	2.4	6.9	11.14	9.94	10.708	0.894	0.24	2.90	3.42
	7.7	5.3	7.0	11.02	9.76	9.390	0.984	1.03	3.94	5.15
	53.6	36.9	7.1	10.04	8.73	7.082	1.161	2.61	12.50	15.21

$$DD = \frac{\left(sCOD^{O_3} - sCOD_0\right)}{\left(tCOD_0 - sCOD_0\right)} \cdot 100 \quad (4)$$

Anaerobic digestion tests

Anaerobic digestion tests were carried out to assess the biodegradability of the sludge before and after the ozone treatment. Continuous stirred tank reactors (CSTRs) maintained at the temperature T = 35 ± 2 °C were used as digesters. Two sets of trials, each one including n. 8 tests, were performed: n. 2 tests were used as a control and therefore run without ozone supply, while n. 6 tests were conducted with ozonated sludge. Each digester was made using a 1 L borosilicate glass flask, with an operating total volume V^t = 0.8 L composed as follows: V^s = 0.6 L of ozonated sludge and V^i = 0.2 L of sludge without any pre-treatment used as inoculum. All the tests were conducted in duplicate and the results obtained averaged.

Specific methane yields (SMY), expressed as ($mLCH_4/gVS_0$), were calculated as the methane volume produced over time with respect to the VS content initially present in the sludge (named VS_0) at the net of the methane produced by the inoculum. At each sampling time, the calculation was made according to the following equation:

$$SMY(t) = \frac{V_{CH_4}(t) - \left(\frac{V^r_{CH_4}(t) \cdot V^i}{V^t}\right)}{V^s \cdot VS_0} \quad (5)$$

where $V_{CH4}(t)$ is the methane volume measured at time t of the test and $V^r_{CH4}(t)$ is the methane volume measured at the same time in the anaerobic digestion test used as control (therefore containing only raw sludge). The methane production was adjusted to the volume at standard temperature and pressure (273 K, 101.325 Pa).

The following equation was used to calculate the specific VS reduction achieved through the combination of ozonation and anaerobic digestion:

$$\Delta VS_{sp} = \frac{V^s \cdot VS_0 - \left(V^t \cdot VS^{O_3}_{AD} - V^i \cdot VS_{AD}\right)}{V^s \cdot VS_0} \cdot 100 \quad (6)$$

where VS_{AD} e $VS_{AD}{}^{O3}$ stand for VS content after anaerobic digestion tests of raw (non-ozonated) and ozonated sludge, respectively.

The specific VS reduction due only to anaerobic digestion was estimated through the following equation:

$$\Delta VS_{AD} = \frac{V^s \cdot VS^{O_3} - \left(V^t \cdot VS^{O_3}_{AD} - V^i \cdot VS_{AD}\right)}{V^s \cdot VS^{O_3}} \cdot 100 \quad (7)$$

Analytical methods

Analyses of TS, VS, and COD were carried out according to standard methods (APHA 2005). The soluble fraction of COD was determined on sludge samples after filtration at 0.45 μm. Biogas produced in the anaerobic digestion tests was monitored daily using the volume displacement principle: eudiometers, connected to each reactor, were filled with a NaCl saturated solution, acidified with HCl to pH = 2 to prevent gas dissolution. The biogas was periodically analyzed through a gas chromatograph (Model 3600 CX, VARIAN) equipped with a thermal conductivity detector and 2-m stainless steel packed column (ShinCarbon ST) with an inner diameter of 1 mm. The operation temperatures of injector and detector were 100 and 130 °C, respectively, with helium as the carrier gas. The oven temperature was initially set at 80 °C and subsequently increased to 100 °C at 2 °C/min.

Specific methane yield modeling

Two kinetic models were used to predict the specific methane yield (SMY): a modified Gompertz equation (GM) (Equation 8) and a modified logistic function (LM) (Equation 9) (Zwietering et al. 1990):

$$SMY = A\exp\left\{-\exp\left[\frac{\mu_m \cdot e}{A}(\lambda - t) + 1\right]\right\} \quad (8)$$

$$SMY = \frac{A}{\left\{1 + \exp\left[\frac{4\mu_m}{A}(\lambda - t) + 2\right]\right\}} \quad (9)$$

In Equations (8) and (9), A is the maximum SMY, μ_m indicates the maximum CH_4 production rate, λ is the lag phase duration, and t represents the cumulative time for biogas production. Kinetic constants were determined using nonlinear regression with the support of Table Curve 2D v. 5.01.

