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ENHANCEMENT OF ANAEROBIC DIGESTION OF WASTE ACTIVATED SLUDGE BY ALKALINE SOLUBILIZATION

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Abstract

The performance of an anaerobic digestion fed with waste activated sludge (WAS) pretreated with NaOH was examined. The sludge was periodically collected from a municipal wastewater-treatment plant. The laboratory work was run in four 1-l semi-continuous anaerobic digestion reactors. Reactor A was fed with untreated WAS at 1% total solids (TS). The other three reactors, B, C and D, were respectively fed with WAS (1% TS) pretreated with 20 meq/l NaOH, WAS (1% TS) pretreated with 40 meq/l NaOH, and WAS (2% TS) pretreated with 20 meq/l NaOH. The reactors were operated at 35°C at four hydraulic retention times — 20, 13, 10 and 7.5 days. The performances of reactors B, C and D, in terms of chemical oxygen demand (COD), volatile solids (VS) removal, and gas production, were superior to that of reactor A. At a retention time of 10 days, the COD removals of reactors A, B, C and D were 38, 46, 51 and 52%, respectively. The gas productions of reactors B, C and D were, respectively, increased by 33, 30 and 163% over that of reactor A. The sludge dewaterability was examined by capillary suction time (CST). The dewaterability of digested sludge was improved in reactors B, C and D. Capillary suction of digested sludges gave times in the range 148–389 s, compared with 309–735 s for undigested sludges.

Key words: Waste activated sludge, anaerobic digestion, hydrolysis, chemical pretreatment, dewaterability.

INTRODUCTION

Anaerobic digestion is a common process for treatment of sludge. Compared with other processes, its advantages are less energy required, a better stabilized product, and usable gas. However, several limitations for anaerobic digestion include the slow reaction, the sensitivity to shock loads and toxic materials, and its complicated operation. One factor influencing efficiency of anaerobic digestion is access to cell-bound organic matter. Digestion of waste activated sludge (WAS), in which most substrate is enclosed within cell membranes, requires release of the cell-bound substrate before it can be utilized by viable anaerobes. Thermal pretreatment (Haug *et al.*, 1983; Hiraoka *et al.*, 1984; Pavlostathis and Gossett, 1988; Li and Noike, 1992), thermochemical pretreatment (Stuckey and McCarty, 1978; Gossett *et al.*, 1982; Samson and Leduy, 1983; Pavlostathis and Gossett, 1985; Sawayama *et al.*, 1995), and alkaline solubilization (Rajan *et al.*, 1989; Ray *et al.*, 1990; Alleman *et al.*, 1994; Woodard and Wukasch, 1994) have been investigated as methods to improve the digestibility of sludge and to increase production of methane. While thermal or thermochemical pretreatment of sludge results in an increase in biodegradability, the thermal process consumes a substantial amount of energy in addition to chemical consumption. The chemical pretreatment is more efficient and cost-effective when carried out at ambient temperature.

Sodium hydroxide at relatively low dosage levels is effective in solubilizing municipal WAS at ambient temperature. Alleman *et al.* (1994) demonstrated that alkaline treatment is effective in solubilizing munitions-grade nitrocellulose into soluble organic carbon forms. Woodard and Wukasch (1994) conducted a laboratory-scale study in the development of a hydrolysis/thickening/filtration technology to improve the efficiency of solid digestion of WAS generated by the biological treatment of a pharmaceutical wastewater. Substantial solubilization (50–60%) of activated sludge suspended solids was achieved at room temperature, with a relatively short hydrolysis time. Rajan *et al.* (1989) showed that low-level alkaline pretreatment of waste activated sludge with NaOH can increase levels of solubilization up to 46%. Furthermore, Ray *et al.* (1990) examined the ability of the single-stage high-rate anaerobic digester to stabilize the alkaline-treated WAS with digesters operated at 35°C and

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five different hydraulic retention times, 20, 13, 10, 7.5 and 5 days. Pretreatment with sodium hydroxide improved the volatile solid reduction by 25–35% and increased gas production by 29–112% over the control sludge samples undergoing no alkaline treatment.

