Optimal process configuration for anaerobic digestion with ozonation

R. Goel*, T. Tokutomi*, H. Yasui* and T. Noike**

* Kurita Water Industries, Research and Development Center, 7-1, Wakamiya, Morinosato, Atsugi, Kanagawa 243-0124, Japan

** Department of Civil Engineering, Tohoku University, Aoba 06, Sendai 980-8579, Japan

Abstract Economical source minimization of excess sludge production is an attractive option to deal with the problem of sludge disposal under strict disposal standards. In this paper long-term operational results for two different process configurations that combine oxidative ozone treatment with anaerobic sludge digestion are described. In the first configuration ozone pretreatment was combined with chemostat anaerobic digestion while in the second configuration ozone pre/post-treatments were combined with an anaerobic digester operated without solid removal. From the results of chemostat experiments, the ozone pretreatment solubilized around 19% and 37% of the solids at 0.015 and 0.05 gO_3/gTS ozone dose respectively. The ozone pretreatment resulted in improved TVS reduction efficiencies and the degradation efficiencies were observed to depend on the applied ozone dose and system SRT. The TVS degradation efficiency for pre-ozonated sludge at an ozone dose of 0.05 gO_3/gTS was 59% as compared to 31% for the control reactor fed with un-ozonated sludge. Test results with the second configuration indicated that overall TVS removal efficiencies for a process scheme with post-ozonation could be improved up to 85% with a minimum ozone dose of 0.045 gO_3/gTVS-fed. However, since no solids (except that for sampling) were withdrawn in this configuration, the accumulated total solids in the reactors increased to 28 g/l to 30 g/l at pseudosteady state. The average specific methane recoveries were observed to be 0.36 l CH_4/gTVS fed which were slightly lower than theoretically expected. Based on the experimental results, important points in the choice of process configuration are discussed.

Keywords Activated sludge; anaerobic digestion; hydrolysis; methane; ozone; sludge treatment

Introduction

Reduction in sludge production from treatment plants is desirable and can be achieved either during wastewater or sludge treatment processes. Theoretically, the specific sludge production (gVSS produced/gCOD removed) in wastewater treatment plants can be reduced by: 1) channeling more energy for biomass maintenance purposes; 2) inducing cryptic growth; 3) promotion of growth of higher organisms like protozoa and metazoa; and 4) control of operating parameters like temperature and DO. Recently, many studies have shown successful application of the above principles for sludge reduction at wastewater treatment plants (Yasui and Shibata, 1994; Ratsak *et al.*, 1994; Rensink and Rulkens, 1997; Low and Chase, 1999; Mayhew and Stephenson, 1998; Strand *et al.*, 1999; Abbassi *et al.*, 2000). During sludge treatment, anaerobic digestion is the most fundamental process for solid reduction. However, enzymatic hydrolysis of solids that is reported to be the rate limiting step (Eastman and Ferguson, 1981) limits the solid degradation efficiencies. Hence, to improve solid degradation efficiencies during anaerobic digestion, many researchers have focused their attention on finding suitable pretreatment methods for enhanced sludge hydrolysis.

In past studies, thermal and thermo-chemical methods have been used for sludge pretreatment and even though substantial improvements in VS degradation following such treatment have been reported, problems related to odor, toxicity (Haug *et al.*, 1978; Stucky and McCarty, 1984) and corrosion have led to only limited application of such pretreatment

Water Science and Technology **Vol 48 No 4 pp 85–96**

methods. Recent studies have tried to explore other pretreatment options like mechanical disintegration using pressurized jets (Choi *et al*., 1997), thickening centrifuge (Dohanyos *et al*., 1997) and ball milling (Kopp *et al*., 1997). Other pretreatment options like ultrasound treatment (Tiehm *et al*., 1997); and ozone oxidation (Weemaes *et al*., 2000) have also been reported. Recent reports (Yasui *et al*., 1996) on full-scale applications of ozone treatment to reduce excess sludge production from a full-scale activated sludge treatment plant highlight the role of ozone in real-world application for sludge hydrolysis and enhancement of biodegradability.

In this work, the main objectives were to evaluate ozone treatment of sludge as a method to improve anaerobic digestion efficiencies and to establish the most suitable process configuration. To achieve these objectives two different process configurations were evaluated under different operational conditions. In the first configuration sludge was pretreated with ozone and fed to chemostat anaerobic digesters. In the second configuration, a new process scheme referred to as "closed-loop operation" having no intentional solid withdrawal was used to maximize the solid reduction. In the closed-loop operation, the conventional step of solid withdrawal was replaced with a recirculation line through post-ozonation (ozonation of digested solids). In this way much longer retention times were maintained for substrate solids, while, for active biomass the retention time was controlled by controlling the amount of solids passing through post-ozonation. With this flow scheme, it is expected that the organic solid degradation efficiencies will improve due to the higher retention time of solid substrate and constant supply of ozonated substrate with enhanced biodegradability. For both the process configurations, experiments were performed to study the effect of important process parameters.

Experimental methods

Process configurations

Two process configurations were studied in the present study. The first configuration (referred to as chemostat experiments hereinafter) was with pre-ozonation in combination with chemostat anaerobic digesters while the second configuration (referred to as closed-loop configuration hereinafter) included centrifugation of digested sludge for solid recovery and a post-ozonation step on digested sludge. The details of operational schemes for each configuration, methods of cultivation of activated sludge and ozonation procedure are described in the following sections.

