Process performance and change in sludge characteristics during anaerobic digestion of sewage sludge with ozonation

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Abstract A new process configuration combining anaerobic digestion with ozonation, and operated at long SRT, was studied with the objective of on-site reduction in sludge quantity and improving biogas recovery. The process performance with respect to solid reduction efficiency and other important process parameters like accumulation of inorganic solids, changes in sludge viscosity and dewatering characteristics were evaluated from the data of long term pilot scale continuous experiments conducted using a mixture of primary and secondary municipal sewage sludge. Due to sludge ozonation and long SRT, high VSS degradation efficiency of approximately 80% was achieved at a reactor solid concentration of 6.5%. A high fraction of inorganic solid (>50%) consisting mainly of acid insoluble and iron compounds was found to accumulate in the reactor. The high inorganic content accumulated in the digested sludge did not, however, contribute to the observed increase in sludge viscosity at high solid concentration. The sludge viscosity was largely found to depend on the organic solid concentration rather than the total solid content. Moreover, higher inorganic content in the digested sludge resulted in better sludge dewaterability. For a quick assessment of the economic feasibility of the new process, an economic index based on the unit cost of digested sludge disposal to unit electric cost is proposed.

Keywords Anaerobic digestion; dewatering; inorganic; ozone; pretreatment; sludge hydrolysis; solubilization; viscosity

Introduction

The option of on-site reduction in sludge quantity presents advantages in terms of downsizing the down-stream requirements for sludge handling, transportation and disposal. The option also presents opportunities for complete treatment of pollution loads at a single site, thus opening a new frontier for overall optimization of the complete treatment process. On-site reduction in sludge production from treatment plants can be achieved either during wastewater (Yasui and Shibata, 1994; Rensink and Rulkens, 1997) or sludge treatment processes. Among the solid treatment processes, anaerobic digestion is one of the most important processes for solid reduction and stabilization. However, the solid reduction during anaerobic digestion is limited due to the rate-limiting step of solid hydrolysis (Eastman and Ferguson, 1981). In an effort to improve sludge hydrolysis, many studies have been performed utilizing different methods of sludge pretreatment. References can be made to pretreatment methods that use thermal, thermo-chemical and mechanical disintegration (Haug *et al*., 1978; Kopp *et al*., 1997; Choi *et al*., 1997), nevertheless, from a practical and operational point of view there still remains a need for new effective pretreatment methods. Sludge ozonation was considered as a new option for sludge pretreatment. The oxidative ozone pretreatment was considered to result in more effective treatment as it not only hydrolyzes the sludge solids but also improves solid biodegradability. The process of sludge ozonation has been incorporated in "modified sludge reduction activated sludge

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process", which has found many practical applications in Japan and thus seems promising (Yasui *et al.*, 1996). To further improve upon the merits of sludge ozonation for sludge reduction, the option of combining sludge ozonation and anaerobic digestion is attractive.

Anaerobic digestion with ozonation has been studied using laboratory batch experiments (Weemaes *et al.*, 2000) and laboratory continuous experiments with different process configurations (Goel *et al.*, 2003a, 2003b). The volatile solid degradation efficiencies of over 80% were estimated for closed loop configuration with high SRT (Goel *et al.*, 2003b) using synthetic sludge. It is however desired to assess the process using sewage sludge and also to collect relevant data for digested sludge characteristics. In the process configurations aiming at improved digestion efficiency, it is expected that characteristically different digested sludge will result due to accumulation of a high fraction of inorganic solids. This high fraction of inorganic solids is expected to change the rheological and dewatering characteristics of sludge. While the change in rheological property will affect the mixing, ozone transfer and pumping requirements, changes in dewatering characteristics are considered to be important for assessing the process impact on down stream solid handling facilities. Pilot scale experiments at a full-scale sewage treatment plant using a mixture of primary and secondary municipal sewage sludge were conducted to 1) assess and compare the digestion efficiency of municipal sewage sludge between the ozonation and conventional process 2) characterize the anaerobically digested sludge with respect to the inorganic composition, viscosity and dewatering characteristics and 3) to develop an economic index (EI) for quick assessment of process applicability.

Experimental methods

Process configurations

Three experimental trains, each with an anaerobic reactor of effective volume 1.1 m^3, were used in the present study. The experimental process configuration for each train is as shown in Figure 1. Experimental train 1 was operated in chemostat mode for collecting background control data. Train 2 was operated with high SRT but without any ozone treatment on the digested sludge.

