Pergamon

Wat. Sci. Tech. Vol. 36, No. 11, pp. 155–162, 1997.

Printed in Great Britain.
0273–1223/97 $17·00 + 0·00

PII: S0273-1223(97)00681-1

ALKALINE AND ULTRASONIC PRETREATMENT OF SLUDGE BEFORE ANAEROBIC DIGESTION

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ABSTRACT

Pretreatment of waste activated sludge (WAS) results in an improved efficiency of the subsequent anaerobic biotransformation of the organic matter to volatile fatty acids. The pretreatment process has been carried out using alkaline treatment, ultrasonic treatment (20 KHz, 120 W) and different combination of these two methods: alkaline followed by ultrasonic, as well as the combining method in which ultrasonic treatment is applied to WAS samples dosed with alkaline. The hydrolysis efficiency was evaluated based on the quantity of soluble COD (SCOD) and organic nitrogen in the pretreated WAS as well as the production of total volatile fatty acids (TVFA) in the following biochemical acid potential (BAP) test. For WAS samples with described pretreatments, the released SCOD varied from 36% to 89% of the total COD (TCOD) and soluble organic nitrogen from 34% to 42%. The TVFA/TCOD ratio of the raw WAS used in this study was less than 10%. For the alkaline pretreated WAS, the TVFA/TCOD ratio increased to 30%, and the following ultrasonic treatment enhanced the ratio 66%. Further, WAS samples pretreated using simultaneous ultrasound and alkaline treatment in which ultrasonic was applied to WAS samples dosed with 40 meq/L NaOH for 14.4 sec/mL could achieve a maximum TVFA/TCOD ratio of 84% in 21 hours. Therefore, the combination of simultaneous alkaline and ultrasound pretreatment is efficient in enhancing the production of volatile acids in WAS in order to achieve recovery of volatile fatty acids from the WAS.

KEYWORDS

Alkaline pretreatment, anaerobic digestion, ultrasonic pretreatment, volatile fatty acids, waste activated sludge.

INTRODUCTION

Anaerobic digestion is generally used to stabilize organic matter in most municipal wastewater treatment plants. The quantity of energy recovered in the form of either volatile acids or methane is an important performance parameter. The process of anaerobic digestion is accomplished through three steps: hydrolysis, fermentation, and methanogenesis (Parkin and Owen, 1986), and the rate limiting step is the hydrolysis of

particulate organic matter to soluble substances (Eastmand and Ferguson, 1981). If the particulate nitrogen-containing organic matter contained in an activated sludge is not properly solubilized, only 30% to 50% of the total COD (TCOD) or volatile solids (VS) in WAS is biodegraded in 30 days (Parkin and Owen, 1986). With increasing solubilization of the organic substances, more VS becomes biodegradable. Thus, the efficiency of anaerobic digestion can be greatly enhanced by improving the rate of the sludge hydrolysis step using physical and/or chemical pretreatment processes.

The pretreatment process may include thermal, thermochemical, alkaline, and ultrasonic methods. In this study, only alkaline treatment and ultrasonic treatment and their combinations will be studies. The alkaline pretreatment which is a chemical process may be used to hydrolyze and decompose lipids, hydrocarbon, and protein into smaller soluble substances such as aliphatic acids, polysaccharides, and amino acids. The ultrasonic energy maintained at frequencies of 20 KHz and 375 W for 1 hour was reported to break up bacterial cells physically and release their content (Everett, 1973). Laboratory results showed that pretreating WAS with 200 W of ultrasonic energy (20 KHz , 1 hour, 20 to 30 °C) could enhance its COD solubilization (Tatsuo *et al.*, 1993). Since these two methods rely on different mechanisms to solubilize particulate organic substances, a combination of these two methods will take advantages of these two mechanisms and achieve a better treatment efficiency. Using combinations such as alkaline treatment followed by ultrasonic treatment, and simultaneous ultrasonic and alkaline treatment for enhancing recovery of volatile fatty acid (VFA) from WAS digestion were studied and the findings are reported in this paper.