The overall objective of this study was to examine the ability of the single-stage high-rate anaerobic digester to stabilize WAS following alkaline chemical pretreatment. Organic removal, gas production, and sludge dewaterability were examined.

Table 1. Changes in organic loading rate and HRT during the experimental period

Phase	Time (weeks)	HRT[a] (days)	OLR[b] (mg COD/day)
I. Collecting database	17	20	595
II. Assessing HRT effects			
a	14	20	595
b	6	13	896
c	6	10	1248
d	3	7.5	2403

[a]HRT, hydraulic retention time.
[b]Organic loading rate.

METHODS

Sludge collection and preparation

The waste activated sludge (WAS) samples were collected weekly throughout the year from the final clarifier of the Min-Shen Sewage Plant, at which inflows and operating parameters fluctuated. This plant uses a conventional activated sludge process, consisting of primary clarification, aeration, and final clarification. The average flow is 13 500 M^3/day, and the sludge retention time of the activated sludge process is 3 days with the food to microorganisms ratio (F/M) of 0.77 kg BOD/kg MLSS/day (BOD = biochemical oxygen demand; MLSS = mixed liquid suspended solid). Collecting samples at different times reflects the variability of feed sludge characteristics. However, after collection, the sludge was adjusted to give a concentration of 10 000 mg/l (1%) total solids (TS) for consistent experiment.

Sludge solubilization

After preparation, the sludge (10 000 mg/l TS) was divided into four portions. The first portion, the control sludge, was returned to the refrigerator for storage. The second and third portions were solubilized by adding sodium hydroxide (NaOH) at 20 and 40 meq/l, respectively. The fourth portion was adjusted to give a final sludge concentration of 2% TS, and then solubilized by adding NaOH at 20 meq/l. The solubilizations were carried out in 1000 ml batch reactors at ambient temperature (25°C) under anoxic conditions for 24 h. A stirring magnet bar was used to ensure sufficient mixing to prevent the sludge from settling and disperse the alkali added. After solubilization, the pretreated sludges were returned to the refrigerator until use.

Experimental apparatus

Four 1-l laboratory-scale single-stage high-rate digesters were employed. Each reactor was a 1000 ml reagent bottle. The top was efficiently sealed air-tight by a rubber stopper. Each reactor was mounted on a magnetic stirrer. A Teflon-coated stirring magnet was used and the stirring speed was maintained so that there was sufficient mixing to keep the sludge from settling and to evenly distribute the sludge fed. The reactors were maintained at 35°C in an incubator. The gas produced from each reactor was collected in a measuring tube over saturated salt solution with 5% H_2SO_4. Sludge was introduced into the four reactors once per day from a glass graduated cylinder, following which the effluent sludge was withdrawn by gravity from each reactor.

Experimental plan

Changes in hydraulic retention time (HRT) and corresponding organic loading rates during the entire experimental period are shown in Table 1. The experimental plan for the project consisted of two phases. Phase I of the project lasted 4 months. This phase included the development of a balanced micro-organism population in the reactors and establishment of a stabilized operation. The experimental procedures were also refined during this period. Initially, each reactor was filled with an anaerobic seed sludge. All four reactors were then fed an untreated sludge (1% TS) and operated at a 20-day HRT and 35°C to allow the biological processes to stabilize with respect to volatile solids (VS) and chemical oxygen demand (COD) removals and gas production rates.

Phase II of the project lasted 7 months. This phase was designed to determine the effect of HRT on the performance of the reactors. At the beginning of this phase, reactor B received the sludge of 1% TS solubilized with NaOH at 20 meq/l, reactor C received the sludge of 1% TS solubilized with NaOH at 40 meq/l, and reactor D received the sludge of 2% TS solubilized with NaOH at 20 meq/l. The feed sludge for reactor A was left unchanged as a control. All four reactors were fed these same sludges for the duration of the project. The characteristics of the feed sludges are presented in Table 2. The temperature was also maintained at 35°C during this phase. After the reactors had reached steady state, i.e., their VS and COD removal rates and gas production rates remained essentially constant with time, data collection began. After sufficient data