Results and discussion

Effect of ozone treatment on sludge solubilization

Table 1 shows average sludge characteristics before and after ozonation at the different oxidant dosages. Particularly, the table highlights the effects on sludge solubilization expressed in terms of change in total and soluble COD (tCOD and sCOD, respectively) and on VS and TS reduction (ΔTS_{ch} and ΔVS_{ch}, respectively) for both mixed sludge (PS+WAS) and WAS. Furthermore, contact time (CT) and pH values of the different dosages are also listed in the table.

The data show that ozone oxidation was capable of affecting tCOD and sCOD, as well as VS and TS content, in both mixed and WAS sludge. Particularly, rising ozone dosage from the lower to the highest values determined an almost linear decrease of total COD (straight line equation for mixed sludge, $y = -0.0677x + 31.085$, $R^2 = 0.9392$; straight line equation for WAS, $y = -0.0633x + 10.426$, $R^2 = 0.9173$) and a linear increase of soluble COD (straight line equation for mixed sludge, $y = 0.0238x + 2.3365$, $R^2 = 0.8965$; straight line equation for WAS, $y = 0.0047x + 0.911$, $R^2 = 0.9329$).

However, tCOD decrease was more pronounced than soluble COD rise: this indicates that ozone dosage was high enough to determine release of internal carbon compounds from the cells and then to partly mineralize them into CO_2 and H_2O. Based on the slopes of the fitting lines, it can be assessed that solubilization was higher in the case of mixed sludge than for WAS, whereas total COD reduction was very similar.

Looking at the effects on solids, a linear increase of both ΔTS_{ch} and ΔVS_{ch} was observed at increasing ozone dosage. Particularly, the straight line equations for mixed sludge were $y = 0.1023x + 2.1167$ ($R^2 = 0.9162$) for ΔTS_{ch} and $y = 0.053x + 1.4582$ ($R^2 = 0.9683$) for ΔVS_{ch}. In the case of WAS, the straight line equations were $y = 0.2287x + 2.9877$ ($R^2 = 0.9963$) for ΔTS_{ch} and $y = 0.1895x + 2.3535$ ($R^2 = 0.9995$) for ΔVS_{ch}. For both types of sludge, TS decrease was more pronounced than that of VS: this confirms that ozonation brought about also mineralization of some solids. From the slope of the lines, it can be noted that solids reduction was higher in the case of WAS than for mixed sludge.

The DD index well reflected these results, and a linear increase was observed as the ozone dosages increased for both mixed sludge (straight line equation: $y = 0.0765x + 0.8728$, $R^2 = 0.8957$) and WAS (straight line equation: $y = 0.042x + 0.3865$, $R^2 = 0.9350$), with higher values obtained in the former case.

The easier solubilization of mixed sludge was likely due to the nature/composition of primary sludge. In the case of WAS alone, being the soluble compounds very low or absent, the ozone acted directly on the cells which were partly mineralized as outlined above.

Looking more in details at the data, it is highlighted that the effects of ozonation resulted to be more important when the ozone supply was increased from the first to the second dosage than from the second to the third one (the highest). This difference was observed in the trends of most of the investigated parameters. It is noteworthy that the third dosage was significantly higher than the lower ones (about 7 times) and therefore its oxidant effect was stronger. In view of the following anaerobic digestion phase, the lower dosages appear to be preferable since capable of a higher sludge solubilization.

Table 1 also shows that there was a slight increase of pH at increasing ozone dosage in both cases of mixed and WAS sludge. As it is known, cell oxidation determines release of ammonia into the medium, along with the other intracellular compounds. This effect is favored as the oxidant supply is increased, and this might explain the slight change in pH under these conditions.

Effect of ozone treatment on sludge reduction during anaerobic digestion

Table 2 shows characteristics of the raw sludge ($SDO_3 = 0$ mgO_3/gTS_0) and of the sludge after the combined anaerobic digestion and ozone treatment (sp index) for both (PS + WAS) and WAS. The same table shows also the contribution due to anaerobic digestion only in the combined process (AD index), reduced by the contribution of the inoculum. Data reported in the table are the average of two duplicates, as described in Section 2.3.

It can be noted that ΔVS_{sp} values were always higher than ΔVS_{AD} and the difference increased with the dosage. Furthermore, this effect was always more evident in the WAS treatment than in the mixed sludge: for instance, at the highest dosage, the difference reached 7.9 and 2.9, respectively. This is in agreement with the observations on solids reported in Section 3.1. It is also worth noting that the presence of pre-treatment was responsible of a higher value of ΔVS_{AD}: for example, in the case of WAS, $AVS_{AD} = 34.1\%$ and $AVS_{AD} = 58.6\%$ for $SDO_3 = 0$ mgO_3/gTS_0 and $SDO_3 = 3.5$ mgO_3/gTS_0, respectively.