MATERIALS AND METHODS

Waste Activated Sludge

The WAS used in the pretreatment study was obtained from a laboratory bench scale activated sludge system. The seeding sludge was collected from the return sludge stream of a municipal wastewater treatment plant. A relatively consistent sludge quality can be achieved by growing the WAS in synthetic wastewater for more than one month using the collected municipal sludge as inocula. The laboratory biological reactor was maintained at an F/M ratio of 0.2 day^{-1} and a solid retention time (SRT) of 10 days. The concentrated feeding stock solution contained 33.3 g/L glucose and 66.7 g/L peptone, with COD ranging from 10,000 to 12,000 mg/L. During the pseudo steady-state, the mix-liquor suspended solids (MLSS) concentration was maintained at about 4,600 mg/L, and its volatile solids/total solids (VS/TS) was about 84%. The excess wasted sludge was collected daily and stored at 4 °C for future use. The collected excess sludge is then subject to various pretreatment studies. Afterward, the pretreated sludge is evaluated for the efficiency of solubilization and the formation of volatile fatty acids (VFAs). The acidifying consortium was collected from a upflow anaerobic sludge blanket (UASB) reactor effluent and incubated by glucose solution at an SRT of 3±0.2 days. Table 1 illustrates the characteristics of the WAS samples and acidifying consortium used in this study. Prior to pretreatment studies, the total solid (TS) of all WAS samples were adjusted to 1% which was considered to be typical for municipal WAS (Huang, 1995).

Pretreatments and Volatile Fatty Acids Production

Figure 1a shows the diagram of the alkaline pretreatment system. Sodium hydroxide (NaOH) which was reported to yield a greater solubilization efficiency than lime (Rajan *et al.*, 1989) was used in the alkaline pretreatment studies. Alkaline pretreatment of WAS was carried out in a 1-L plastic bottle at ambient temperature. After addition of NaOH, the dissolved oxygen in the reactor was purged with nitrogen gas and the bottle was then sealed with a rubber stopper. A magnetic stirrer was used to mix the contents continuously during the treatment period. Ultrasonic pretreatment was carried out in a 1-L wide-mouth glass bottle reactor (Figure 1b). The ultrasonic energy output (Branson Ultrasonic Model 250 Sonifier) was rated at 120 W and its frequency was set at 20 KHz. The biochemical acid potential (BAP) test, which is a simplified version of the biochemical methane potential (BMP) test (Owen *et al.*, 1979), was used to examine

the VFA productions of pretreated WAS samples. The apparatus shown in Figure 1a was also used to carry out the BAP test. In this test, the pretreated WAS was mixed with acidifying consortium in 1:3 (v/v) and the mixture was incubated in the 1-L wide-mouth glass bottle reactor at room temperature.

Table 1. Characteristics of waste activated sludge and acidifying consortium used in this study.

Item	Incubated WAS	Acidifying consortium
pH	6.8 ± 0.1	6.0 ± 0.2
TCOD (mg/L)	6,968 ± 343	9,034 ± 273
SCOD (mg/L)	230 ± 25	268 ± 32
NH_3-N (mg-N/L)	71	43
MLSS (mg/L)	4,613 ± 293	6,780 ± 163
VS/TS (%)	83.6 ± 0.3	72.9 ± 2.3
TKN (mg-N/L)	350	256
Alkalinity (mg-$CaCO_3$/L)	2,900	2,400

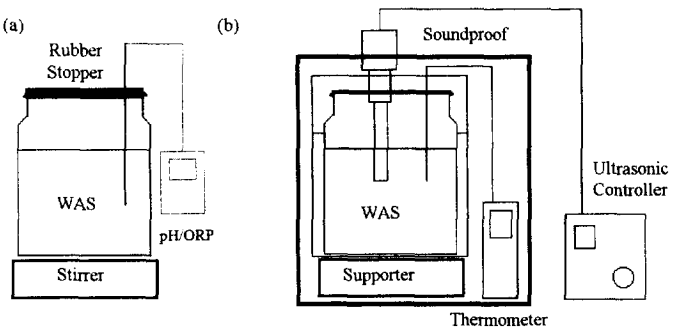

Figure 1. Schematic diagram of (a) alkaline pretreatment and BAP test, and (b) ultrasonic pretreatment.

Analytical Methods

After the pretreatment procedure, samples collected from the reactor were filtered through 0.45 μm filter papers and the filtrates were stored at 4 °C for subsequent analyses. The Anthrone carbohydrate method (Raunkjer *et al.*, 1994) was used for measuring the concentration of carbohydrates in the sample. Determination of organic nitrogen was performed in accordance with method 420B of the 18th edition of Standard Methods. Measurements of COD, pH, and ORP were carried out following the procedures described in the 18th edition of Standard Methods. The composition of the VFA produced from the BAP test were measured using the GC-FID system (GC-8900, China Chromatography Co.) equipped with a stainless steel column (3 mm i.d., 1.6 m) and Porapak Q (mesh 80/100) packing using nitrogen as the carrier gas.