Table 2. Average[a] characteristics of feed sludges

Reactor	A	B	C	D
Pretreated with NaOH	0 meq/l	20 meq/l	40 meq/l	20 meq/l
Total solids (mg/l)	10150±410	10530±338	12484±213	18069±1376
Volatile solids (mg/l)	7643±118	7225±222	8588±128	13242±1051
Total COD (mg/l)	11905±238	11942±109	12484±213	21932±1518
Soluble COD (mg/l)	251±37	2962±277	4783±225	3368±983
pH	6.86±0.13	8.07±0.87	12.26±0.10	7.78±0.18
Alkalinity (mg/l)	512±44	1705±269	2714±352	1883±193
Dewaterability, CST (s)	28.15±9.86	363.15±59.63	662.75±99.73	570.40±50.76

[a]Averages of four analyses.

were obtained at the 20-day HRT, the loading rate was increased to the 13-day HRT. After the organic removal rates and gas production had stabilized, data were again collected. This process was repeated for the 10- and 7.5-day HRTs.

Experimental analyses

The reactor pH, temperature, and gas production were monitored daily. The effluent total and volatile solids (TS and VS), and total and soluble COD were monitored at least every 2 days. Other parameters that were monitored less frequently included organic acids, alkalinity, and gas composition. Most experimental analyses followed the procedure recommended in Standard Methods (1992) (18th edition). The sludge dewaterability was examined by capillary suction time (CST). The instrument for this purpose was a Capillary Suction Time Filterability Test (Model 200, Triton Electronics Ltd, Gt. Dunmon, Essex, UK). This device consists of a timer, a sludge holder (18-mm cylinder), and blotter paper (Whatman No. 17, size 6.0 cm × 9.8 cm).

RESULTS AND DISCUSSION

The major parameters measured were influent and effluent strength, using both solids (TS and VS) and COD as indicators, influent and effluent soluble COD, and gas production. Results of tests of anaerobic digestion of sludge pretreated with sodium hydroxide are summarized in Table 3, which compares the performance of the digesters.

Sludge characteristics

As organic material in pretreated sludge was hydrolysed, the soluble fraction of feed sludge was greater in reactors B, C and D than in reactor A. The soluble fraction (represented by soluble COD) of feed sludge into reactor A was in the range 2–10%, into reactor B 22–27%, into reactor C 36–40%, and into reactor D 10–20%. As bacteria utilized the hydrolytic products and as anaerobic digestion proceeded in reactors B, C and D, the digested sludges [Fig. 2(b)] contained a smaller soluble fraction than the feed sludges [Fig. 2(a)]. The soluble fraction of digested sludge from reactor A was 5–8%, from reactor B 6–12%, from reactor C

Table 3. Summary of digester performances

Digesters	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
HRT (days)	20	20	20	20	13	13	13	13	10	10	10	10	7.5	7.5	7.5	7.5
VS removal (%)	35	36	42	45	35	37	39	24	28	31	31	36	19	26	33	45
COD removal (%)	39	47	47	47	38	46	47	37	38	46	51	52	21	39	37	47
Gas composition																
CH_4 (%)	71	76	84	74	72	76	86	75	73	77	84	74	74	77	86	74
CO_2 (%)	12	11	2	15	16	14	2	18	14	9	3	18	12	12	4	19
Gas production rate (l/m^3/day)	83	113	113	164	123	150	146	282	158	210	205	416	133	258	247	514
CH_4 production rate (l/m^3/day)	59	86	86	121	89	114	126	212	115	162	172	308	98	199	212	380
CH_4 production/VS removed (l gas/kg VS)	437	688	531	432	422	558	495	927	544	726	642	600	506	753	549	449
CH_4 production/COD removed (l gas/kg COD)	253	307	332	247	261	264	272	370	251	297	275	255	300	325	343	264
Total solids (mg/l)	7485	7560	8555	11690	7110	7460	9005	12785	7320	7647	9965	13585	8340	8460	10000	11860
Volatile solids (mg/l)	4930	4485	4945	6745	5080	4535	5221	9335	5415	4980	5850	8953	6140	5540	5880	7860
Total COD (mg/l)	7249	6278	6510	11184	7304	6485	6649	12830	7646	6459	6128	11228	9312	7311	8012	12356
Soluble COD (mg/l)	387	390	648	544	530	740	1154	1408	422	798	1290	1249	745	788	1724	1100
pH	7.07	7.41	7.84	7.41	7.18	7.48	7.96	7.45	7.09	7.44	7.85	7.45	7.11	7.41	7.78	7.55
Alkalinity (mg/l)	1440	2332	2976	3080	1699	2976	3870	3635	1427	3100	3848	4317	1395	2776	3683	3844
Dewaterability, CST (s)	34	148	209	263	55	214	274	389	27	160	227	299	38	167	254	291