Therefore, ozonation pre-treatment contributed to improve total VS reduction, particularly for WAS. However, comparison of ΔVS_{sp} and ΔVS_{AD} highlights that anaerobic digestion process remained the main responsible of total VS reduction in the combined process.

Effect of ozone treatment on methane production

Figures 1 and 2 show the specific methane yield (SMY) of (PS + WAS) and WAS, respectively, measured over time during the anaerobic digestion batch tests using either raw sludge (without ozonation pre-treatment) or ozonated sludge. For mixed sludge, the SMY time profiles show that at the lowest dosage, which was 4.8 mgO_3/gTS_o, ozonation was capable of increasing methane production with respect to the non-treated sludge: particularly, at the end of the tests, production reached 190 $NmLCH_4/gVS_0$ versus 175 $NmL\ CH_4/gVS_0$ of the non-ozonated sludge. However, at dosages of 9.5 and 73.2 mgO_3/gTS_o, values of SMY decreased progressively and were always lower than those produced by the raw sludge. In agreement, looking at the values of the model parameters listed in Tables 3 and 4, it can be noted that for mixed sludge, the value of A, which represents the maximum SMY, was higher only at the lowest oxidant dosage. The higher solubilization enhanced methane production in the anaerobic digestion.

Table 2 Sludge characteristics due to the combined anaerobic digestion and ozone treatment (sp index) and due to anaerobic digestion only (AD index) (sd = standard deviation)

Type of sludge	SDO_3	TS		VS		ΔVS_{sp}	ΔVS_{AD}
	(mgO_3/gTS_0)	(g/L)	sd	(g/L)	sd	(%)	(%)
PS + WAS	0	11.700	0.699	7.021	0.408	69.7	69.7
	4.8	12.154	0.459	6.872	0.240	70.6	70.1
	9.5	10.495	1.379	6.517	0.531	72.6	71.4
	73.2	9.202	0.167	6.587	0.182	72.2	69.3
WAS	0	8.716	1.007	6.786	0.733	34.1	34.1
	3.5	6.082	0.271	4.783	0.151	60.0	58.6
	7.7	6.110	1.318	4.829	0.371	59.4	57.2
	53.6	6.640	1.333	5.089	0.609	56.1	48.2

A similar same trend was also noted in the case of WAS: the highest SMY increase at the end of the tests was observed at the lowest dosage (3.5 mgO_3/gTS_o), 150 $NmLCH_4/gVS_0$ in the ozonated sludge versus 112 $NmLCH_4/gVS_0$ in the non-ozonated sludge. At dosages of 7.7 and 53.6 mgO_3/gTS_o, methane production decreased progressively; however, in this