RESULTS AND DISCUSSION

Hydrolysis Model

Figure 2 shows variations of SCOD and ORP of WAS under three different pretreatment schemes: (1) pretreated with 40 meq/L NaOH for 24 hours, (2) pretreated with 40 meq/L NaOH for 24 hours followed by ultrasonic vibration for 24.0 sec/mL, and (3) simultaneous ultrasonic (14.4 sec/mL) applied to samples dosed

with 40 meq/L NaOH. The ORP of the three pretreatments samples showed the same variation pattern. As shown in Figure 2, all ORP curve initially decreased with a significant increase of SCOD in the first 2 hours. Afterward, the ORP curves become increasing while the SCOD curves become leveling off. The observed variations of ORP values are similar to those reported by Yu *et al.* (1996) and Huang (1995). Based on the ORP measurement, the first 2-hour reaction period was defined as the first phase of hydrolysis and the second phase starts after the 2-hour reaction period. For future studies as well as field application the ORP measurement can be used as an on-line parameter for monitoring the hydrolysis resulted from alkaline pretreatment.

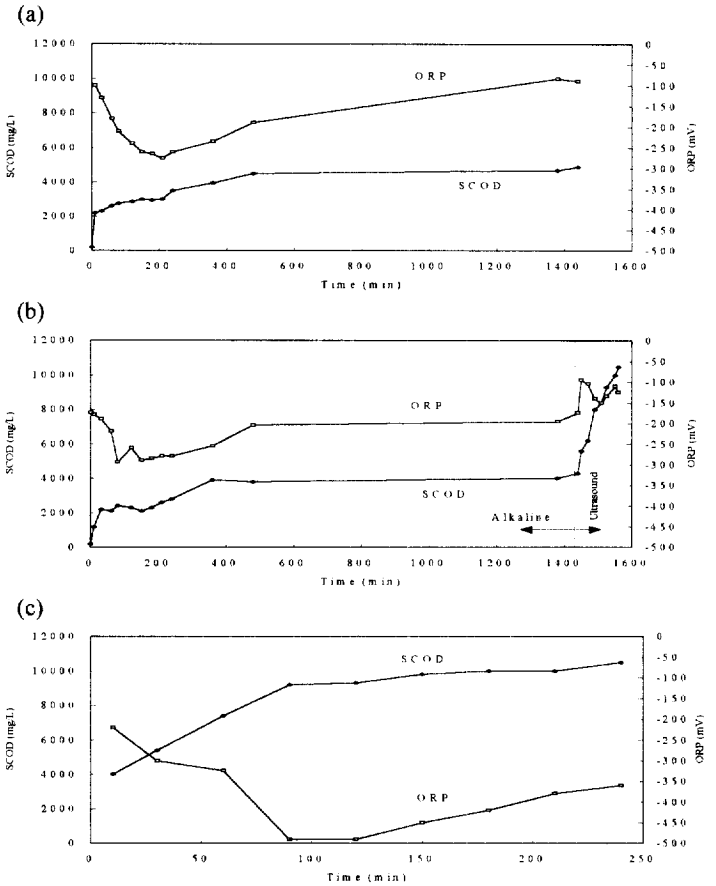

Figure 2. SCOD and ORP profiles of different pretreatments. (a) 40 meq/L NaOH for 24 hr, (b) 40 meq/L NaOH for 24 hours then ultrasound for 24.0 sec/mL, (c) ultrasonic vibration with 40 meq/L NaOH for 14.4 sec/mL.

First Hydrolysis Phase. For the first phase of alkaline hydrolysis of municipal WAS, Lin *et al.* (1995) proposed the following polynomial equation (Eq. 1) to delineate the reaction kinetics:

$$C = a_0 + a_1 \times t + a_2 \times t^2 + a_3 \times t^3 \quad (1)$$

where C = soluble COD (SCOD, mg/L).
t = reaction time (min).
a_0, a_1, a_2, a_3 = coefficients.

Derivation of Eq. (1) is shown as :

$$dC/dt = a_1 + 2 \times a_2 \times t + 3 \times a_3 \times t^2 \quad (2)$$

If the term "t" in equation (2) approaches zero, the first term on the right-hand side of the equal sign, that is "a_1", can be used to represent the initial hydrolysis rate (mg/L/min). The higher alkaline dosage or WAS concentration resulted in an enhanced hydrolysis rate was seen by an increase of the "a_1" term in Equation (2) (Huang, 1995). The initial hydrolysis rate for WAS sample undergoing the various pretreatment schemes can then be calculated and listed in Table 2. Obviously, the initial hydrolysis rate (211.9 mg/L/min) for the WAS sample pretreated using the simultaneous ultrasonic and alkaline treatment was much higher than the initial rates for other pretreatment schemes.

