

Effects of ozone treatment on the biodegradability of sludge from municipal wastewater treatment plants

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Abstract The effects of ozone pretreatment on the biodegradability of municipal wastewater sludge were determined. Three types of experiments were conducted: anaerobic digestion, aerobic biodegradation, and denitrification using ozone-treated sludge as a carbon source. For 5 days, ozonated sludge at 0.1 gO₃/g-SS showed about 2–3 times greater biodegradation compared to the raw sludge in both aerobic and anaerobic conditions. In anaerobic experiments, biodegradation increased with ozone dosage up to 0.2 gO₃/g-SS. Further increase of ozone dosage did not improve the biodegradation. In aerobic condition, about 77% of the ozonated sludge at 0.1 gO₃/g-SS could be biodegraded after 15 days and is compared with 36% degradation of the untreated sludge. Most of the biodegradation of the ozonated sludge occurred within 5 days while the raw sludge was biodegraded steadily throughout the experimental period. The biodegradation enhancement of ozonated sludge was confirmed in batch denitrification experiments.

Keywords Anaerobic digestion; biodegradability; ozone treatment; sludge; sludge pretreatment

Introduction

Ozone treatment of municipal sludge has been proposed for improvement of anaerobic digestion processes (Scheminski *et al.*, 1999; Weemaes *et al.*, 2000). It was suggested that partial oxidation and solubilization of sludge solids enhance the biodegradability of the raw sludge or digested sludge. Recently, ozone treatment followed by recirculation of the treated sludge into a bioreactor for further aerobic biodegradation was reported to effectively reduce excess sludge production (Yasui and Shibata, 1994; Yasui *et al.*, 1996; Sakai *et al.*, 1997). For more than 6 months, a full-scale wastewater treatment plant could be operated in a relatively stable condition without sludge withdrawal (Yasui *et al.*, 1996). The basic assumption in these processes is that ozone treatment and subsequent solubilization of sludge solids increases the biodegradability of the sludge. In this study, the effects of ozone treatment on the biodegradability of municipal sludge were evaluated. Three types of experiments were conducted to quantify the biodegradability enhancement of ozone-treated sludge: anaerobic digestion, aerobic biodegradation, and denitrification using ozone-treated sludge as a carbon source.

Methods

Sludge was taken from one of the municipal wastewater treatment plant in Seoul. The sludge was passed through a standard sieve to remove large debris and its concentration was adjusted to 1.2% total solid before ozonation. The ratio of VSS/MLSS was about 0.74. The sludge was ozonated in a cylindrical shape column reactor with 50 mg-O₃/L-gas. A mechanical foam breaker was used for foaming control during ozonation. The effects of

ozone treatment on the biodegradability of sludge were determined at various ozone dosages from 0.02 to 5 g-O₃/g-MLSS. Anaerobic digestion experiments were conducted in a series of 160 mL serum bottles for 30 days. Each bottle contained 50 mL of ozonated sludge and 50 mL of anaerobic seed sludge. The production of methane was monitored by a GC system (HP 6890 series) equipped with a TCD detector. Total gas production was also measured by connecting a 50 mL glass syringe into the serum bottle. Aerobic biodegradation experiments were conducted in 2 L bioreactors containing 250 mL raw sludge and 250 mL ozonated sludge. The degradation of sludge was determined by monitoring oxygen consumption in the reactor. Oxygen consumption was determined by measuring the change in headspace pressure created by oxygen consumption. NaOH solution (1N) was used to trap the generated CO₂. The CO₂ trap solution was periodically replaced with fresh solution and the head space was flushed with pure oxygen. The nitrate concentration in the solution was also monitored and is subtracted from the total oxygen consumption. The biodegradability of the sludge supernatant after ozone treatment was also evaluated by batch denitrification experiments. A series of 250 mL flasks containing 30 mg/L NO₃, 50 ml seed sludge, and the sludge supernatant after ozone treatment were sealed and incubated with slow agitation. The added supernatants were properly diluted to make the target SCOD concentrations for each flask.

Results

Figure 1 shows the fate of sludge particles after ozone treatment at various dosages. Solubilization of sludge is dominant at relatively low ozone dosages. At higher dosages, the rate of mineralization become greater, resulting in the decrease of solubilized organics. Unsettled micro particles reached the maximum at 0.1 g/g-SS.

Anaerobic digestion

The results from anaerobic digestion experiments were shown in Figure 2. Both the methane and total gas production rates increased with ozone dosage up to 0.2 g/g-SS. Further increase of ozone dosage to 0.5 g/g-SS did not increase the biodegradation. Considering the 1:1 volume ratio of the feed and the seed sludge, methane production from the treated sludge at 0.2 g/g-SS is about three times greater than that from raw sludge. The methane production or biodegradation consists of two phases; initial rapid biodegradation is followed by slower, but steady degradation. Interestingly, both the initial and the 2nd phase biodegradation rates do not change much with ozone dosage. Most of the differences in gas and methane production between the raw sludge and the treated sludge can be attributed to the differences in the duration of the initial fast degradation phase.