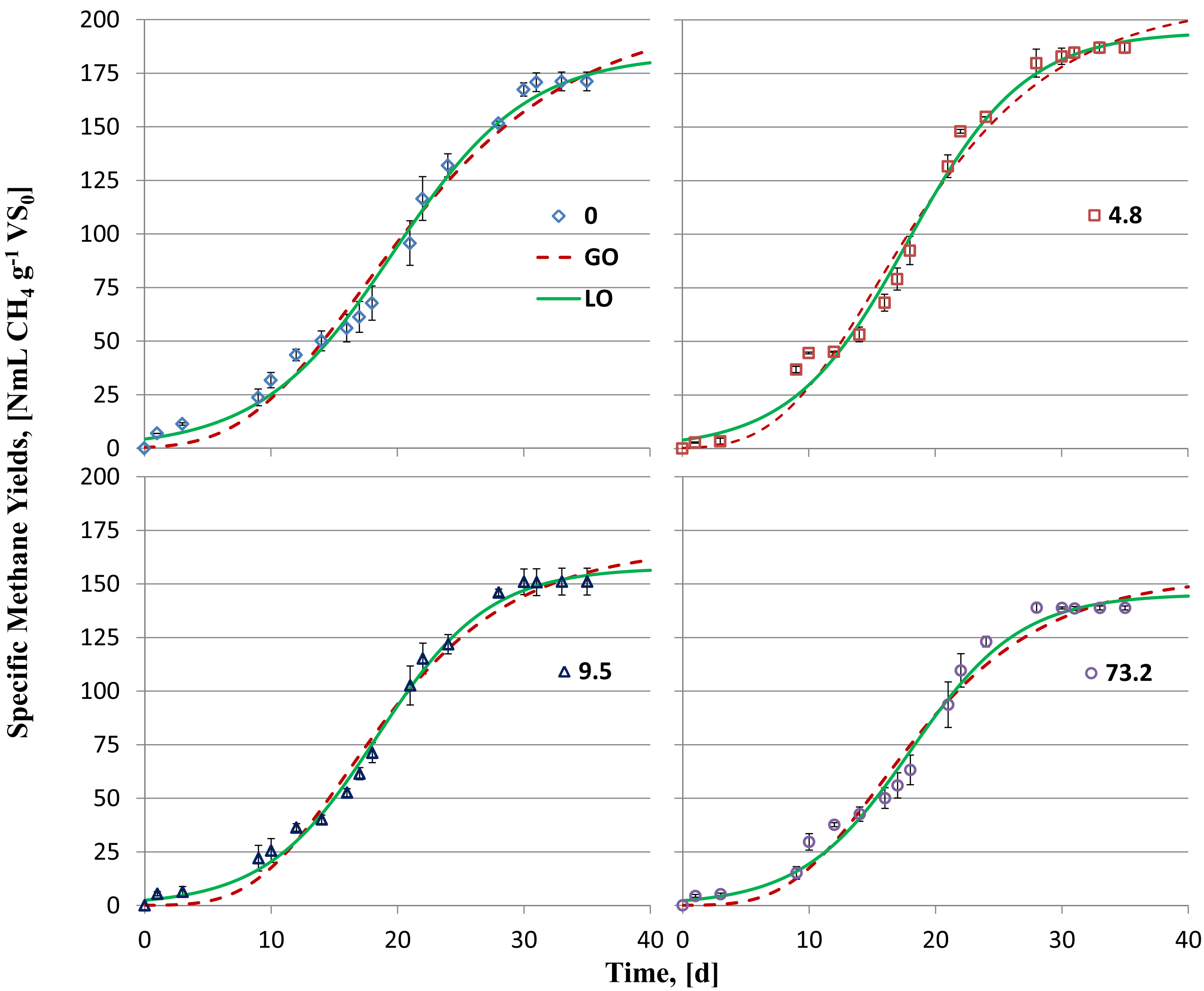

Fig. 1 SYM for (PS + WAS) experimental (symbols) and modeled by Gompertz (red) and modified logistic function (green) (error bars indicate sd)