In Train 3, a part of the digested sludge was withdrawn, ozonated and returned back to the reactor. A comparison of the performance results of Train 1 and Train 3 provided a

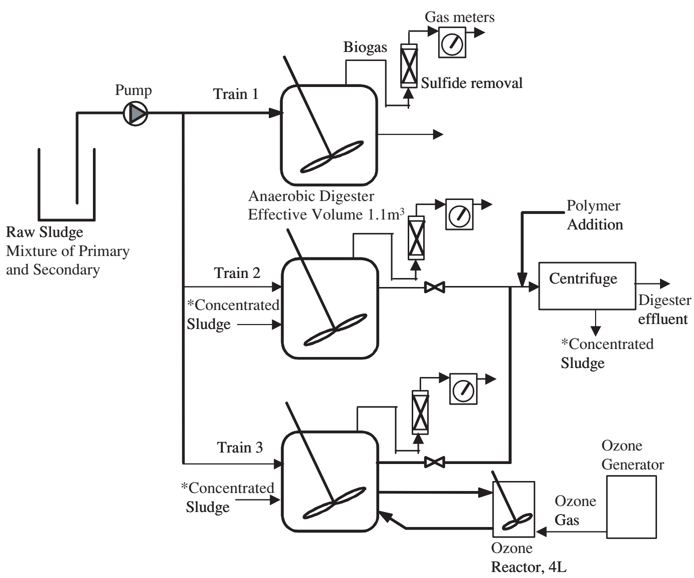


Figure 1 Process configuration for different experimental trains

means to assess the improvement over the conventional process, while comparison of Trains 2 and 3 was used to clearly demonstrate the effectiveness of ozonation by eliminating the effect of solid accumulation.

Sludge characteristics and operational conditions

The mixed municipal sewage sludge used in the pilot scale experiments consisted of primary and secondary sludge in the ratio of 1:3.5 (w/w). The activated sludge plant producing the secondary sludge was operated at a F/M ratio ranging between 0.24–0.32 kgBOD/kgSS·d. The SRT of the plant was about 6–7days. The characteristics of primary, secondary and mixed sludge are as shown in Table 1. The three large contributors to ash (inorganic solid) were identified to be acid insoluble fraction (presumably silica, 26–43%), iron (21–23%) and phosphorus (14–27%). The source of iron was identified to be from the ground water which is used and discharged by industries. In addition to this, iron was also contributed from the runoff of the ground water used for snow melting during winter. This large percentage of iron reduced the TVS/TS ratio of mixed sludge to 0.76. The operational details of three experimental digesters are as summarized in Table 2. For Train 3, a part of the sludge was withdrawn (~70 l/d) and returned back to the reactor after ozonation. The ozonation of digested sludge was performed in a completely mixed reactor. An average ozone dose of 0.026 kgO_3/kgTVS was applied during ozonation. The pH in the anaerobic digester was observed to be between 7.0–7.5.

Analytical methods

Total solids (TS), Total volatile solids (TVS) were performed as described in Goel *et al.* (2003a). The ozone gas measurements were done using a UV detector based ozone meter (Nippon ozone Co.). The inorganic solid analysis was conducted by using sequential steps of acid solubilization and heat drying using 50% HCl and conc. HNO_3. The heat dried residue from the last step was solubilized in 50% HCl and after filtration through 0.45 μm filter, inorganic content was analyzed using ICP. Dewaterability studies were performed by compressing polymer-coagulated sludge at a pressure of 1.0 kg/cm^2 for 60 seconds and measuring the water content of the dewatered cake. An organic cationic polymer with doses of 1.0% dry solid basis was used in the experiments. Viscosity measurements were made using the Brookfield-type rotational viscometer. The viscosity measurement was performed using No. 2 or 3 spindle in accordance with the sample viscosity at rotation rates of 3, 6, 12, 30 and 60 rpm. Sample sludge was put in a 500 ml beaker and viscosity measurements were performed as soon as possible. Initial values of the viscosity were used for each sample to eliminate the effect of thixotropic behavior of the sludge.