Operational schemes

Four 2-litre jar fermenters equipped with temperature and mixing control were used for each configuration. The closed-loop configuration was studied after the tests were completed on the chemostat configuration. The temperature of the digesters was controlled at 35°C during the study. The startup of the anaerobic reactors was done using a mixture of ground UASB sludge, thermophilic anaerobic digested sludge and mesophilic anaerobic digested sludge from a full-scale treatment plant.

Chemostat reactors. The typical configuration details for the chemostat configuration are shown in Figure 1. The four anaerobic digesters were either fed with raw sludge (control run) or the ozonated sludge (test run). The operation of chemostat reactors was divided into three phases (Phase I, Phase II and Phase III). The details of operational conditions for each of the four reactors in different phases are given in Table 1. The AS and ozonated sludge were batch-fed once every day to the digesters after removing an equivalent amount from the digesters. From the experimental results using the operational scheme, it was possible to estimate the effect of SRT and applied ozone dose on sludge digestion efficiency for control and test (ozonated sludge fed reactors) runs.

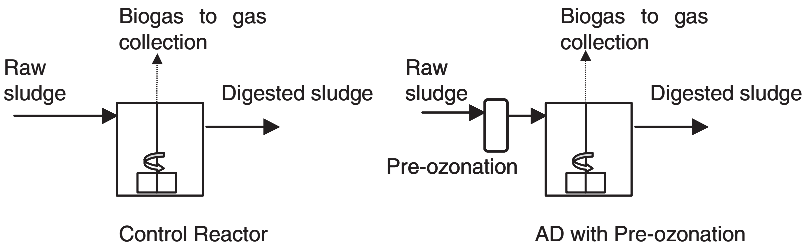

Figure 1 Chemostat anaerobic digesters with and without pre-ozonation

Closed-loop reactors. The typical configuration details for the closed-loop configuration are shown in Figure 2. As shown in Figure 2, two different ozonation schemes were studied for closed-loop configuration. In the first scheme (denoted as I) only post-ozonation of digested sludge was used while in the second configuration (denoted as II) both the pre-ozonation and post-ozonation were applied. For each ozonation scheme, two alternatives (1 and 2) having differences with respect to ozone doses were operated simultaneously to understand the role of applied ozone on the process performance. The operational schemes for the four digesters operated as closed-loop configuration are shown in Table 2. The digesters used in the study were started up with anaerobic sludge well acclimated to the ozonated substrate from chemostat experiments. The initial TVS concentration in the reactors was around 12 g/l.

Table 1 Operating conditions for chemostat reactors

Run no.	SRT/HRT (days)	Average solid loading (kg TVS/m^3.d)	Characteristic of feed	O_3 dose (gO_3/gTS)	Operation period (days)	Comment
Phase I						
I-1[1]	28	0.77	Lab. AS	0.0	35	Control
I-2	28	0.77	Ozonated sludge	0.015	35	Test 1
I-3	14	1.54	Lab. AS	0.0	35	Control
I-4	14	1.54	Ozonated sludge	0.015	35	Test 2
Phase II						
II-1	28	0.77	Lab. AS	0.0	120	Continuation of I-1
II-2	28	0.77	Ozonated sludge	0.05	120	Increased ozone dose
II-3	14	1.54	Lab. AS	0.0	120	Continuation of I-3
II-4	14	1.54	Ozonated sludge	0.05	120	Increased ozone dose
Phase III						
III-1	28	0.77	Lab. AS	0.0	30	Continuation of II-1
III-2	28	0.77	Ozonated sludge	0.05	30	Continuation of II-2
III-3	7	3.08	Lab. AS	0.0	30	Decreased SRT
III-4	7	3.08	Ozonated sludge	0.05	30	Decreased SRT

[1] I-1 denotes reactor 1 during phase I

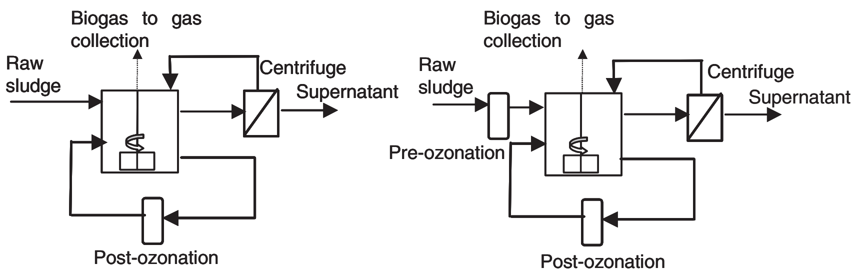

Figure 2 Closed-loop operation with post-ozonation and pre/post-ozonation

Table 2 Operational details for closed-loop reactors

Configuration no.	Feed sludge			Digested sludge for postozonation		SRT[2] (d)	Target volumetric loading[3] (kgTVS/m^3.d)
	Characteristics	Amount (ml/d)[1]	Ozone dose (gO_3/gTS)	Amount (ml/d)[1]	Ozone dose (gO_3/gTS)		
I-1	Raw AS	72	0.0	72	0.03	28	0.79
II-1	Pre-ozonated AS	72	0.015	72	0.04	28	0.79
I-2	Raw AS	72	0.0	72	0.06	28	0.79
II-2	Pre-ozonated AS	72	0.03	72	0.02	28	0.79