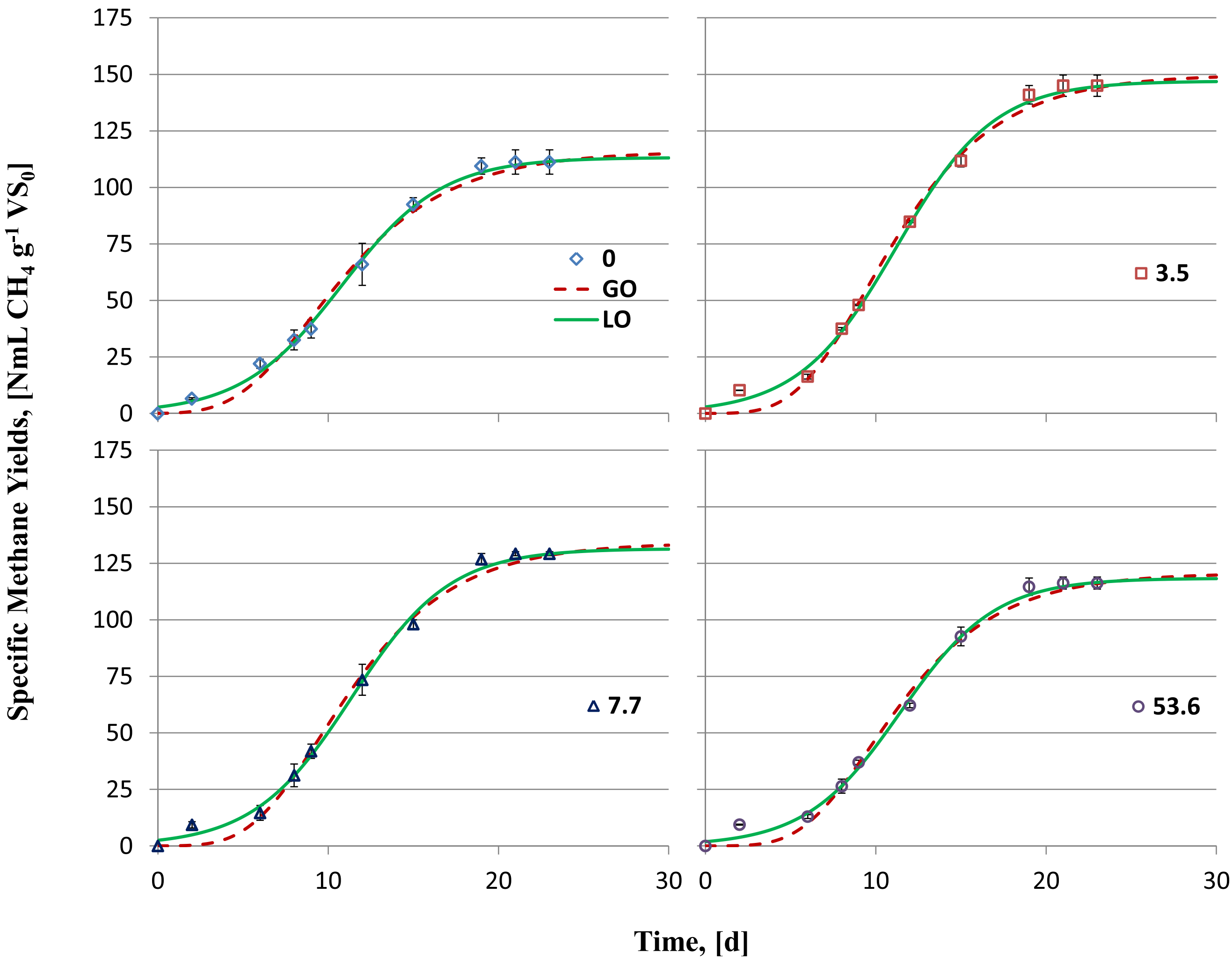

Fig. 2 SYM for WAS experimental (symbols) and modeled by Gompertz (red) and modified logistic function (green) (error bars indicate sd)

case, values of SMY always remained above those measured in the non-ozonated sludge. Data obtained by modeling and shown in Tables 3 and 4 indicate values of A being always higher in the presence of ozonation pre-treatment.

Methane production was always higher for mixed than WAS sludge, due to the more abundant biodegradable and soluble fractions

As highlighted by Figs. 1 and 2, both Gompertz and modified logistic modeling provided a very good fitting of the experimental data of specific methane yield production; nonetheless, due to the R^2 values, the logistic model was assumed to better represent the results. By applying this model, the ozone oxidation at the optimal dose (4.8 and 3.5 mgO_3/gTS_0, for mixed and WAS sludge,

Table 3 Results of Gompertz modeling

Type of sludge	SD_{O3} (mgO_3/gTS_0)	A ($NLCH_4/kgVS_0$)	μ_m ($NLCH_4/kgVS_0$•d)	λ (d)	R^2 (−)
PS + WAS	0	203.098	7.966	7.905	0.983
	4.8	208.695	9.686	7.503	0.983
	9.5	167.502	8.374	8.625	0.987
	73.2	153.886	7.816	8.397	0.980
WAS	0	115.936	9.597	4.576	0.992
	3.5	149.920	13.140	5.271	0.995
	7.7	134.094	11.641	5.386	0.994
	53.6	120.635	10.839	5.637	0.992

Table 4 Results of logistic modeling

Type of sludge	SD_{O3} (mgO_3/gTS_o)	A ($NLCH_4/kgVS_0$)	μ_m ($NLCH_4/kgVS_0$•d)	λ (d)	R^2 (−)
PS + WAS	0	183.775	8.703	9.185	0.992
	4.8	194.524	10.562	8.697	0.991
	9.5	157.536	8.933	9.563	0.995
	73.2	145.241	8.401	9.432	0.989
WAS	0	113.214	9.631	4.920	0.998
	3.5	147.016	12.804	5.466	0.998
	7.7	131.440	11.377	5.610	0.997
	53.6	118.355	10.651	5.896	0.997

respectively) resulted to give rise to an additional methane production of about 6% and 30% for (PS + WAS) and WAS, respectively, with respect to non-ozonated sludge. Therefore, although the mixed sludge provided higher methane production with respect to WAS, the increment in comparison to the value obtained by the non-ozonated sludge was lower.

Furthermore, at the optimal dosages, there was an increment of the maximum CH_4 production rate (μ_m) of 21% and 33% for (PS + WAS) and WAS, respectively; for the mixed sludge, it was also observed a decrease (of about 5%) of the initial lag phase of methane production (λ).

Figure 3 compares SMY and ΔVS_{sp} versus ozone dosage for mixed and WAS sludge.

In the case of mixed sludge, the effect on specific VS reduction became appreciable only at the higher dosages (9.5 and 73.2 mgO_3/gTS_o); by contrast, a significant increase of methane production was obtained for the lowest ozone level (4.8 mgO_3/gTS_o) when the soluble compounds were more abundant.

In the case of WAS, significant increases of both SMY and VS reduction with respect to the non-ozonated sludge were obtained at all the tested dosages; however, the higher enhancement was obtained at the lowest ozone supply.

Table 5 compares the results obtained in the present study with data referred by other authors and achieved through anaerobic digestion batch tests conducted under similar conditions (temperature, T; hydraulic retention time, HRT). The listed ozone doses are referred as the most effective for the applied operating conditions; in Table 5, ΔCH_4 and ΔVS represent the corresponding percentage increase of methane production and VS reduction, respectively, achieved at these dosages as compared to the values due to anaerobic digestion without ozonation pre-treatment.