Table 2. The initial hydrolysis rate in the first phase of different pretreatment methods.

Reference	Substrate	Pretreatment	Initial Hydrolysis Rate (mg/L/min)	R^2
This Study	1%TS WAS	40 meq/L NaOH (24 hr)	97.8	0.96
		40 meq/L NaOH (24 hr) +Ultrasound (24.0 sec/mL)	150.7	0.97
		Ultrasonic vibration with 40 meq/L NaOH (14.4 sec/mL)	211.9	0.96
Huang (1995)	1%TS WAS	40 meq/L NaOH (24 hr)	79.8	0.96
		Ultrasound (13.5 sec/mL) + 40 meq/L NaOH (24 hr)	197.1	0.93
Lin *et al.* (1995)	1%TS WAS	40 meq/L NaOH (24 hr)	26.5	0.63

Second hydrolysis phase. The kinetics of the second-phase hydrolysis which follows a first order reaction and can be express by Eq. (3) as suggested by Lin *et al.* (1989).

$$d(C_p - C_u)/dt = -K \times (C_{po} - C_u) \quad (3)$$

where C_p = particulate COD concentration (mg/L).
C_{po} = initial particulate COD concentration (mg/L).
C_u = unsolube particulate COD concentration (mg/L).
K = first order reaction constant (1/min).

Since there is a stoichiometric relation between the alkaline dosage applied and the quantity of WAS hydrolyzed, Eq. (3) could be expressed in the form of Eq. (4), and further reorganized and expressed as Eq. (5).

$$dC/dt = K \times (C_{max} - C) \quad (4)$$

$$\ln [(C_{max}-C)/C] = - K t \quad (5)$$

where C_{max} = maximum soluble particulate COD (mg/L).
C = soluble particulate COD at time t (mg/L).

t = reaction time of second hydrolysis phase (min).

The integrated results of the second hydrolysis phase data using to Eq. (5) is shown in Table 3. The pretreatment with only alkaline alone for 24 hours could not effectively hydrolyze the particulate COD in the second phase. In contrast, the ultrasonic treatment alone increased the maximum soluble particulate COD (C_{max}) to 10,480~10,632 mg/L while samples pretreated using the simultaneous ultrasonic and alkaline treatment resulted in a lower C_{max} and a higher reaction constant (K) than either alkaline followed by ultrasound treatment or ultrasound followed by alkaline treatment. The SCOD and soluble organic nitrogen of WAS after different pretreatments are listed on Table 4. The WAS samples pretreated with described methods released from 36% to 89% of total COD (TCOD) in the form of SCOD and from 34% to 42% of soluble organic nitrogen. The pretreatment using simultaneous alkaline and ultrasound treatment was found to be more effective in releasing both SCOD and soluble organic nitrogen than alkaline treatment, and be close to the results of alkaline treatment followed by ultrasound treatment. Therefore, the process of simultaneous ultrasonic and alkaline treatment could shorten the WAS pretreatment time and result in a prolific production of SCOD.

Table 3. The hydrolysis in the second phase of different pretreatment methods.

Reference	Substrate	Pretreatment	C_{max} (mg/L)	K (1/min)	R^2
This Study	1%TS WAS	40 meq/L NaOH (24 hr)	4,880	0.108	0.76
		40 meq/L NaOH (24 hr) +Ultrasound (24.0 sec/mL)	10,632	0.600	0.77
		Ultrasonic vibration with 40 meq/L NaOH (14.4 sec/mL)	10,480	0.882	0.97
Huang (1995)	1%TS WAS	40 meq/L NaOH (24 hr)	4,700	0.005	0.96
		Ultrasound (13.5 sec/mL) + 40 meq/L NaOH (24 hr)	13,840	0.328	0.96

Table 4. Summary of different pretreatments of waste activated sludge.

