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BMP test on chemically pretreated sludge

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Abstract

Municipal waste activated sludge (WAS) was treated with NaOH to solubilize the particulate organic matter in order to improve its digestibility when the sludge was stabilized in an anaerobic digestion process. For the WAS of 1% TS treated with 20 and 40 meq/l NaOH at ambient temperature for 24 h, the SCOD/TCOD values increased from 3.5 to 39 and 55%, respectively. Results of the BMP (biochemical methane potential) test showed that recoveries of carbon and nitrogen reached 94–105% and the methane produced was 349 ml (at 1 atm and 35°C) for 1 g of COD removed. The improvement in VS removal for sludge treated with 40 meq/l of NaOH was as high as 41% over the control sludge sample, with COD removal and gas production improved by 30 and 34%, respectively, over the control. Results of the cumulative COD removal appeared to follow first-order reaction kinetics. Parameters of the first-order model such as ultimate biodegradable COD (L_u), reaction rate coefficient (k) and ultimate biodegradability (μ), were calculated using the Thomas method. The BMP test can be used as a valuable tool to study the kinetics and efficiency of anaerobic digestion processes.

Keywords: Anaerobic digestion; Biochemical methane potential; Chemical pretreatment; Hydrolysis

1. Introduction

Most municipal wastewater treatment plants use the activated sludge process to treat wastewater, and the resulting excess waste activated sludge (WAS) consists largely of biological mass, mainly protein (approximate 30%), carbohydrate (approximate 40%) and lipids (approximate 30%) in particulate forms. The WAS must be stabilized sufficiently to reduce its organic content so that it can be safely disposed of without causing odor problems and/or pathogen contamination. Anaerobic biological digestion is the most commonly used WAS stabilization method in modern wastewater treatment plants. The anaerobic digestion is a complex microbiological process including hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Parkin and Owen, 1986). However, the hydrolysis step is considered to be the rate-limiting step in the overall anaerobic digestion process for municipal WAS (Li and Noike, 1987; Ray et al., 1990).

If the efficiency of sludge digestion for WAS is to be improved, the logical approach is to increase the rate of hydrolysis (Woodard and Wukasch, 1994) using physical or chemical techniques, such as thermal pretreatment (Haug et al., 1977, 1978, 1983; Haug, 1977; 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; Lin et al., 1997, 1998). While the thermal or thermochemical pretreatments of sludge result 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 more cost-effective and can be carried out at ambient temperature (Lin et al., 1997).

Sodium hydroxide at relatively low dosage levels is effective on solubilizing municipal WAS at ambient temperature. Alleman et al. (1994) demonstrated that alkaline treatment is effective in solubilizing munitions-

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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 time of hydrolysis. Rajan et al. (1989) showed that the 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 performance of the single-stage high-rate anaerobic digester to stabilize the alkaline-treated WAS with digesters operated at 35°C and five different hydraulic retention times, 20, 13, 10, 7.5 and 5 d. Pretreatment with sodium hydroxide improved the volatile solid reduction from 25 to 35% and increased gas production from 29 to 112% over the control sludge samples undergoing no alkaline treatment. Lin et al. (1997) proposed that the alkaline pretreatment does significantly enhance the amount of the soluble organic matter from the WAS of sewage plant. After an alkaline pretreatment, the performances of pretreated samples for COD and VS removal and gas production were superior to unpretreated samples.

In the past, a long experimental time has been required to observe and evaluate the digestion of WAS by conducting a laboratory-scale reactor study. The duration of experiment usually includes the development of a balanced microorganism population in the reactors and establishment of a stable operation. Therefore, a more efficient alternative method to study the kinetics and efficiency of the anaerobic digestion process is needed. Owen et al. (1979) presented the methods of anaerobic toxicity assay (ATA) and biochemical methane potential (BMP) to evaluate the anaerobic treatability of organics in wastewater. After preliminary screening studies, the BMP test was considered the most suitable method for a relatively easy evaluation of the anaerobic digestion process. The objectives of this study were to apply the BMP test as a tool for evaluating the anaerobic sludge digestion process, its kinetics and efficiency; and to demonstrate that the alkaline treatment of municipal WAS improves its digestibility, reduction of the volatile suspended solids and methane gas production.