[1] Daily-feeding rates were 100 ml/d, but since no feeding was done on Saturdays and Sundays, weekly average of daily feed and sludge for post-ozonation was 72 ml/d
[2] SRT is calculated as (volume of reactor)/(volume withdrawn daily for post-ozonation)
[3] The actual average applied loading was lower and was estimated to be 0.6 (kgVS/m^3.d) based on the operation data

Cultivation of activated sludge

A 160 l activated sludge SBR was operated for cultivating the activated sludge required for feeding to the anaerobic digesters. The SBR was operated at a sludge age of 10 days. The 500 ml of concentrated substrate (BOD_5 300,000 mg/l) containing yeast extract, fish extract, fructose syrup and phosphoric acid was batch fed to the reactor daily. The MLSS in the reactor was around 5,000–6,000 mg/l.

Ozonation

Activated sludge and digested sludge. The ozonation of activated sludge during chemostat experiments was performed at pH of 2. The pH of the activated sludge was adjusted to 2 by using 4N HCl acid before ozonation. A precalculated ozone dose of either 0.015 or 0.05 gO_3/gTS was applied during ozonation. After ozonation the pH was readjusted to 7–7.2 using 4N NaOH. The raw activated sludge and ozonated sludge were stored in a refrigerator. The amount of stored sludge was enough for 3–5 days of feeding to the jar fermenters. Thus fresh substrate was prepared every 3–5 days during the period of this study. Activated sludge ozonation during closed-loop reactor study was performed in a similar way except that no pH adjustments were performed before and after ozonation. The ozonation of digested sludge in the closed-loop configuration was performed twice per week and the ozonated sludge was stored in a refrigerator.

Analytical methods

Total solids (TS) and total volatile solids (TVS) in the feed sludge and reactors were measured according to *Standard Methods*. Suspended solid (SS) and volatile suspended solids (VSS) were measured after centrifuging the sludge sample twice at 12,000 rpm for 10 minutes. The supernatant of first centrifugation was filtered using 0.45 μm and used for soluble fraction analysis. The TOC in the soluble fraction was measured using a Shimadzu TOC 5000. The COD concentration was measured by using Hach COD measurement apparatus. The VFA concentration in soluble samples was measured using a liquid chromatograph equipped with a visible detector at 410 nm. Soluble ammonia concentration was measured calorimetrically using a flow injection analyzer. The ozone gas measurements were done using an ozone meter (Nippon Ozone Co.) based on a UV detector. For the closed-loop configuration, a sample volume of 10–20 ml per week was withdrawn from each reactor for analysis. The solids, thus withdrawn, were included in the preparation of the solid mass balance.

Results

Chemostat studies

Solid solubilization in ozonation. A plot between measured VSS before and after ozonation is as shown in Figure 3(a). From the correlation, it is estimated that about 37% of the solids are solubilized at 0.05 gO_3/gTS ozone dose. By similar experiments at lower ozone dose of 0.015 gO_3/gTS, the expected solubilization ratio was estimated to be about 19% (data not shown). From Figure 3(a), it can also be deduced that at a particular ozone dose, the solubilization ratios do not change significantly for sludge concentrations ranging from 18 g/l to 26 g/l.

Solid mineralization in ozonation. TVS before and after ozonation were measured to assess the sludge mineralization during the ozonation stage. A plot between TVS in raw sludge and ozonated sludge (ozone dose = 0.05 gO_3/gTS) is as shown in Figure 3(b). The regression line suggests that about 5% of the TVS is mineralized during ozone treatment at 0.05 gO_3/gTS of ozone dose.

Other parameters. Table 3 shows a summary of the parameters for assessing the change in sludge characteristics after ozonation. It can be seen that ammonia and VFA concentration only increase slightly after ozone treatment. The VFA analysis also revealed that formic acid was the major constituent of whatever little VFA was produced during ozone treatment. The increase in soluble PO_4-P was significant and almost 25% of the TP in the sludge was observed to solubilize after ozone treatment.

Solid reduction during anaerobic digestion. The time course of TVS in anaerobic digesters during different phases is shown in Figure 4. A summary of results is also presented in Table 4. The TVS reduction efficiencies for the raw activated sludge at 28 days SRT during

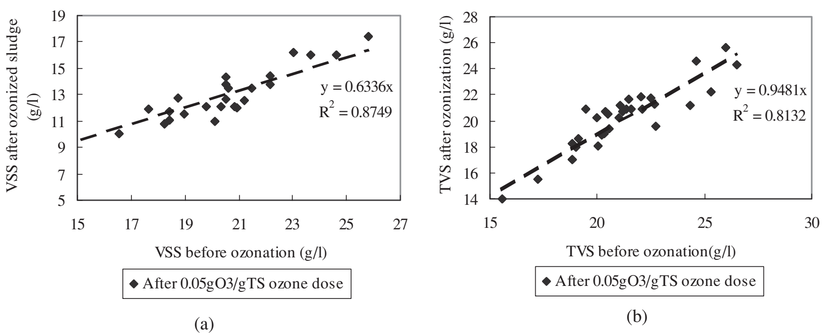

Figure 3 (a) Sludge solubilization during ozone treatment; (b) sludge mineralization during ozone treatment