10–22%, and from reactor D 5–11%. The soluble fraction of digested sludge in reactor A was slightly greater than that of the feed sludge, as the hydrolysed products were produced slowly by enzymes; hydrolysis is the limiting step of anaerobic digestion of WAS, but the degradable organic material of hydrolysed products was utilized quickly, and the refractory material from hydrolysed products accumulated gradually.

Organic removal

The reactors had varied rates of removal of substrate in terms of COD and VS. The reactors fed with pretreated sludge had substrate removed more rapidly. As for COD removal, reactor A was in the range 21–39%, reactor B 39–47%, reactor C 37–51% and reactor D 37–52%. Pretreatment offers little advantage with prolonged retention if the objective is to obtain greater volumetric removal of organics. However, if greater stabilization is required, solubilization increases the removal. In contrast, at the shorter periods of retention, solubilization is required to attain a satisfactory organic stabilization. At 7.5-day HRT, the pretreatment resulted in at least twice the organic stabilization measured as removal of COD.

The fractional improvement of digester performance is shown in Table 4. Improvement in VS removal of reactor C attained 72% over reactor A at 7.5 days of retention. For the same period, COD removal improved 76%. Comparison of reactors B, C and D showed that organic removal increased as the concentration of either NaOH or sludge solids increased. The performance of reactor D was better than that of reactor C; e.g., increasing the concentration of sludge solids proved more effective for organic removal than increasing the concentration of NaOH. Solubilization by thermal pretreatment increased COD removals by 18–22% over sludge that lacked thermal treatment (Haug *et al.*, 1983). The digesters fed with autoclaved sludge showed 30–56% greater organic destruction than those fed with intact activated sludge (Pavlostathis and Gossett, 1988). Pretreatment with sodium hydroxide improved VS reduction in the range 25–35% over no pretreatment (Ray *et al.*, 1990). By thermochemical treatment, a maximum of 85% organics was converted to methane compared with approx. 53% in non-treated controls (Stuckey and McCarty, 1978).

Gas production and methane yield

The average content of methane in gas was 72%, 76%, 85%, and 74% for reactors A, B, C and D, respectively. The reactor fed with pretreated sludge had greater methane, and methane increased as the concentration of NaOH increased. The rate of gas production also increased when feed sludge was pretreated with NaOH; the reason was that pretreated sludge hydrolysed much organic material into solution, and the anaerobic digestion process used it immediately; hence reactors B and C had greater rates of gas production than reactor A. The influent substrate concentration of reactor D was the greatest and caused a greater rate of gas production than of the others. The fractional increase in gas production of reactors B, C and D was 22–94%, 19–86%, and 106–287%, respectively. The fractional increase of methane in reactors B, C and D was 29–102%, 42–116% and 106–287%, respectively. Thermal pretreatment resulted in a 30% increase in production of digestion gas (Hiraoka *et al.*, 1984).