2. Methods

2.1. Chemical pretreatment

The WAS sample was collected from a municipal wastewater treatment plant located in northern Taiwan, and its concentration was adjusted to 1.0% total solids. Sodium hydroxide of 20 and 40 meq/l was used to carry out the hydrolysis pretreatment study in a 1-l batch reactor at ambient temperature under anoxic conditions for 24 h. A stirring magnet bar was used to ensure mixing sufficient to prevent the sludge from settling and disperse the alkali added. Total chemical oxygen demand (TCOD) and soluble chemical oxygen demand (SCOD) of the reactor content were measured and the ratio of soluble COD to total COD (SCOD/TCOD) was used to reflect the extent of hydrolysis. The soluble COD was obtained by measuring the COD of the filtrate collected by filtering the sludge sample through a 0.45-μm filter. After the chemical pretreatment, the sludge was divided into two parts. One part was centrifuged to separate the sludge sample into supernatant and particulate portions. The unfiltered sludge sample, supernatant, and particulate were used in the subsequent anaerobic digestion study and the digestion efficiencies were evaluated using the BMP tests.

2.2. Biochemical methane potential (BMP)

The BMP tests performed in this study followed the procedure as described by Owen et al. (1979) in 100-ml serum bottles at a temperature of 35°C. Variables used to assess the efficiency of the anaerobic digestion on the BMP test were volatile solids (VS), total organic carbon (TOC), total inorganic carbon (TIC), ammonia nitrogen, organic nitrogen, gas production, and gas composition. The organic carbon was determined with an Astro Model 2001 TOC Analyzer. Gas production for each BMP test was measured once every 2 or 3 days over a period of 30 days. Gas analyses were performed using an HP Model 5890 Gas Chromatography. The other variables were measured at the beginning and end of the BMP test. Each test carried out under different conditions was run once.

3. Results and discussion

The organic content of a sludge sample is usually measured as VS, COD, and TOC. In this study VS, TOC, and COD for all samples were taken from the BMP tests. A total of 54 data points were plotted in Fig. 1. Through linear regression between VS or TOC versus COD, the squared correlation coefficient of the determination (R^2) was generally close to '1' and ratios of TOC:VS:COD can be expressed as 0.3:0.6:1 with confidence.

The methane yield for an anaerobic digestion process is commonly expressed as a function of the reduction of either volatile solids or COD. In this study, the methane production per gram of COD

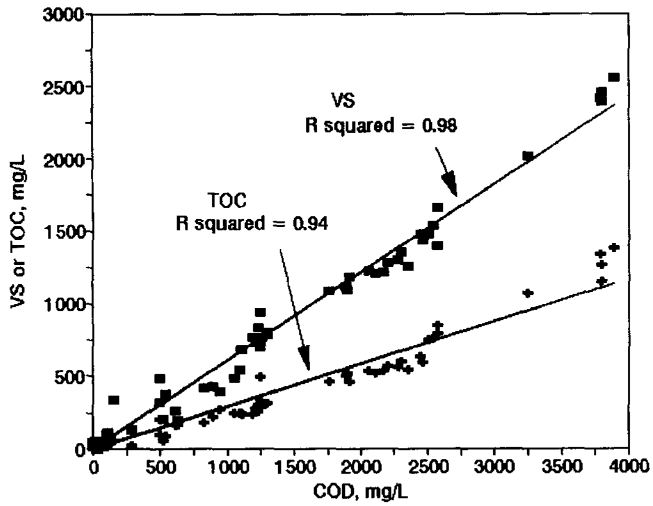

Fig. 1. Relationship between VS or TOC versus COD ($n = 54$).