Table 3 Average characteristics of raw and ozonated sludge

Parameter	Raw sludge	Ozonated sludge
TVS (g/l)	21.4 ± 1.8	20.6 ± 2.0
VSS (g/l)	20.5 ± 1.7	12.7 ± 1.7
Soluble TOC (g/l)	0.34 ± 0.24	2.62 ± 0.43
TVS/TS	0.92 ± 0.01	0.84 ± 0.02
VSS/SS	0.92 ± 0.01	0.93 ± 0.01
Soluble NH_4-N(g/l)	0.04 ± 0.02	0.05 ± 0.02
Kjeldhal N(g/l)	2.2	2.1
Total P(g/l)	0.56	0.56
Soluble PO_4-P(g/l)	0.019	0.13
VFA (g/l)	–	0.2 ± 0.05

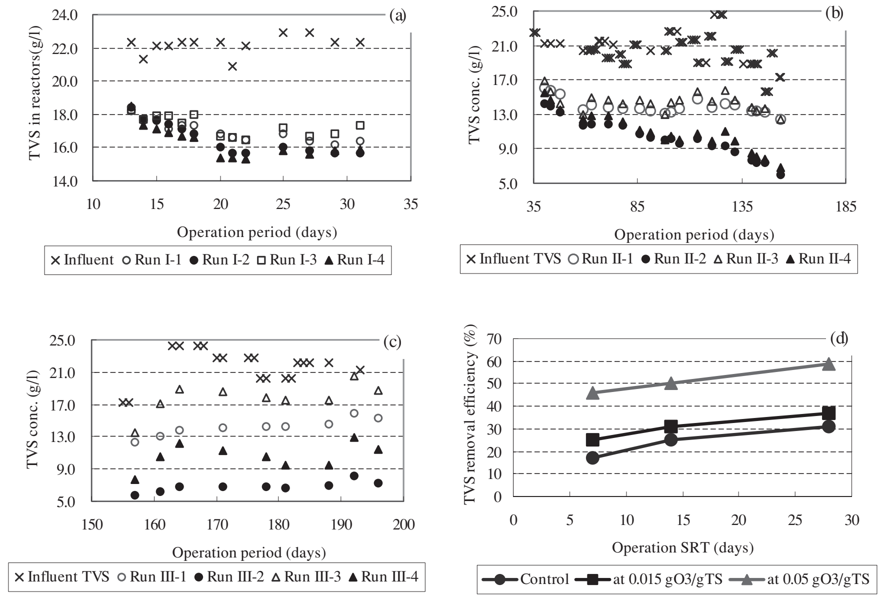

Figure 4 The trend of TVS during: (a) phase I; (b) phase II; (c) phase III; and (d) TVS removal efficiencies with SRT and Ozone dose

Table 4 Summary of different process parameters

Run no.	SRT/HRT (days)	O_3 dose (gO_3/gTS)	Solid degradation efficiency TVS (%)	VSS (%)	TVS/TS ratio (–)	Specific methane production ($lCH_4/gTVS$ fed)	Soluble NH_4-N (mg-N/l)	Soluble TOC (mg/l)	VFA COD (major component) (mg COD/l)
Phase I[1]									
I-1	28	0.0	35	38	0.85	0.20	745	68	
I-2	28	0.015	37	42	0.83	0.21	824	129	90 (IB)[4]
I-3	14	0.0	24	28	0.87	0.12	647	493	1,506(P)
I-4	14	0.015	31	36	0.84	0.14	770	689	1,924(P)
Phase II[2]									
II-1	28	0.0	31	35	0.87	0.12	830	1,013	2,136(A,P)
II-2	28	0.05	59	65	0.73	0.25	1,357	1,876	3,791(A,P)
II-3	14	0.0	27	30	0.89	0.11	718	743	1,833(A,P)
II-4	14	0.05	50	60	0.74	0.20	1,302	2,126	3,691(A,P)
Phase III[3]									
III-1	28	0.0	25	–	0.87	0.15	643	113	–
III-2	28	0.05	58	60	0.65	0.31	1,224	466	–
III-3	7	0.0	17	–	0.89	0.07	422	217	–
III-4	7	0.05	46	52	0.73	0.19	1,055	1,590	–

[1] Startup, control reactors 1 and 3 operated at different SRT, ozonated sludge fed reactors 2 and 4 operated at SRT same as 1 and 3 respectively. The applied ozone dose was 0.015 gO_3/gTS

[2] The ozone dose for sludge fed to reactors 2 and 4 was increased from 0.015 to 0.05 gO_3/gTS

[3] The SRT for reactor 3 and 4 was reduced from 14 days to 7 days. Trace metals of Fe, Ni and Co were also added in the fed sludge

