Hydrogen as a quick indicator of organic shock loading in UASB

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Abstract This study investigates the influence of organic shock loading on H_2 production in an upflow anaerobic sludge bed (UASB) reactor. An esterification wastewater produced from a polyethylene terephthalate (PET) manufacturing plant was applied; the major organic pollutants are ethylene glycol and acetaldehyde. Experiments of two influent modes were performed here: a continuous-flow mode with a step input of shock loading and a batch mode with a pulse input of shock loading. Results of the continuous-flow experiments indicate that biogas production parameters such as H_2 concentration and biogas production rate are more sensitive than water quality parameters such as pH, ORP, COD and TOC. In particular, H_2, increasing by 140% within 1 hour, is a very important index upon the organic shock loading. It changes from 120 ppm to over 600 ppm as the organic loading rate increases from 4.4 to 13.2 kgCOD/m^{3}·day through 4 hours of shock loading. Experiments of the batch shock loading with different pulse dosages of ethylene glycol, acetaldehyde and the raw wastewater were also investigated. The amount of H_2 production increased in proportion to an increase of organic load. Furthermore, the sequence of H_2 production among the three types of shock loading is acetaldehyde> ethylene glycol> raw wastewater. To sum up, H_2 shows a faster response rate than the other parameters. Therefore, H_2 can be adopted as an important parameter for organic shock loading in UASB.

Keywords Upflow anaerobic sludge bed (UASB), esterification wastewater, hydrogen (H_2)

Introduction

The up-flow anaerobic sludge bed (UASB) has been extensively applied in wastewater treatment in recent years. In the anaerobic digestion process, hydrogen (H_2) has been found as an important intermediate product through the methanogenic stage. H_2 is consumed by H_2-utilizing methanogens for reducing carbon dioxide to methane (Gujer and Zehnder, 1983). In highly efficient methanogenic digesters, H_2 is rarely detected unless the methanogenesis is disturbed by shock loading (Archer *et al*., 1986; Guwy *et al*., 1997) or by toxicants (Hickey *et al.*, 1989; Mosey and Fernandes, 1989). McCarty and Smith (1986) found that the H_2 concentration approached 500–1000 ppm after shock loading in the laboratory-scale digester. Hickey *et al.* (1989) showed that H_2 concentration in the biogas of a digester responded rapidly to toxicant shocking such as chloroform and heavy metals.

This study primarily presents the application of an H_2 sensor in a UASB reactor for treating an esterification wastewater that is generated from the polyethylene terephthalate (PET) manufacturing plant. The COD concentration of this wastewater ranges from 35,000 to 45,000 mg/l, containing ethylene glycol (EG), acetaldehyde and some other intermediate components. In this investigation, the feasibility of applying an H_2 sensor to monitor the variation in H_2 concentration was examined. Influences of other parameters such as pH, COD, TOC, ORP and volatile acids on the shock loading were also studied. The effects of different dosages of EG and acetaldehyde with pulse addition to the reactor were discussed as well.

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Materials and methods

Bench-scale UASB reactor

A 10-litre bench-scale UASB reactor (10 cm-Lx10 cm-Wx100 cm-D) was applied to treat this esterification wastewater. The influent in the storage tank was regulated to the desired COD concentration. Figure 1 schematically depicts this system.

On-line monitoring and control system

The monitoring and control system consists of the computer, PLC controller and meters. The meters included a pH meter with sensor (Suntex), an ORP meter with sensor (Suntex), an H_2 detector (WINTER gas-wamanlagen TH2W200) and a gas meter (SHINAGAWA SEIKI DC-1) was installed. The IBM compatible PC (pentium-II) for Windows system with the software (Visual Supervisory Control and Data Acquisition, VSCADA) was used for data acquisition and process control. On-line data sampled every 1 minute were displayed on screen. The PLC controller (Omron) includes an AD/DA converter, communication module and a terminal panel connected to the computer and meters.