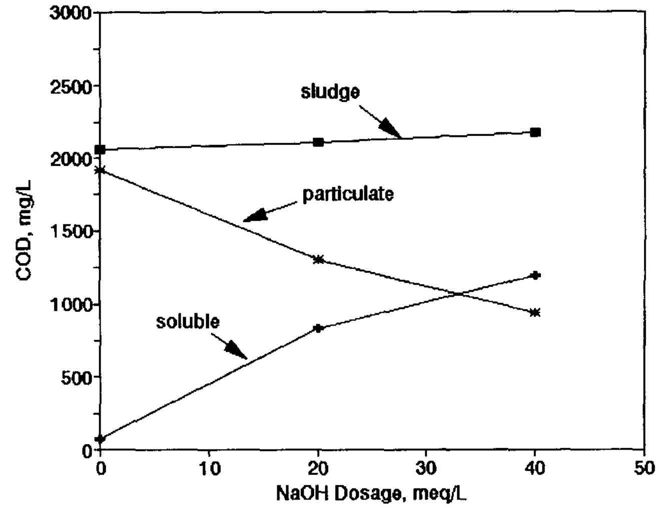

Fig. 3. Profiles of COD versus NaOH dosage for a sludge of 1% TS.

destroyed from the BMP tests averaged 349 ml (at 1 atm and 35°C), as shown in Fig. 2. For 1 g of COD removed, the theoretical methane produced would be 350 ml at STP. Literature values for methane gas production may vary considerably, but representative values are usually in the range of 490 to 730 ml methane per gram VS destroyed (Metcalf and Eddy, Inc., 1991).

3.1. BMP test results

Figure 3 shows the variation of COD measured in particulate and soluble portions for a sludge of 1% TS with no NaOH treatment and treated with 20 and 40 meq/l NaOH. Without the chemical treatment, the total COD of the sludge was approximately 2000 mg/l.

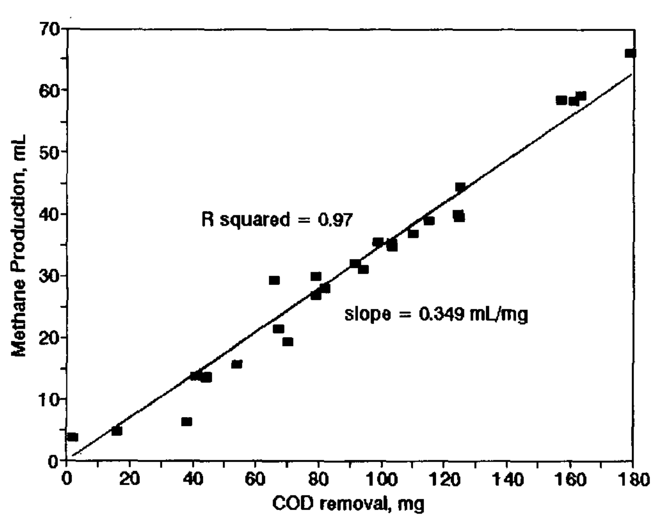

Fig. 2. Relationship between methane production versus COD removed ($n = 27$).

But most of the COD was in particulate form, as evidenced by the high COD of the particulate portion of the sludge sample (≅2000 mg/l) and a low COD of 70 mg/l in the soluble portion. The ratio of SCOD/TCOD of the untreated sludge sample was 3.5%. With increased NaOH concentrations, the total COD of the control remained at the 2000 mg/l level. But the particulate portion showed a decreasing COD with a corresponding increasing COD in the soluble portion. When the NaOH concentration was increased from 20 to 40 meq/l the COD in the soluble portion increased from 830 to 1190 mg/l, and SCOD/TCOD increased from 39 to 55%. These data demonstrate that the alkaline pretreatment at ambient temperature significantly solubilized municipal WAS. This observation is also supported by the results reported by Rajan et al. (1989).