[4] IB: Iso-butyric acid, P: Propionic acid, A: Acetic acid

different runs (I-1, II-1 and III-1) ranged between 25–35%. The TVS reduction efficiencies for the sludge treated with 0.015 gO_3/gTS (I-2 and I-4) were only 10–30% higher than the efficiencies for untreated sludge (I-1 and I-3). As the operation was continued in Phase II with an increased ozone dose of 0.05 gO_3/gTS, the TVS reduction efficiencies gradually improved to 59% and 50% for the SRT of 28 and 14 days (II-2 and II-4) respectively, suggesting an improvement of 85 to 90% over the control efficiency respectively. It can be seen that after switching to phase II, it took a long time (2 months) before differences between the control and ozonated sludge fed reactors became significant. Thus it appears that some acclimation to ozonated sludge was necessary before the full degradation potential was realized. Considering this point, it is possible that degradation efficiencies for ozonated sludge at 0.015 gO_3/gTS ozone dose may have been slightly underestimated due to the relatively short operation period.

In Phase III, the SRT of reactors III-3 and III-4 was further reduced to 7 days. At reduced SRT, the TVS reduction efficiency for control reactor (III-3) dropped significantly from 27% to 17% whereas efficiency for ozonated sludge fed reactor (III-4) only reduced from 50% to 46%.

The observed TVS removal efficiencies and their relation to SRT and ozone dose are as shown in Figure 4(d). The comparison of TVS degradation efficiency for ozonated sludge and control sludge at different SRTs suggests that ozone treatment produces at least two organic fractions out of which one (ca. 30% at 0.05 gO_3/gTS) has significantly higher hydrolysis rates than the original sludge and is consumed during the initial phase (≤7days) of digestion. Judging from the degradation efficiencies at higher SRT, the degradation behavior of remaining fraction (ca. 70%) is not much different from the solids in the original sludge. The percent solubilization of 19% at 0.015 gO_3/gTS and 37% at 0.05 gO_3/gTS resulted in about 30% and 80% improvements in TVS removal efficiencies respectively. Thus, the improvement in TVS degradation efficiency at different ozone doses seems to correlate well with percent solubilization during ozone treatment.

From the summary of parameters in Table 4, the observed ammonia levels in the reactors with pre-ozonation were consistently higher than that observed in the control reactors. These higher levels corroborate well to the higher degradation efficiencies in the reactors fed with ozonated sludge. The observed specific methane production ($lCH_4/gTVSfed$) was also higher.

Apparent first-order hydrolysis rates of ozonated sludge. Based on the continuous operational data, the observed hydrolysis rates of ozonated sludge and raw sludge are calculated and are presented in Table 5. The apparent first-order hydrolysis rates (k), have been calculated assuming steady-state conditions in the reactors. The expression $k = \eta/(1-\eta)\tau$ is used for calculating apparent first-order coefficient from the data of continuous experiments, here τ is the sludge retention time (= HRT) in days and η is the TVS degradation efficiency. The apparent first-order hydrolysis coefficient is found to depend on sludge retention time. The value of the apparent first-order hydrolysis coefficients for ozonated sludge was two to four times higher than that of activated sludge.

Performance of closed-loop reactors

Organic and inorganic solid accumulation. The observed trend of organics and inorganic solids in all the reactors is as shown in Figure 5(a) and (b). After about 140 days of operation, the TVS and inorganic solid concentrations in the reactors were observed to achieve stable concentration. The TVS accumulation in the reactor of configuration II-1 and II-2

Table 5 Estimated apparent first-order hydrolysis rate

Condition	SRT/HRT (d)	TVS reduction efficiency (%)		Apparent first-order hydrolysis coefficient, k (d^{-1})	
		Control	Ozonated sludge	Control	Ozonated sludge
1	28	35	59	0.020	0.051
2	14	27	50	0.026	0.071
3	7	17	46	0.030	0.120

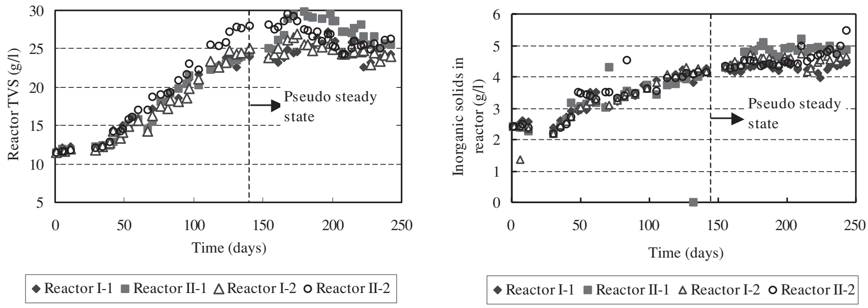

Figure 5 Trend of: (a) TVS in reactors; (b) inorganic solids in reactors

was observed to be slightly higher than that of configuration of I-1 and II-2 despite two point ozonation in the later case.

TVS removal efficiencies based on organic solid balance. A mass balance was prepared for the period after pseudosteady-state was achieved. The mass balance is presented in Table 6. According to the mass balance, 9–13% of the TVS were lost in the effluent and 5–6% of the TVS were lost during sampling of sludge samples for TS, TVS and other measurements. The TVS degradation efficiency was estimated to be 85%, 82%, 86%, 86% for reactors I-1, II-1, I-2, II-2 respectively. The calculated TVS removal efficiency for different reactor configurations did not differ much, suggesting that two-point ozonation (pre- and post-ozonation) did not result in any additional benefit as compared to only post-ozonation.