Table 1 Inorganic and Organic characteristics of sewage sludge (Average of 5 data sets)

Parameter	Unit	Primary sludge	Activated sludge	Mixed sludge
TS	(mg/L)	30,700	44,000	39,600
TVS	(mg/L)	25,000	32,700	30,100
TVS/TS	(–)	0.81	0.74	0.76
Acid insoluble fraction as SiO_2	(mg/L)	2,320 (43.8)	3,060 (26.3)	2,810 (29.6)
Fe_2O_3	(mg/L)	1112 (21.0)	2689 (23.1)	2159 (22.7)
P_2O_5	(mg/L)	733 (13.8)	3184 (27.4)	2359 (24.8)
CaO	(mg/L)	414 (7.8)	907(7.8)	743 (7.8)
MgO	(mg/L)	144(2.7)	512 (4.4)	390 (4.1)
Al_2O_3	(mg/L)	557 (10.5)	1058 (9.1)	890 (9.4)
MnO	(mg/L)	9 (0.2)	212 (1.8)	145 (1.5)

The values in parentheses are the values of % fraction as ash

Table 2 Operational details for experimental trains

Train no.	Amount of feed sludge (L/d)	Digested Sludge for post-ozonation Amount (L/d)	Ozone dose (gO_3/gTVS)	SRT[1] (d)	Average volumetric loading[3] (kgTVS/m^3.d)
1	20	0	0.0	58	0.51
2	20	0	0.0	144	0.51
3	20	70	0.03	275	0.51

[1]SRT is calculated as (Solid mass in reactor)/(daily solid mass withdrawn)

Results

Solid accumulation and solid degradation efficiency

The trend of TS concentration in the reactors during the experimental period of 6 months is as shown in Figure 2. For Train 3, a continuous increase in TS concentration was observed for the first 4 months. After this, the TS concentration stabilized at about 6.5% (65g/l). The TS concentration in reactors of Train 1 and Train 2 were measured to be about 2.3% and 4.5% respectively. TVS, TIS (Total Inorganic Solid) and TS balance were prepared for the final three months of the experimental period and are as shown in Table 3.

The organic solid digestion efficiency in experimental Trains 1, 2 and 3 was calculated to be 52%, 59% and 81% respectively. On the other hand, the TS removal efficiency for the three trains was estimated to be 39%, 43% and 61% respectively. As the accumulated volatile solids in Train 2 and Train 3 (Table 3) were almost in a similar range, it is suggested that the increase in solids degradation efficiency in Train 3 was due to the effect of ozonation of digested sludge. Even though the observed organic removal efficiencies were almost similar to that previously observed during laboratory scale experiments (Goel *et al.*, 2003b), the concentration of accumulated solid was different. In the case of pilot scale experiments, the total solids accumulated in the reactor were about 6.5% (65 g/l) as compared to 3% (30 g/l) in the case of laboratory scale experiments (Goel *et al.*, 2003b). This difference in the concentration of accumulated solid is thought to be mainly due to the differences in the TVS/TS ratio of the feed sludges in the two cases.

Characterization of accumulated inorganic solids

Characteristics of the digested sludge from the three reactors are as shown in Table 4. The TVS/TS ratio of the digested sludge from Train 3 was the lowest (0.47) corroborating the

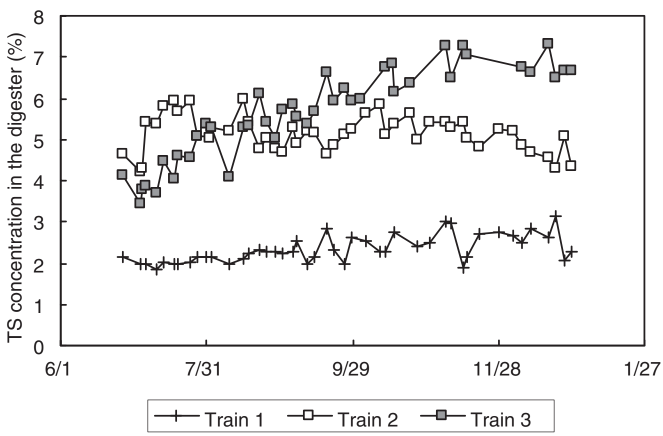


Figure 2 Trend of total solid accumulation in the experimental trains

higher organic degradation efficiency in this train. Although the mass of accumulated inorganic in the digesters was different, the percentage distribution of measured concentration of ash components in digested sludge did not reveal any significant differences. Based on the measured total concentration of inorganic species in sludge, Visual MINTEQ version 2.12 (KTH, 2002) was used to predict expected precipitated/soluble components. The analysis results suggested precipitation of over 98% of the inorganic and the major expected precipitants of iron were predicted to be vivianite ($Fe_3(PO_4)_2 8H_2O$) and pyrite (Fe_2S). A small amount of magnesium and phosphorus were suggested to be present in the soluble phase. The low measured soluble concentration in the digester effluent (Data not shown) matched reasonably well with the predictions of MINTEQ.