It can be noted that in the previous studies, the specific ozone dosages were significantly higher and the increment percentages of both methane production and VS reduction resulted to be more relevant than in the present work. The paper by Weemaes et al. (2000) reported that ozonating mixed primary and activated sludge required a significantly higher dosage to obtain appreciable results. Therefore, the low improvement observed in the present study was likely due to the scarce oxidant dosage.

Cost analysis

A preliminary cost analysis was carried out to obtain a draft evaluation of the potential cost saving achievable

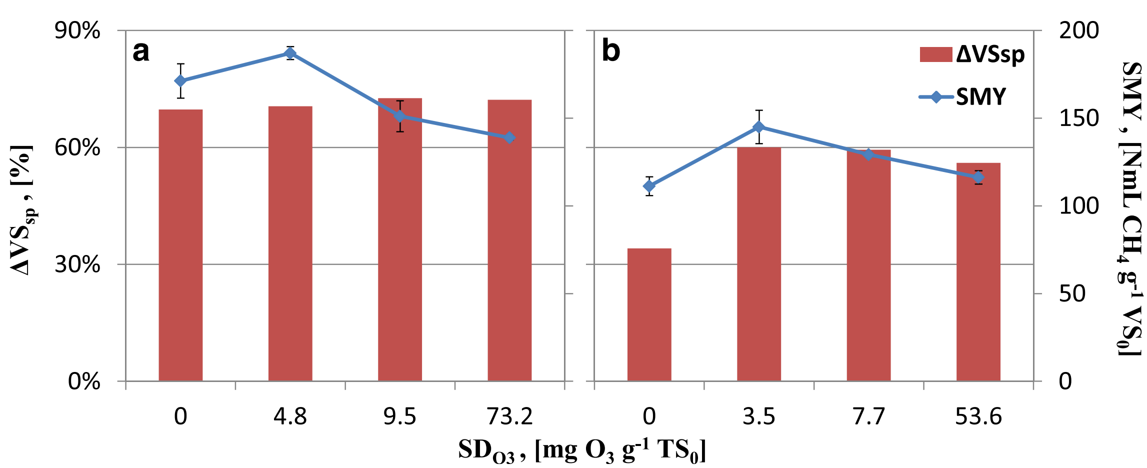

Fig. 3 SMY and ΔVS_{sp} versus ozone dosage for: **a** (PS + WAS) and **b** WAS (error bars indicate sd)

Table 5 Comparison of experimental and literature data

Type of substrate	O_3 Dosage		HRT	T	CH_4 production		ΔCH_4	ΔVS	Ref.
	($gO_3/gCOD_0$)	(gO_3/gTS_0)	(d)	(°C)	($NmLCH_4/gCOD_0$)	($NmLCH_4/gVS_0$)	(%)	(%)	
Primary and activated sludge	0.1		30	33	220		100	58	Weemaes et al. 2000
Activated sludge (synthetic)		0.05	28	35		310	107	90	Goel et al. 2003
Activated sludge		0.15	18	35	367		144	143	Bougrier et al. 2007
Activated sludge		0.10	50	37				19	Salsabil et al. 2010
Activated sludge		0.10	6	35		89.6 (190 NmL)		4	Pei et al. 2015
Activated sludge		0.10	15	35		467	233	39	Pei et al. 2016
Digested sludge	0.086		19	35	123		52	49	Chacana et al. 2017
Dewatered sludge		0.055	15	37		33	88	31	Wenjing et al. 2019
Primary and activated sludge	0.0039	0.0048	33	35	150	194	6	1	This study
Activated sludge	0.0033	0.0035	21	35	138	147	30	76	

using the ozone dosages which in the present study resulted to be more convenient.

Assuming a specific cost of final disposal equal to 150 €/t, which falls in the common range of the costs afforded in Italy, and a sludge production of 1500 t/y, in the absence of pre-treatment, the final cost of disposal would be 225,000 €/y. As observed in the present study, ozonation pre-treatment improves the volatile solids reduction in the anaerobic digestion process, ΔVS_{AD}: this determines a decrease in the total sludge production of the same percentage. In the present experimental work, at the optimal dosage $SDO_3 = 3.5\ mgO_3/gTS_0$, the net increase of WAS solid reduction accounted for 24.5% (=58.6−34.1). Assuming these values, the total sludge production would decrease from 1500 t/y to 1133 t/y, giving rise to a cost saving for final disposal of 55125 €/y. The application of ozone oxidation determines an additional operating cost for oxidant production and application which can be assumed equal to 4.5 €/kg (for generators up to 10 kg/h). At the optimal dose, $SDO_3 = 3.5\ mgO_3/gTS_0$, the cost of ozonation would be equal to 23625 €/y. Therefore, the net cost saving in the presence of ozonation pre-treatment would account for 31500 €/y.