Ozone requirements. The specific ozone requirement in the reactor configuration I-1 was found to be lowest at 0.054 gO_3/gTVS removed. For configurations I-2, II-1 and II-2, the specific ozone requirements worked out to be 0.079, 0.085 and 0.072 gO_3/gTVS removed respectively. Comparing I-1 and I-2 in which the flow schemes were identical except that the ozone dose on the digested sludge in I-2 was twice as much, it appears that giving a high ozone dose was ineffective as no significant difference in the overall performance of these reactors was observed.

Other parameters. The observed specific methane production was 0.36, 0.34, 0.36 and 0.33 lCH_4/g TVS-fed for I-1, II-1, I-2 and II-2 respectively. Considering theoretical specific gas production of 0.5 lCH_4/gTVS-removed, a TVS reduction efficiency of 80–85% should result in specific methane production of 0.4–0.42 lCH_4/gTVS-fed. Thus the observed specific methane production was 10–15% lower than the theoretical values. The lower values of specific methane production were typical for reactors II-1 and II-2 having two-point ozonation (pre- and post-ozonation) with higher ozone doses. The lower methane recoveries may be considered to be mainly due to partial mineralization of COD

Table 6 Mass balances after pseudo steady state

Configuration no.	TVS fed to the reactors (g)	TVS wasted in effluent (g)	TVS wasted in sampling (g)	TVS increase in reactor[2] (g)	Net miner-alized (g)	TVS removal efficiency (%)
I-1	113.61	10.45 (9.2%)[1]	6.23 (5.5%)	(0.45)	97.38	85.72
II-1	111.97	13.00 (11.6%)	6.98 (6.2%)	0.79	91.20	81.46
I-2	113.59	13.13 (11.6%)	6.24 (5.5%)	(3.32)	97.53	85.87
II-2	107.96	14.09 (13.0)	6.65 (6.2%)	(5.74)	92.96	86.11

[1] Percent of the feed solids
[2] The numbers in brackets indicate the decrease in solids during the period used for mass balancing

and slight increase in the oxidation state of the organics during the ozonation stage. As higher ozone doses can increase both the COD mineralization and the oxidation state of organics, it is reasonable to expect lower methane recoveries at higher ozone doses. However, as the methane recoveries from I-2 reactor were not affected despite application of a higher ozone dose on the digested sludge, it is tempting to think that during post-ozonation the effect of COD mineralization and increase in oxidation are not as significant as that for pre-ozonation.

The filtered effluent COD in all the reactors during the pseudosteady state was observed to be in a range of 875–1,055 mg/l. The measured VFA concentrations were always lower than 100 mg/l. The unfiltered COD concentrations in the supernatant after centrifugation were consistently higher than the filtered COD concentrations, suggesting fine particles and colloids could not be completely removed by centrifugation. The observed supernatant COD ranged from 3,000 to 4,400 mg/l. The higher values were typically associated with the reactors I-2, II-1 and II-2 which all had much higher ozone doses as compared to reactor I-1. Thus, from the results of this study it appears that too high ozone doses can result in an increase in effluent COD.

Discussion

Ozone is reported to react and break the main cell constituents of polysaccharides, proteins and lipids to smaller molecular chain compounds (Bablon *et al.*, 1991). Further, at higher ozone doses organic compounds may oxidize to organic acids, aldehydes and alcohols. In addition to the action of hydrolyzing long chain polymers, it is also reported that the biodegradability of humic compounds (Bablon *et al.*, 1991) can be improved after ozonation. Consistent with such observations, the results of this long-term continuous experimental study clearly establishes that the ozonation of activated sludge not only increases the subsequent solid degradation rates but also improves the fraction of degradable solids.

The observed TVS degradation efficiencies of 59% (ozone dose 0.05 gO_3/gTS, SRT = 28 days) are considered to be a significant improvement over the control efficiency of 31%. Moreover, the observed high degradation efficiencies of 46% even at low SRT (SRT = 7 days) present new opportunities to apply pre-ozonation to handle increased sludge amounts at existing facilities without new constructions. As seen from the results, significant improvements in solid degradation efficiencies could be achieved only after a lengthy acclimation period. The required acclimation period may be indirectly related to the change in substrate characteristics and increased redox potential of the ozonated substrate. Weemaes *et al.* (2000) observed a lag phase in gas production from the anaerobic batch reactor fed with high ozone dosed substrate suggesting that higher redox potential may negatively affect the methanogenic activity. It is not clear whether the redox potential affected the start up procedure, but during the later periods of study, no negative effects of high redox potential of ozonated sludge was observed. The dilution rate could be an important factor when considering the effect of redox potential of ozonated sludge on anaerobic digestion and may require some consideration at high dilution rates.