MINTEQ analysis suggested that in the presence of excess iron, complete precipitation of phosphorus could be expected. When iron species was excluded in the analysis, almost 30% of the phosphorus in the feed was suggested to be present in the digester effluent. Based on this analysis, it became clear that the distribution of inorganic species and their interaction can affect the inorganic accumulation pattern in anaerobic digestion.

Sludge viscosity

Increase in sludge viscosity at higher TS concentration is a matter of concern as it can affect the operations of reactor mixing, ozone transfer, sludge pumping and dewatering. The experimental results suggested non-Newtonian pseudo-plastic behavior of the digested sludge. The expression $\tau = k\,(dv/dy)^n$ was used for experimental data fitting. The calculated values of "k" and "n" at different TS concentrations are as expressed in Figure 3a. While the values of "n" were found to be almost independent of the sludge type and TS concentration, the value of "k" depended on both. The calculated relationships between "k" and "X"(TS

Table 3 TVS, TIS, TS balance in anaerobic digesters

	TVS mass balance			TIS mass balance			TS mass balance		
	Train 1	Train2	Train 3	Train 1	Train 2	Train3	Train1	Train2	Train 3
Solid mass fed to digester	61.2	62.7	60.5	19.3	20.2	19.4	80.5	82.9	79.9
Solid mass increase in digester	–0.4 (–1%)	0.0 (0%)	0.6 (1%)	1.0 (5%)	0.1 (1%)	10.1 (52%)	0.6 (1%)	0.1 (0%)	10.7 (13%)
Solid mass withdrawn as excess solid	29.9 (49%)	22.6 (36%)	4.4 (7%)	18.9 (98%)	19.5 (96%)	7.0 (36%)	48.8 (61%)	42.1 (51%)	11.4 (14%)
Solid mass in the effluent	_	3.3 (5%)	6.6 (11%)	_	1.6 (8%)	2.3 (12%)	_	4.9 (6%)	8.8 (11%)
Solid amount removed	31.7 (52%)	36.8 (59%)	49.0 (81%)	–0.6 (–3%)	–1.0 (–5%)	–0.0 (–0%)	311 (39%)	35.8 (43%)	49.0 (61%)

Table 4 Characteristics of digested sludge

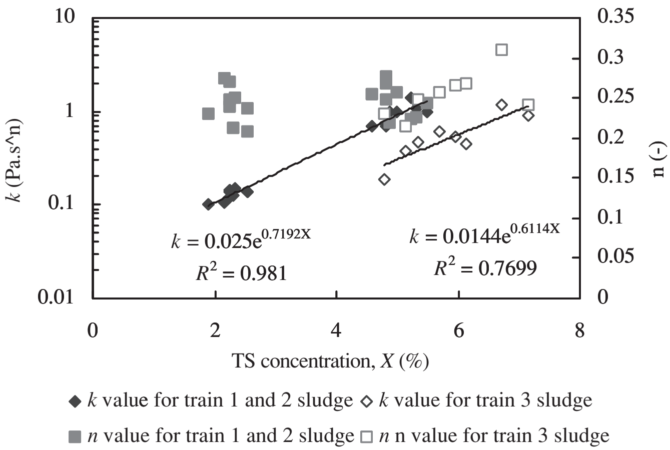
Parameter	Unit	Train 1	Train 2	Train 3
TS	(mg/L)	27,500	52,700	65,200
TVS	(mg/L)	16,300	27,800	30,400
TVS/TS	(–)	0.59	0.53	0.47
Acid insoluble fraction as SiO_2	(mg/L)	2810 (32.6)	8,320 (33.0)	11,450 (32.8)
Fe_2O_3	(mg/L)	1902 (22.0)	6321 (25.1)	8738 (25.0)
P_2O_5	(mg/L)	1981 (22.9)	5130 (20.4)	7054 (20.2)
CaO	(mg/L)	693 (8.0)	1848 (7.3)	2618 (7.5)
MgO	(mg/L)	315 (3.6)	1071 (4.3)	1495 (4.3)
Al_2O_3	(mg/L)	819 (9.5)	2116 (8.4)	3022 (8.7)
MnO	(mg/L)	136(1.6)	373 (1.5)	521 (1.5)