Reference	Sludge	Pretreatment Method	SCOD/TCOD (%)	Soluble Org-N (%)
This Study	1%TS WAS	40 meq/L NaOH (24 hr)	36.3	42.1
		40 meq/L NaOH (24 hr) +Ultrasound (24.0 sec/mL)	89.3	52.5
		Ultrasonic vibration with 40 meq/L NaOH (14.4 sec/mL)	77.9	44.6
Huang (1995)	1%TS WAS	40 meq/L NaOH (24 hr)	28	53.4
		Ultrasound (13.5 sec/mL)	36	39.9
		Ultrasound (13.5 sec/mL) + 40 meq/L NaOH (24 hr)	80.6	82.2
Prohaska *et al.* (1994)	1%TS PS	Anaerobic Hydrolysis 25 (2~3 days)	-	10~15
Kenzevic *et al.* (1994)	PS+WAS	12.5 meq/L NaOH (0.5 hr)	45	-
Liao (1993)	1%TS WAS	40 meq/L NaOH (24 hr)	36.3	49.5
Lin *et al.* (1989)	1%TS WAS	40 meq/L NaOH (12 hr)	42	-
Haug *et al.* (1978)	1%TS WAS	175 ^{0}C+250 meq/L NaOH (24 hr)	68	-
Stuckey & McCarty (1978)	4.3%TS WAS	175 ^{0}C+300 meq/L NaOH (1 hr)	55	-
		Ultrasound (90 sec/mL)	20	-

PS: Primary Sludge

Biochemical Acid Potential Test

The productions of the various volatile fatty acids including acetic acid, propionic acid, n-butyric acid, iso-butyric acid, n-valeric acid, and iso-valeric acid for WAS samples undergoing different pretreatment schemes were examined using the BAP test. The summation of all the acids produced was reported as the Total Volatile Fatty Acid (TVFA). Figure 3 shows the profile of TVFA produced from various pretreated WAS samples. Less than 10% of TCOD in the WAS sample without pretreatment was converted to TVFA. With only alkaline pretreated, the TVFA/TCOD ratio increased to 30%, and the following ultrasonic treatment further enhanced the ratio up to 66%. However, the pretreatment of ultrasonic vibration of the WAS sample dosed with 40 meq/mL NaOH reached a maximum TVFA/TCOD ratio of 84% in 21 hours verifying that the simultaneous ultrasonic and alkaline pretreatment can efficiently enhance the production of volatile acids from WAS for the TVFA recovery.

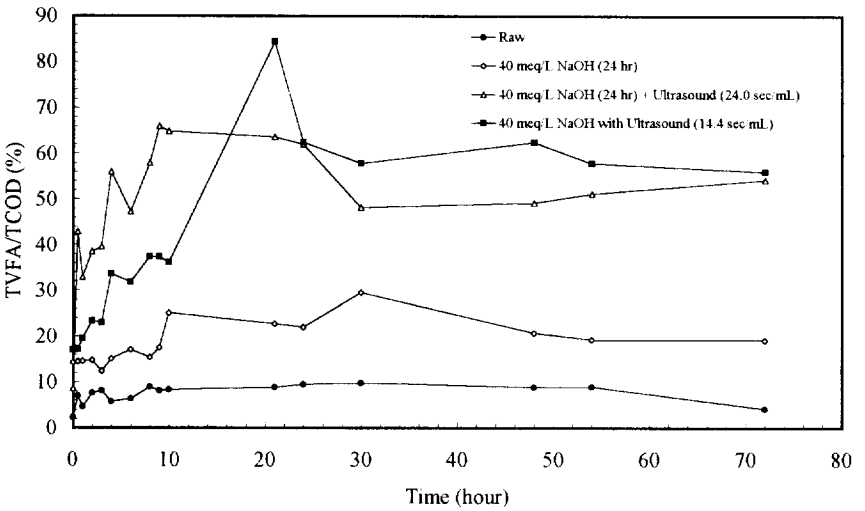

Figure 3. Transformation ratios of volatile fatty acids under different pretreatments.

CONCLUSION

Synthetic municipal WAS has been used in the hydrolysis pretreatment studies to increase the rate of solubilizing particulate organic matter in order to enhance the production of volatile fatty acids in the subsequent anaerobic biological digestion process. The ORP measurement may have a potential as an indicator for monitoring the hydrolysis resulted from alkaline pretreatment. Among the three pretreatment schemes: alkaline treatment only, alkaline treatment followed by ultrasonic treatment, and the simultaneous ultrasonic treatment of the sample dosed with alkaline, the initial hydrolysis rate of the simultaneous ultrasonic and alkaline treatment is the highest being 211.9 mg/L/min. The simultaneous ultrasonic and alkaline treatment was found to be close to the results of alkaline followed by ultrasound pretreatment in releasing both SCOD and soluble organic nitrogen but is more effective than alkaline treatment alone. Using the simultaneous ultrasonic and alkaline treatment, the pretreatment time for municipal WAS can be greatly shortened resulting in a high amount of SCOD released. This method can be used to enhance the production of volatile acids from WAS for recovery of TVFA recovery.

ACKNOWLEDGEMENT

We thanks the National Science Council of Republic of China for providing financial assistance to complete this work.

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