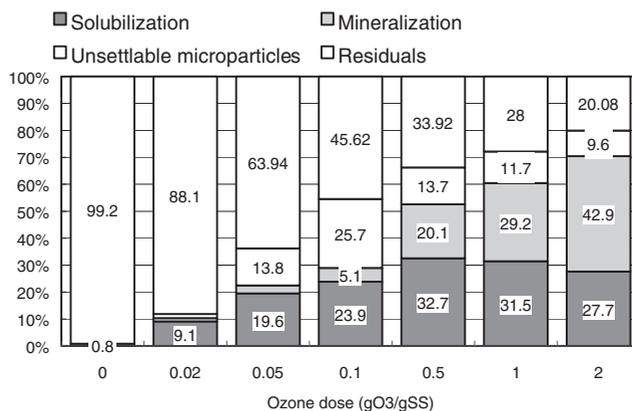


Figure 1 The fate of sludge after ozone treatment at various ozone dosages

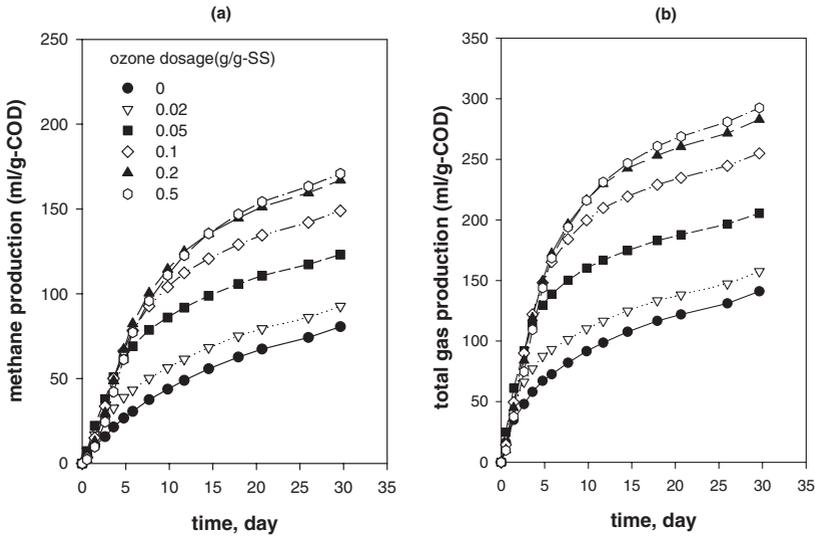


Figure 2 Production of methane and total gas during anaerobic biodegradation of ozone treated sludge; a) methane production, b) total gas production

Aerobic biodegradation

The biodegradability enhancement after ozone treatment was also demonstrated in aerobic biodegradation experiments. Figure 3 shows the oxygen consumption by ozone treated sludge in an aerobic bioreactor. The two phases of biodegradation, similar to the observation in anaerobic experiments, were observed. The duration of the fast degradation phase increases with ozone dosage. Although it is obvious that biodegradability of sludge is enhanced by ozonation, accurate quantification of the biodegradability of the ozonated sludge is not easy because the seed sludge itself consumes oxygen. Considering the volume ratio of the feed and the seed sludge (1:1), the total biodegradation rates can be regarded as the average values between the ozonated sludge and the seed sludge. Based on the assumption and the initial and the final TCOD for each sample (Table 1), the estimated biodegradation for the ozonated sludge after 15 days are 36.0, 45.4, 63.0, 77.1% at ozone dosages of 0, 0.02, 0.05, and 0.1 g/g-SS, respectively. In fact, most of the biodegradation for ozonated sludge occurs within 5 days. One of the interesting observations is the suppression of biodegradation rate at relatively high ozone dosages (>0.1 g/g-SS). This was observed in both aerobic and anaerobic biodegradation experiments (Figure 2 and 3), although the extents are smaller in anaerobic experiments. Weemaes *et al.* (2000) reported the presence of a lag period in anaerobic biodegradation of ozone treated sludge at 0.2 g/g-SS, although clear explanation for the observation was not given.