After the alkaline pretreatment, efficiencies of anaerobic digestion of the unfiltered sludge, supernatant, and particulate were evaluated with BMP tests. Figure 4 provides a representative set of the cumulative methane production data obtained with the BMP test for all three samples, including the unfiltered sludge sample (the control), the filtrate and the particulate portions. The methane gas production obtained at the 30-day digestion time for samples treated with 20 or 40 meq/l NaOH was higher than that for sludge samples without the chemical treatment. With 40 meq/l NaOH, the observed gas production increased by 34% over the control. In addition, the methane production from the soluble portion was significantly greater than that for the particulate portion. Thus, the biodegradability of the soluble portion was superior to that of the particulate portion. The data of COD and VS collected from BMP tests are listed in Table 1. The sample treated with 40 meq/l NaOH showed better VS removal (up to 41%) and

COD removal (30%) efficiencies than samples without the chemical treatment. It is obvious that alkaline pretreatment could enhance not only solubilization (Fig. 3) but also biodegradability (Fig. 4 and Table 1) of municipal WAS.

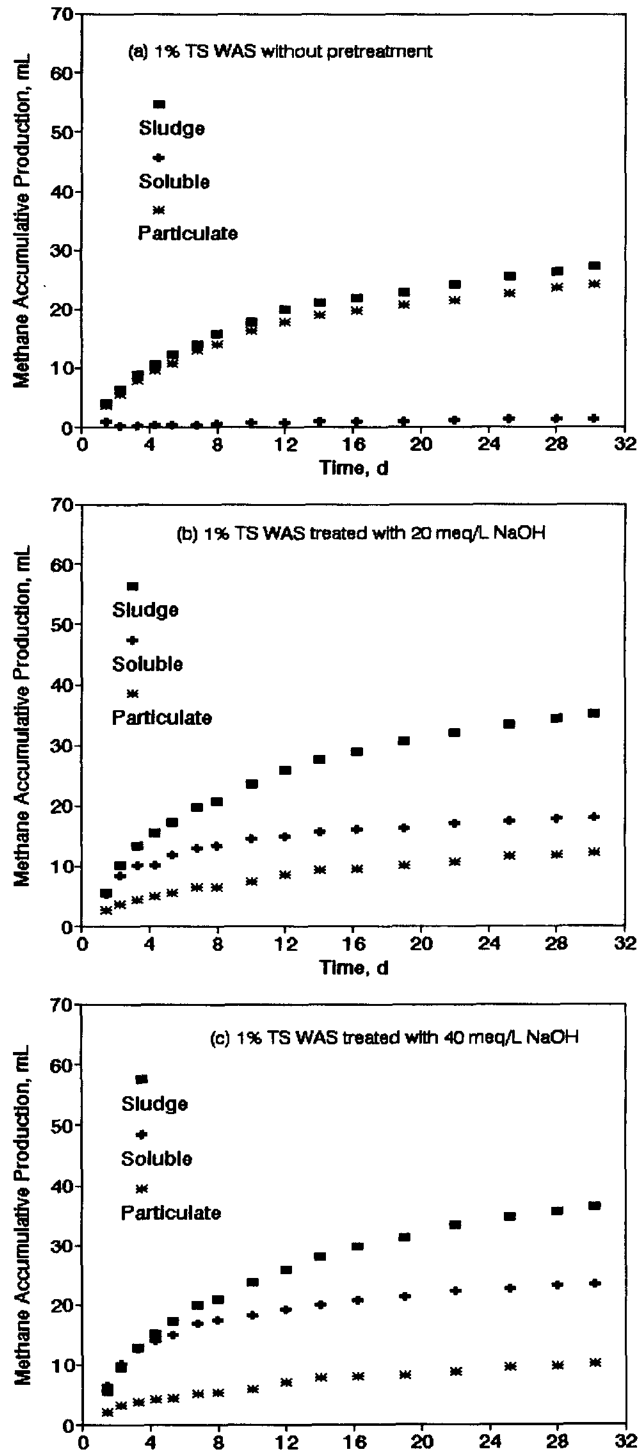

Fig. 4. Profiles of methane production versus reaction time in BMP study.