In real cases, the cost analysis must be carried out based upon the specific conditions and characteristics of the full-scale WWTP and the type of sludge, either WAS or mixed.

The optimal ozone dosage to be applied will be selected considering the cost of ozone production (depending on the type of ozonator) and of sludge disposal in the specific case. The cost analysis leads to find out the ozonation conditions that enhance performance of the anaerobic digestion and make the pre-treatment to be really profitable. This analysis is site specific. Economic and energy saving with respect to the higher dosages come as a consequence.

Conclusions

Ozonation pre-treatment at dosages below 100 mgO_3/gTS_0 was effective in enhancing volatile solids reduction and methane production in the following anaerobic digestion process of waste-activated sludge. Lower effects were observed in the treatment of the mixed sludge. Indeed, at the optimal dosage, methane production increased by 6% and 30% for mixed and WAS, respectively, and the maximum CH_4 production rate was enhanced by 21% and 33% for mixed and WAS, respectively. The optimal dosage for methane production was the lowest one among the values tested; that was 4.8 and 3.5 mgO_3/gTS_0 for mixed and WAS sludge, respectively. For VS reduction, the effects increased with the dosage.

It is noteworthy that the specific ozone dosages applied in the present study were much lower than those usually referred by the literature, while the improvement obtained in the specific methane production in the case of WAS remained still significant. Therefore, the present study demonstrated the importance of investigating the application of ozone dosages below 100 mgO_3/gTS_0, when ozonation is being evaluated to enhance the anaerobic digestion performance in comparison to other pre-treatments. Taking into account that sludge disposal costs in the WWTP are often above 100 €/ton TS and are expected to increase further, it is highlighted that the potential cost saving can be achieved by reducing final sludge quantity and increasing methane production, even if by only few percentage points.

References

APHA (2005) Standard methods for the examination of water and wastewater, 20th edn. American Public Health Association, Washington, DC

Bougrier C, Albasi C, Delgenès JP, Carrère H (2006) Effect of ultrasonic, thermal and ozone pre-treatments on waste activated sludge solubilisation and anaerobic biodegradability. Chem Eng Process: Process Intensif. 45(8):711–718

Bougrier C, Battimelli A, Delgenes JP, Carrere H (2007) Combined ozone pretreatment and anaerobic digestion for the reduction of biological sludge production in wastewater treatment. Ozone-SciEng 29(3):201–206

Carlsson M, Lagerkvist A, Morgan-Sagastume F (2012) The effects of substrate pre-treatment on anaerobic digestion systems: A review. Waste Manag 32:1634–1650

Carrère H, Dumas C, Battimelli A, Batstone DJ, Delgenes JP, Steyer JP, Ferrer I (2010) Pretreatment methods to improve sludge anaerobic degradability: a review. J Hazard Mater 183:1–15

Chacana J, Alizadeh S, Labelle M-A, Laporte A, Hawari J, Barbeau B, Comeau Y (2017) Effect of ozonation on anaerobic digestion sludge activity and viability. Chemosphere 176:405–411

Chiavola A, D'Amato E, Gori R, Lubello C, Sirini P (2013) Techno-economic evaluation of the application of ozone-oxidation in a full-scale aerobic digestion plant. Chemosphere 91:656–662

Chu L, Yan S, Xing X-H, Sun X, Jurcik B (2009) Progress and perspectives of sludge ozonation as a powerful pretreatment method for minimization of excess sludge production. Water Res 43:1811–1822

Dhar BR, Nakhla G, Ray MB (2012) Techno-economic evaluation of ultrasound and thermal pretreatments for enhanced anaerobic digestion of municipal waste activated sludge. Waste Manage 32(3):542–549

Fall C, Silva-Hernández BC, Hooijmans CM, Lopez-Vazquez CM, Esparza-Soto M, Lucero-Chávez M, van Loosdrecht MCM (2018) Sludge reduction by ozone: Insights and modeling of the dose-response effects. J Environ Manag 206:103–112

Feki E, Khoufi S, Loukil S, Sayadi S (2015) Improvement of anaerobic digestion of waste-activated sludge by using H_2O_2 oxidation, electrolysis, electro-oxidation and thermo-alkaline pretreatments. Environ Sci Pollut Res 22:14717–14726

Gao Y, Duan Y, Fan W, Guo T, Huo M, Yang W, Zhu S, An W (2019) Intensifying ozonation treatment of municipal secondary effluent using a combination of microbubbles and ultraviolet irradiation. Environ Sci Pollut Res 26:21915–21924