The values in parentheses are the values of % fraction as ash concentration) for different sludges are as shown in Figure 3a. For a comparative evaluation of viscosity change, using viscosity values at 30 rpm, a relationship between TS concentration and viscosity of sludge from different reactor configurations was plotted in Figure 3b. The viscosity of anaerobically digested sludge from the ozonation train was found to be lower than that of digested sludge from the control run at the same TS concentration. An increase in TS concentration from 2.7% (conventional process) to 6.3% (ozonation process) resulted in about 2.5 fold increase in viscosity. When the viscosity data was plotted against the TVS concentration (Figure 4), it was found that at the same TVS concentration the viscosity of the digested sludge from the ozonation train is only slightly lower than the viscosity of the digested sludge from the conventional process. Thus, it seems that sludge viscosity directly depends on the TVS concentration rather than the TS concentration. The slight reduction in the viscosity for the ozonation train at the same TVS concentration is thought to be due to the positive effect of viscosity reduction after ozonation. At a TS concentration 4.78%, the viscosity was observed to decrease from a value of 500 mPa·s to 300 mPa·s after ozonation.

Sludge dewatering characteristics

Based on the results of more than 15 dewatering tests on digested sludge from the three trains, it was established that water content of the dewatered cake of anaerobically digested sludge from train 3 with ozonation was about 10% lower than that of the control sludge under similar dewatering conditions. The water content data when plotted with the TVS/TS

(a)



(b)

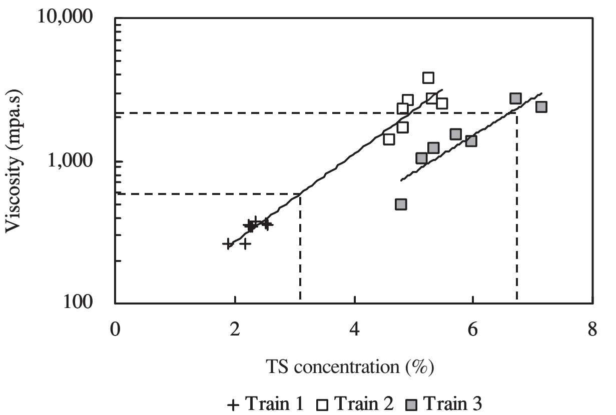


Figure 3 (a) Non-Newtonian viscosity parameters; (b) change in viscosity with TVS concentration

ratio (Figure 5) revealed a direct correlation between the water content and inorganic content of sludge.

Discussion

Based on the result of both the laboratory scale (Goel *et al.*, 2003b) and pilot scale experiment, the new process scheme combining anaerobic digestion with ozonation to achieve higher organic solid removal efficiency is considered to be technically and practically feasible. The process could be operated at high TS concentration of 6.5% without any operational problems. The changes in the sludge properties with respect to viscosity and dewatering characteristics showed an encouraging trend for the applicability of this process. Although the viscosity of digested sludge increased with the increased TS concentration, due to negligible contribution of inorganic solid to viscosity and the positive effect of ozonation in viscosity reduction, the values were lower than could be expected for conventional digested sludge at the same solid concentration. The experimental observation that the sludge ozonation reduces the sludge viscosity probably results from the fact that the floc structure during ozonation is broken (Yasui *et al.*, 1994), reducing the interfloc resistance. The observed improvement in dewatering characteristics of the anaerobic