Table 1
Results of COD and VS in BMP tests

	Initial (day 0)		Final (day 30)			
	COD mg/l	VS mg/l	COD mg/l	VS mg/l	COD Removal (%)	VS Removal (%)
Control sludge						
No pretreatment	3910	3550	2969	3020	39	43
20 meq/l NaOH	3960	3530	2811	2860	48	55
40 meq/l NaOH	4020	3540	2778	2800	51	61
Supernatant						
No pretreatment	1920	2340	1757	2320	–	–
20 meq/l NaOH	2680	2740	2011	2450	65	69
40 meq/n NaOH	3040	3080	2247	2530	56	72
Particulate						
No pretreatment	3770	3500	2950	3150	36	30
20 meq/l NaOH	3150	3120	2612	2750	31	46
40 meq/l NaOH	2790	2710	2349	2520	33	49
Blank	1850	2320	1720	2320		

3.2. Kinetics

Anaerobic digestion is generally described as a first-order reaction. The experimental results shown in Fig. 4 can be delineated by a first-order reaction kinetics (eqn (1)).

$$dC/dt = -kC \tag{1}$$

in which C is the concentration of organics (mg/l COD) and k is reaction rate coefficient (d^{-1}). After integration, eqn (1) can be rearranged as:

$$Y = L_u(1 - e^{-kt}) \tag{2}$$

in which Y is the organic removal at time t (mg/l COD), L_u is ultimate biodegradable organics (mg/l COD), and t is time (d). Using eqn (2) the ultimate biodegradability for organic (μ) can be calculated as L_u/TCOD.

Based on the methane production per gram of COD destroyed (Fig. 2), the quantity of COD destroyed at time t can be calculated using the methane production data (Fig. 4), and the COD reduction rate constant can be estimated according to eqn (2).

Using the Thomas method, the values of k, L_u, and μ for the untreated and treated sludge are calculated and listed in Table 2. Among the control sludge samples, supernatant, and particulate, the values of k and μ for the supernatant portion were the greatest indicating that the alkaline pretreatment was effective in solubilizing the particulate organic matter and improving the biodegradability of the solubilized municipal WAS. The squared correlation coefficient of the determination (R^2) was generally close to unity, being greater than 0.95 for the various NaOH dosages. Thus, the kinetics of COD removal or gas production are satisfactorily predicted with the first-order model. This also demonstrates that the BMP test is useful for studies of kinetics of the anaerobic sludge digestion process.

3.3. Evaluation of BMP test

The results of carbon and nitrogen mass balances for BMP tests are listed in Table 3. Total carbon was calculated from both aqueous and gaseous phases. For the gaseous phase the total carbon was theoretically converted from the CH_4 and CO_2 values obtained in the study. Results of mass balance for COD and TKN for BMP test systems ranged from 98 to 105%; close to 100%.

Table 2
Values of L_u, k and μ in the anaerobic digestion model

	k (d^{-1})	L_u (mg/l)	μ (%)	R^2
Control sludge				
No pretreatment	0.10	880	43	0.99
20 meq/l NaOH	0.17	1100	52	0.97
40 meq/l NaOH	0.16	1200	55	0.98
Supernatant				
No pretreatment				
20 meq/l NaOH	0.17	625	75	0.97
40 meq/n NaOH	0.16	763	64	0.97
Particulate				
No pretreatment	0.10	753	39	0.99
20 meq/l NaOH	0.12	432	33	0.94
40 meq/l NaOH	0.12	336	36	0.93

Figure 5 shows the comparison of VS and COD removals versus the ultimate biodegradable COD (L_u) (shown in Table 1). The data points were experimental results obtained from BMP tests for a digestion time of 30 days. These data points were fitted by solid lines which represent the theoretical results calculated using eqn (2). The squared correlation coefficients of the determination (R^2) were 0.99 and 0.85 for COD and VS data, respectively. The experimental results obtained from the BMP test were consistent with the results predicted with the model. Additionally, using the BMP test, the time needed to evaluate the anaerobic digestion process for municipal WAS can be greatly reduced.