From the closed-loop experiments, it can be seen that the configuration with post-ozonation is most efficient as it: 1) required minimum ozone dose of 0.054 gO_3/gTVS-removed (0.45 gO_3/gTVS-fed); 2) resulted in better effluent quality and; 3) gave better gas recoveries. As the relative fraction of degradable and inert organics in raw sludge and those in digested sludge are different, ozonation with digested sludge may have been more efficient as it has a relatively higher fraction of inert fraction than the raw activated sludge. From the results of this study post-ozonation appears to be efficient, however, in practical applications it may be essential to estimate the consumption of ozone by the reductants (reduced metals and sulfides) usually present in higher concentration in anaerobically digested sewage sludge. In the present study, the effect of such reductants is considered to be small as the synthetic sludge did not contain compounds that lead to significant concentration of reduced species.

One of the important considerations in a closed-loop configuration is the accumulation of organic and inorganic solids in the reactor. At higher solid loadings, the maximum concentration of solids that can be easily maintained in the reactor should govern the solid digestion efficiencies. To predict the expected accumulated total solid concentration a simplified steady-state model based on the mass balancing of organics and inorganic solids is proposed. Figure 6 shows the system boundary for the system to be modeled. The mass balance for volatile solids and inorganic solids can be described by following equations.

Mass balance for organic solids:

$$Q_1.X_{1,o}.(1-\eta_1)+Q_r.X_{2,o}.(1-\eta_2)=Q_r.X_{2,o}+(Q_1-Q_e).X_{3,o}+Q_e.X_{2,o} \tag{1}$$

Mass balance for inorganic solids:

$$Q_1.X_{1,i}.=Q_e.X_{2,i}+(Q_1-Q_e).X_{3,i} \tag{2}$$

In writing the above mass balance for solids, it is assumed that there is no mineralization during the ozonation stage. For estimating the total solid concentration in the reactor, Eq. (1) and (2) can be rearranged to result in Eq. (3). In deriving the simplified form of Eq. (3), the smaller contribution of mass flow from the effluent stream is neglected ($Q_1.X_{3,o}$ = $Q_1.X_{3,i}=0$).

$$X_{2,TS}=X_{2,o}+X_{2,i}=\frac{Q_1.X_{1,o}}{V}.\left[\frac{(1-\eta_1)\theta_e\theta_r}{\theta_e\eta_2+\theta_r}+\theta_e\frac{(1-r_1)}{r_1}\right] \tag{3}$$

where subscript *i* and *o* represent the inorganic and organic solids and

Q_1 : Flow rate of raw sludge (m^3/d)
Q_r : Flow rate of recirculated ozonated sludge (m^3/d)
Q_e : Excess sludge withdrawal flow rate (m^3/d)
$X_{1,}$: Concentration in the raw sludge (kg/m^3)
$X_{2,}$: Concentration in the recirculated sludge(kg/m^3)
$X_{3,}$: Solid in the effluent (kg/m^3)
$X_{2,TS}$: Total solid concentration in reactor ($X_{2,o}+X_{2,i}$) (kg/m^3)
V : Volume of reactor (m^3)
η_1 : Organic solid removal efficiency for raw sludge (%)
η_2 : Organic solid removal efficiency for recirculated ozonated sludge (%)
θ_e : SRT of solids defined as $\{V/Q_e\}$ (days)

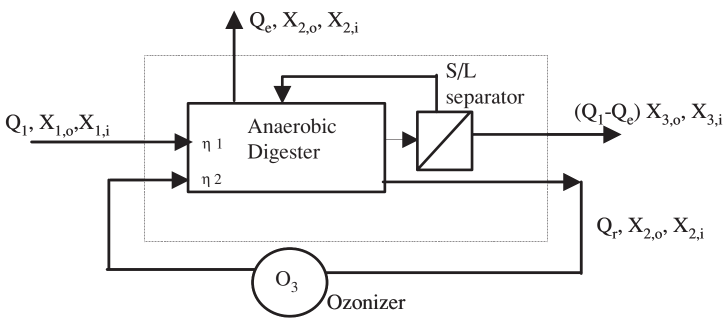

Figure 6 System boundary for mass balancing

θ_r : SRT of ozonated solids defined as $\{V/Q_r\}$ (days)
r_1 : TVS/TS ratio $\{X_{1,o}/(X_{1,o}+X_{1,I})\}$ in feed sludge (–)

In the above equation, by knowing the value of η_1 and η_2, the steady-state value of solids in the reactors can be predicted. The values of η_1 and η_2 depend on the system sludge retention time $[\theta_e\theta_r/(\theta_e+\theta_r)]$, applied ozone doses and temperature (Goel *et al.*, 2002). Eq. (3) can be used to understand the effect of process parameters the volumetric organic loading $(Q_1.X_{1,o}/V)$, TVS/TS (r_1) and the SRT of solid (θ_e).

Based on the above discussion, it is clear that both the chemostat configuration and closed-loop configuration are effective in improving the solid degradation efficiencies in anaerobic digestion. The choice of the configuration, however, depends on the desired level of improvements in solid degradation efficiencies and the volumetric loading. For example, the chemostat configuration is considered to be effective in cases where higher solid loading with moderate level of improvements in solid degradation efficiencies are desired. On the other hand, the closed-loop configuration should be the process of choice where high solid degradation efficiencies are desired at low solid loading.

Conclusions

Improvement in solid degradation efficiency in anaerobic digestion using sludge ozonation was studied through long-term operation of laboratory-scale continuous reactors. Based on the results of different process configuration tried in this study following conclusions can be drawn.