Denitrification experiments

Batch denitrification experiments were conducted using only the supernatant after ozone

Table 1 Total COD before and after aerobic biodegradation experiments

Samples	Raw seed sludge		Ozonated sludge (1:1) before biodegradation			Seed + ozonated sludge after biodegradation		
	before	after	0.02 g/g-SS	0.05 g/g-SS	0.1 g/g-SS	0.02 g/g-SS	0.05 g/g-SS	0.1 g/g-SS
TCOD (mg/L)	12,820	8,200	12,210	11,930	11,720	7,420	6,250	5,330

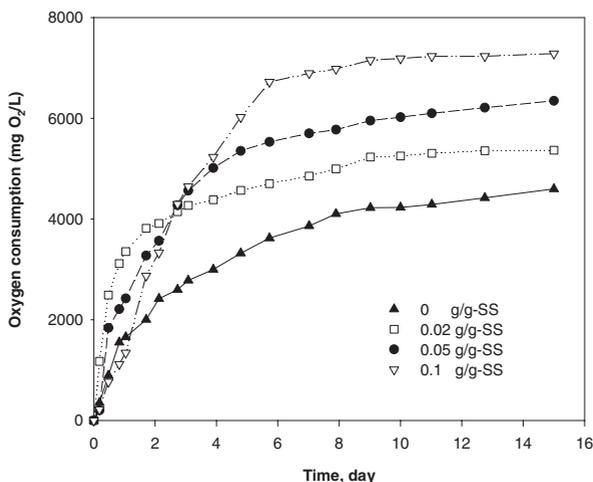


Figure 3 Oxygen consumption during aerobic biodegradation of ozone treated sludge

treatment including SCOD and unsettled particles. Figure 4a shows the progress of denitrification at various carbon/nitrogen (C/N) ratios using the supernatant treated at 0.1 g/g-SS. On the other hand, the denitrification for the supernatants at different ozone dosages with the C/N ratio fixed at 10 is shown in Figure 4b.

It is clear that the solubilized and/or the unsettled microparticles are available for biodegradation as a good carbon source regardless of ozone dosage. The specific denitrification rate for ozonated treated supernatant was 0.05 g $\text{NO}_3\text{-N/gVSS}\cdot\text{d}$ on average, which is comparable to the values for domestic wastewater (0.03–0.11 g $\text{NO}_3\text{-N/gVSS}\cdot\text{d}$) (US EPA, 1975).

Conclusions

The effects of ozone treatment on the biodegradability of municipal sludge were estimated in anaerobic and aerobic biodegradation experiments. Solubilization increased with ozone dosage up to 0.5 g/g-SS and decreased at higher dosages. In both anaerobic and aerobic biodegradation experiments, ozonated sludge at 0.1 g $\text{O}_3\text{/g-SS}$ showed about 2–3 times

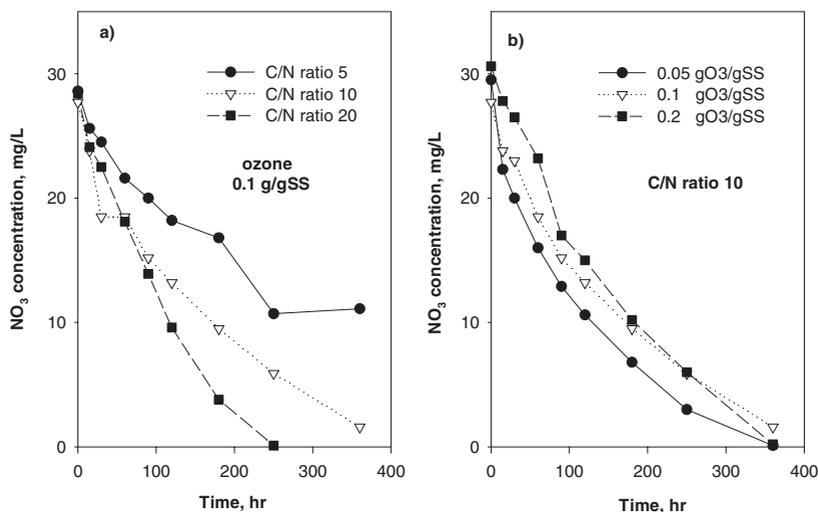


Figure 4 The progress of denitrification using ozonated sludge as a carbon source: a) at varying C/N ratio, b) at varying ozone dosages with C/N ratio fixed

greater biodegradation compared to the raw sludge. In anaerobic experiments, biodegradation increased with ozone dosage up to 0.2 gO₃/g-SS. Further increase of ozone treatment did not improve the biodegradation. In the aerobic condition, about 77% of the ozonated sludge at 0.1 gO₃/g-SS could be biodegraded after 15 days and is compared with 36% degradation of the untreated sludge. The biodegradation of the ozonated sludge mostly occurred within 5 days while the raw sludge was steadily biodegraded for more than 15 days, indicating the conversion of sludge into readily degradable substrate by ozone treatment. The fact that the extent of biodegradation enhancement by ozone treatment is much higher than the magnitude of solubilization suggests that even the biodegradability of the residual solids after ozone treatment is greater than the untreated sludge. The biodegradation enhancement of ozonated sludge was also confirmed in batch denitrification experiments.

Based on the observations, it can be concluded that ozone treatment of sludge combined with the biodegradation process can greatly reduce the amount of sludge production. Further study will be necessary to compare ozone treatment of sludge with other mechanical and biological pretreatments in terms of biodegradability enhancement.

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