Goel R, Tokutomi T, Yasui H, Noike T (2003) Optimal process configuration for anaerobic digestion with ozonation. Water Sci Technol 48(4):85–96

Meng X, Liu D, Frigon M (2015) The process of activated sludge ozonation: effect of ozone on cells, flocs, macromolecules and nutrient release. Water Sci Technol 71:1026–1032

Metcalf & Eddy (2003) Wastewater Engineering. McGraw-Hill, New York

Özön E, Erdinçler A (2019) Effects of microwave, H_2O_2/MW and H_2O_2/heat pre-treatments on the methane production from wastewater sludges: experimental and modeling approach. Environ Sci Pollut Res Int. https://doi.org/10.1007/s11356-019-05190-2 Published on line 20 May 2019

Park KY, Maeng SK, Song KG, Ahn KH (2008) Ozone treatment of wastewater sludge for reduction and stabilization. J Environ Sci Health Part A 43:1546–1550

Parkin G, Owen WF (1986) Fundamentals of anaerobic digestion of wastewater sludges. J Environ Eng 112(5):867–920

Pei J, Yao H, Wang H, Shan D, Jiang Y, Ma L, Yu X (2015) Effect of ultrasonic and ozone pre-treatments on pharmaceutical waste activated sludge's solubilization, reduction, anaerobic biodegradability and acute biological toxicity. Bioresour Technol 192:418–423

Pei J, Yao H, Wang H, Ren J, Yu X (2016) Comparison of ozone and thermal hydrolysis combined with anaerobic digestion for municipal and pharmaceutical waste sludge with tetracycline resistance genes. Water Res 99:122–128

Pérez-Elvira S, Fdz-Polanco M, Plaza FI, Garralón G, Fdz-Polanco F (2009) Ultrasound pre-treatment for anaerobic digestion improvement. Water Sci Technol 60(6):1525–1532

Qiang Z, Nie Y, Ben W, Qu J, Zhang H (2013) Degradation of endocrine disrupting chemicals during activated sludge reduction by ozone. Chemosphere 91:366–373

Qiang Z, Wang L, Dong H, Qu J (2015) Operation performance of an A/A/O process coupled with excess sludge ozonation and phosphorus recovery: a pilot-scale study. Chem Eng J 268:162–169

Salsabil MR, Laurent J, Casellas M, Dagot C (2010) Techno-economic evaluation of thermal treatment, ozonation and sonication for reduction of wastewater biomass volume before aerobic or anaerobic digestion. J Hazard Mater 174:323–333

Tian X, Wang C, Trzcinski AP, Lin L, Ng WJ (2015) Interpreting the synergistic effect in combined ultrasonication–ozonation sewage sludge pre-treatment. Chemosphere 140:63–71

Vlyssides AG, Karlis PK (2004) Thermal-alkaline solubilization of waste activated sludge as a pre-treatment stage for anaerobic digestion. Bioresour Technol 91(2):201–206

Weemaes M, Grootaerd H, Simoens F, Verstraete W (2000) Anaerobic digestion of ozonized biosolids. Water Res 34(8):2330–2336

Wenjing L, Chao P, Lama A, Xindi F, Rong Y, Dhar BP (2019) Effect of pre-treatments on biological methane potential of dewatered sewage sludge under dry anaerobic digestion. Ultrasonics-Sonochem 52:224–231

Xu G, Chen S, Shi J, Wang S, Zhu G (2010) Combination treatment of ultrasound and ozone for improving solubilisation and anaerobic biodegradability of waste activated sludge. J Hazard Mate 180:340–346

Yan ST, Chu LB, Xing XH, Yu AF, Sun XL, Jurcik B (2009) Analysis of the mechanism of sludge ozonation by a combination of biological and chemical approaches. Water Res 43:195–203

Yang S-S, Guo W-Q, Cao G-L, Zheng H-S, Ren NQ (2012) Simultaneous waste activated sludge disintegration and biological hydrogen production using an ozone/ultrasound pretreatment. Bioresour Technol 124:347–354

Yasui H, Shibata M (1994) An innovative approach to reduce excess sludge production in the activated sludge process. Water Sci Technol 30(9):11–20

Yasui H, Nakamura K, Sakuma S, Iwasaki M, Sakai Y (1996) A full-scale operation of a novel activated sludge process without excess sludge production. Water Sci Technol 34(3–4):395–404

Zhang G, Yang J, Liu H, Zhang J (2009) Sludge ozonation: disintegration, supernatant changes and mechanisms. Bioresour Technol 100: 1505–1509

Zwietering MH, Jongenburger I, Rombouts FM, Van 't Riet K (1990) Modeling of the bacterial growth curve. Appl Environ Microbiol 56: 1875–1881