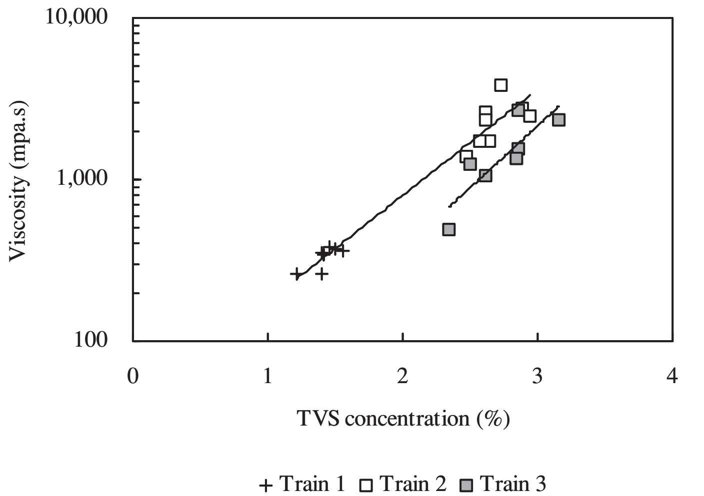


Figure 4 Change in viscosity with TVS concentration

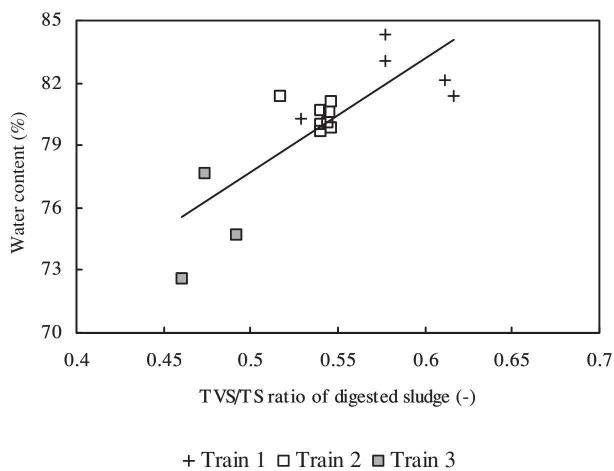


Figure 5 Relationship between water content in dewatered sludge and TVS/TS

Table 5 Solid disposal and energy cost for different alternatives

Component	Train 1	Train 2	Train 3
1. Solid balance			
a. Total solid fed (kgDS/d)	100	100	100
b. Total solid after anaerobic digestion (kgDS/d)	61	57	39
c. Volume of wet sludge cake(m^3/d)	244	211	130
d. Cost of disposal (Euro/d)	–244*Us[1]	–211*Us	–130*Us
2. Energy balance			
e. Energy produced (kWh/d)	43.5	49.3	67.7
f. Energy input during ozonation (kWh/d)	–0.0	–0.0	–50.0
g. Other energy input (dewatering, pumping etc.) (kWh/d)	–0.0	–25.0	–25.0
h. Net energy (kWh/d)	43.3	39.3	–7.3
i. Energy cost (Euro/day)	43.3*Ue[2]	39.3*Ue	–7.3*Ue

[1] U_s is the unit solid disposal cost (Euro/kg wet cake)
[2] U_e is the unit energy cost (Euro/kWh)

digested sludge at lower TVS/TS ratio was found to be consistent with the negative correlation of cake dry matter and TVS/TS reported by Mikkelsen and Keiding (2002).

As the sludge reduction process using sludge treatment invariably needs additional energy input for sludge hydrolysis, the economic benefits of these options shall mainly depend on the relative cost of additional energy input and corresponding decrease in sludge disposal cost. Considering this, an economy index defined as the ratio of energy cost (Euro/kWh) to sludge disposal cost (Euro/kg wet sludge) is defined to make a quick identification of the areas where the ozonation process could be economically applied. For the processes under study, the calculations for sludge disposal cost and the required energy input are presented in Table 5.

From Table 5, for train 3 to be operationally as cost effective as train 1, expression in the following equation shall hold:

$$-130 \bullet U_s - 7.3 \bullet U_e \geq -244 \bullet U_s + 43.3 \bullet U_e$$
$$U_s / U_e \geq 0.44$$

So, for the value of economic index (U_s/U_e) equal to 0.44 kWh/kg wet cake, the operational cost of the ozonation process shall break-even with that of the conventional process. However, for situations where the actual cost of sludge disposal is much higher than the electricity cost, the process shall be able to provide capital recovery. Sludge disposal cost normally will depend on the choice of downstream processes (drying, incineration, co-incineration, land application) and unit cost of ultimate disposal option can be used for assessment. The current value of the economy index for Japan can be estimated to be approximately 1.5 (unit energy cost 0.10 Euro/kWh and unit sludge disposal cost for land-filling 0.15 Euro/kg wet cake), making it beneficial for Japanese conditions.

Conclusions

A new process scheme combining anaerobic digestion with sludge ozonation was studied through continuous pilot scale experiments using municipal sewage sludge. The process resulted in organic solid degradation efficiency of 81%, while total solid degradation efficiency of 61% was estimated. The accumulation of inorganic solids increased the TS concentration in the reactor to 6.5%. Adequate planning for handling the inorganic solid accumulation in the reactor is considered to be vital for maintaining high organic degradation efficiencies. Although the increased solid concentration resulted in an increase in digested sludge viscosity, the increase did not result in any operational problems. The dewatering characteristics of the digested sludge improved significantly and are thought to result in significant reduction in the down-stream disposal cost of excess sludge. The theoretical minimum value of the economic index based on the ratio of unit energy cost and sludge disposal cost was estimated to be 0.44 and it is considered that the process could be applicable to situations where actual value of this ratio is higher than the calculated minimum.

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