Table 4. Summary of improvements in digester performances

Retention time (days)	Reactor A	Reactor B	Percent[a] increase	Reactor C	Percent[a] increase	Reactor D	Percent[a] increase
			VS removal (%)				
20	35	36	1	42	19	45	29
13	35	37	6	39	11	24	—
10	28	31	10	31	12	36	29
7.5	19	26	37	33	72	45	133
			COD removal (%)				
20	39	47	21	47	20	47	20
13	38	46	23	47	26	37	—
10	38	46	22	51	35	52	38
7.5	21	39	84	37	76	47	123
			Gas production (l/m^3)				
20	83	113	36	113	36	164	98
13	123	150	22	146	19	282	129
10	158	210	33	205	30	416	162
7.5	133	258	94	247	86	514	286

—, Negative value.
[a]Increase, expressed as percentage over reactor A.

Pretreatment with sodium hydroxide increased gas production by between 29 and 112% over the control sludge (Ray *et al.*, 1990).

Reactors B and C had greater fractional increases of methane production than gas production, coinciding with the fact that reactors B and C had greater proportions of methane in the gas (Table 3). The fractional increase of methane and gas production was almost the same for reactor D, which indicated that the main gas composition did not vary much compared with reactor A. All pretreated sludges increased the fraction of gas and methane production as HRT decreased. The methane production per gram of VS destroyed in this project averaged 580 ml per gram of VS; methane production per gram of COD destroyed averaged 290 ml per gram of COD. Literature values for methane gas production vary considerably, but representative values are in the range 490–730 ml methane per gram VS destroyed (Metcalf and Eddy, 1991). For 1 g of COD removed, the theoretical methane produced would be 350 ml at standard temperature and pressure (STP).

pH Values and alkalinity

The pH of the feed sludge varied considerably for the four reactors, as the feed sludges of reactors B, C and D were pretreated with NaOH (Table 2). The pH of the digested sludge of the four reactors was almost the same (Table 3). The pH of all four reactors remained relatively constant for varied HRT, although the feed sludge of reactor C had an extreme pH. The alkalinity of the four reactors of feed and digested sludges varied greatly, increasing as the concentration of NaOH increased. The alkalinities of the feed sludges are shown in Table 2, and of digested sludges in Table 3. Compared with the feed sludge and digested sludge of the four reactors, the alkalinity in all increased during anaerobic digestion.

Effects of digestion on dewaterability

The CSTs for feed sludges and digested sludges of reactors A, B, C and D at different HRT are shown in Table 2 and Table 3. In a previous study, Lin *et al.* (1996) found that CST had a large correlation coefficient of 0.92 with specific resistance filtration (SRF). The correlation between CST and SRF was:

$$SRF\ (s^2/g) = 6.55 \times 10^8\ \mathrm{CST\ (s)} - 1.8 \times 10^9$$

for waste activated sludge collected from the Min-Shen Sewage Plant. Anaerobic digestion alters the distribution of particle size in sludges. When digestion works well, particles of all sizes are destroyed, but there is a preferential removal of particles of small sizes, a consequent loss of specific surface area, and therefore an improvement in dewaterability (Lawler *et al.*, 1986). The dewaterability of digested sludge was improved in reactors B, C and D. The CST values of digested sludges were in the range 148–389 s, whereas undigested sludges were 309–735 s. For reactors B, C and D, the best dewaterability of digested sludge occurred at 20-day HRT. The CST of digested sludge of reactor A was in the range 27–55 s, greater than that of feed sludge. Karr and Keinath (1978) reported that anaerobically digested sludge was more difficult to dewater, measured by CST and specific resistance, than either primary or activated sludge.

CONCLUSION

Four reactors were employed to evaluate the ability of a single-stage high-rate digester to treat waste activated sludge at retention tomes of 20, 13, 10 and 7.5 days at 35°C. Reactor A was fed with untreated WAS (1% TS). The other three reactors B, C and D were respectively fed with WAS (1% TS) pretreated with NaOH (20 meq/l), WAS (1% TS) pretreated with NaOH (40 meq/l), and WAS (2% TS) pretreated with NaOH (20 meq/l). The performances of reactors B, C and D, for COD and VS removal, and gas production were superior to that of reactor A. The dewaterability of digested sludge was improved in reactors B, C and D.

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