4. Conclusions

The BMP test was used to evaluate the kinetics and efficiency of the anaerobic process for digesting chemically pretreated municipal sludge. For a sludge of 1% total solids treated with NaOH at ambient temperature for 24 h, the particulate organic matter in the sludge was solubilized leading to an increase in the soluble COD in the treated sludge. When the NaOH concentration was increased from 20 to 40 meq/l, the SCOD/TCOD ratio increased from 39 to 55%. After the chemical pretreatment, the control sludge, supernatant, and particulate were subject to anaerobic digestion and the efficiency was evaluated with BMP tests. The

Table 3
Carbon and nitrogen mass balance

	Initial (day 0)			Final (day 30)				
	TC mg	Norg. mg/l	NH_3– mg/l	TC mg	Norg. mg/l	NH_3– mg/l	Carbon Recovery %	TKN Recovery
Control sludge								
No pretreatment	104	160	162	106	106	213	102	99
20 meq/l NaOH	103	157	165	106	92	238	103	102
40 meq/l NaOH	104	165	160	109	84	238	104	99
Supernatant								
No pretreatment	55	53	160	56	53	170	103	105
20 meq/l NaOH	68	104	162	71	61	207	104	101
40 meq/l NaOH	76	126	162	79	70	221	104	101
Particulate								
No pretreatment	96	162	152	101	106	201	105	98
20 meq/l NaOH	81	109	148	84	86	170	103	100
40 meq/l NaOH	77	95	148	76	78	168	98	101
Blank	50	56	148	51	44	148	102	94

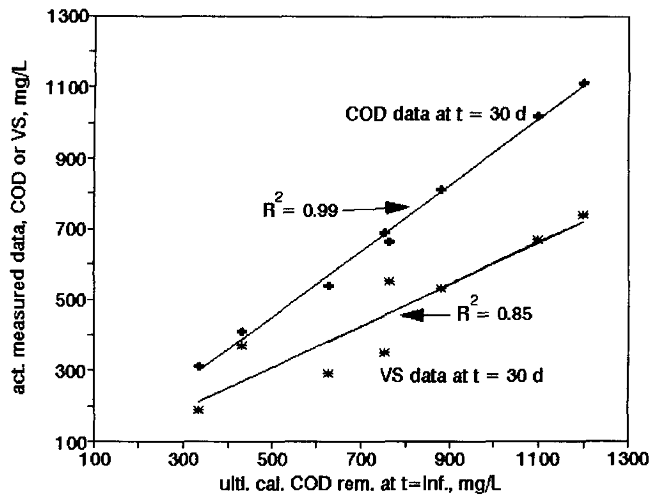

Fig. 5. Comparison of VS and COD removal versus COD removal using BMP results.

results of BMP tests showed that carbon and nitrogen had 94–105% recoveries and the methane produced was 349 ml (at 1 atm and 35°C) for 1 g of COD removed. For sludge samples treated with 40 meq/l of NaOH, removal of its VS in the anaerobic digestion process was as high as 41% over the control. With the same alkali concentration, COD removal was improved by 30% and gas production increased by 34% over the control. The cumulative COD removal appeared to follow first-order reaction kinetics. Parameters of the model, ultimate biodegradable COD (L_u), reaction rate coefficient (k) and ultimate biodegradability (μ), were calculated by the Thomas method. In this study, the BMP test was shown to be a valuable tool for studying the kinetics and efficiency of an anaerobic digestion process. Chemical pretreatment of municipal WAS to convert the particulate into soluble portion was shown to be effective in enhancing the digestibility of the WAS.

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