1. The pre-ozonation of activated sludge solubilized about 19% and 37% of the solids at 0.015 and 0.05 gO_3/gTS ozone dose, respectively. No significant mineralization of organics is observed during the ozonation stage.
2. The chemostat configuration with pre-ozonation at 0.05 gO_3/gTS improved the solid degradation efficiencies to 59% (SRT = 28 days). This was a significant improvement as compared to solid degradation efficiency of 31% for the control run. The solid degradation efficiencies for lower SRT of 14 days and 7 days also improved to 50% and 46%, suggesting possibilities of higher loading with pre-ozonation. An acclimation period lasting more than 60 days was observed before improved degradation was observed for the ozonated sludge fed reactors.
3. The closed-loop configuration studies indicated that TVS degradation efficiencies of 85% can be achieved with this configuration. Further, the configuration with postozonation was found to be most effective as it required minimum ozone doses of 0.045 gO_3/gTVS-fed and had better performance with respect to other process parameters of gas production and effluent COD.
4. In the closed-loop configuration, the filtered COD were low (ca.875–1,055 mg/l), but the COD in the supernatant after centrifugation were observed to be high (ca. 3,000 to 4,400 mg/l) and represent about 9–13% of the input COD. Moreover, the effluent COD were higher for the reactors having higher ozone dose.
5. Both the chemostat configuration and closed-loop configuration were found to be effective in improving the solid degradation efficiencies in anaerobic digestion. The choice of the process, however, needs to be made depending on the desired solid loading and the expected level of improvements in solid degradation efficiency.

References

Abbassi, B., Dullstein, S. and Rabiger, N. (2000). Minimization of excess sludge production by increase of oxygen concentration in activated sludge floc; experimental and theoretical approach. *Wat. Res.*, **34**(1), 139–146.

Bablon, G. *et al.* (1991). *Fundamental Aspects in Ozone in Water Treatment – Application and Engineering*, ed. Langlais, B., Reckhow, D.A. and Brink, D.R., Lewis Publishers, pp 11–132.

Choi, H.B., Hwang, K.Y. and Shin, E.B. (1997). Effects on anaerobic digestion of sewage sludge pretreatment. *Wat. Sci. Tech.*, **35**(10), 207–211.

Dohanyos, M., Zabranska, J. and Jenicek, P. (1997). Enhancement of sludge anaerobic digestion by using of a special thickeing centrifuge. *Wat. Sci. Tech.*, **36**(11), 145–153.

Eastman, J.A. and Ferguson, J.F. (1981). Solubilization of particulate organic carbon during the acid phase of anaerobic digestion. *JWPCF*, **53**, 352.

Goel, R., Yasui, H. and Noike, T. (2002). Closed loop anaerobic digestion using pre/post sludge ozonation and effect of low temperature on process performance, Conference Proceedings, *Anaerobic Digestion of Solid Wastes 2002 conference*, Munich, 18–20 Sep 2002.

Haug, R.T., Stucky, D.C., Gossett, J.M. and McCarty, P.L. (1978). Effect of thermal treatment on digestibility and dewaterability of organic sludges. *JWPCF*, **50**, 73–85.

Kopp, J., Muller, J., Dichtl, N. and Schwedes, J. (1997). Anaerobic digestion and dewatering characteristics of mechanically disintegrated excess sludge. *Wat. Sci. Tech.*, **36**(11), 129–136.

Low, E.W. and Chase, H.A. (1999). The effect of maintenance energy on biomass production during wastewater treatment. *Wat. Res.*, **33**(3), 847–853.

Mayhew, M. and Stephenson, T. (1998). Biomass yield reduction: Is biochemical manipulation possible without affecting activated sludge process efficiency? *Wat. Sci. Tech.*, **38**(8–9), 137–144.

Ratsak, C.H., Kooi, B.W. and Van Vereveld, H.W. (1994). Biomass reduction and mineralization increase due to ciliate *Tetrahymena pyriformis* grazing on the bacterium *Pseudomonas fluorescens*. *Wat. Sci. Tech.*, **29**(7), 119–128.

Rensink, J.H. and Rulkens, W.H. (1997). Using metazoa to reduce sludge production. *Wat. Sci. Tech.*, **36**(11), 171–179.

Strand, S.E., Harem, G.N. and Stensel, H.D. (1999). Activated sludge yield reduction using chemical uncouplers. *Wat. Environ. Res.*, **71**(4), 455–458.

Stuckey, D.C. and McCarty, P.L. (1984). The effect of thermal pretreatment on the anaerobic biodegradability and toxicity of waste activated sludge. *Wat. Res.*, **18**(11), 1343–1353.

Tiehm, A., Nickel, K. and Neis, U. (1997). The use of ultrasound to accelerate the anaerobic digestion of sewage sludge. *Wat. Sci. Tech.*, **36**(11), 121–128.

Weemaes, M., Grootaerd, H., Simoens, F. and Verstraete (2000). Anaerobic digestion of ozonized biosolids. *Wat. Res.*, **8**, 2330–2336.

Yasui, H. and Shibata, M. (1994). An innovative approach to reduce excess sludge production in the activated sludge process. *Wat. Sci. Tech.*, **30**(9), 11–20.

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