Off-line analytical methods

The COD concentration was analyzed according to the Methods suggested by APHA (1995). The total organic carbon (TOC) concentration was measured using a TOC analyzer (Dohrmann DC-190). Levels of individual volatile acids and EG were determined by HPLC (column: ORH801, mobile phase: $0.1H_3PO_4$) ; acetaldehyde was also determined by HPLC (column: Zorbax ODS, mobile phase: 75 methane / $25H_2O$). The biogas production was measured using a gas flowmeter (SHINAGAWA SEIKI DC-1).

Experimental procedures

The digested swine sludge was seeded into the 10-litre UASB reactor with 153 gVSS. The bicarbonate alkalinity in UASB was maintained about 1190 mg/l (as $CaCO_3$) by adding $NaHCO_3$ as a buffer solution. After 3 months of acclimation, the organic loading (F/V) reached 4.4 kgCOD/m^3·day with the COD removal efficiency about 94% under 10.4 ml/min influent flow rate, then the experiments of shock loading were started. This investigation can be divided into two parts. The first part was performed in a continuous-flow mode with a 4-hour step input of shock loading by increasing to 3 folds of influent COD. The wastewater compositions for the step change of shock loading are shown in Table 1. The on-line parameters including pH, ORP, H_2 and biogas production rate were monitored; the off-line parameters including COD, TOC, volatile acids, EG and acetaldehyde were analyzed. The second part was conducted in a batch mode with a pulse input of shock loading by feeding different amounts of EG, acetaldehyde and raw wastewater into the recycling tank. The H_2

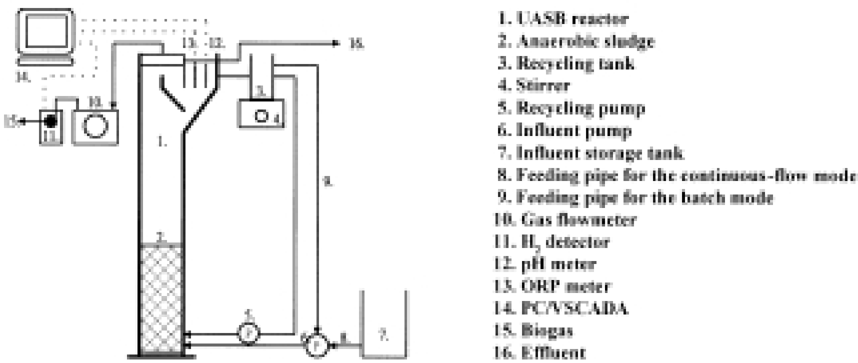

Figure 1 Schematic diagram of the bench-scale UASB reactor

Table 1 The compositions of the influent for the step change of shock loading

COD	pH	acetate	propionate	butyrate	EG	acetaldehyde
8,944	7.63	181	113	N.D.	2,473	3,247

The unit is mg/l except the pH. The word "N.D." means "not detected".

Table 2 The compositions of the influent for batch shock loading

COD (g/batch)	0.77	1.15	1.53	3.06	4.59	9.18
(A) acetaldehyde (g/batch)	0.5	0.75	1.0	2.0	3.0	6.0
(B) EG (g/batch)	0.59	0.88	1.18	3.36	3.53	7.07
(C) raw wastewater (ml/batch)	16.4	24.6	32.8	65.6	98.4	197

concentration was on-line monitored during the experiment. The experiment on each chemical group was performed with six different dosages that are equivalent to 0.77, 1.15, 1.53, 3.06, 4.59 and 9.18 gCOD/batch separately. Table 2 summarizes the compositions of the influent for batch shock loading.

Results and discussion

Continuous-flow mode with a step input of shock loading

pH. In the anaerobic biological reactor, the optimal pH range was demonstrated as 6.6 ~ 7.6 (McCarty and Smith, 1986). At pH < 6.2, the methanogenesis is inhibited but the acetogenesis can still function well. Figure 2 shows the change in pH profile during the shock loading. The pH value decreased from 7.02 to 6.56 due to the accumulation of volatile acid. The slight decrease of pH was owing to buffer capacity of $NaHCO_3$ in the UASB reactor.

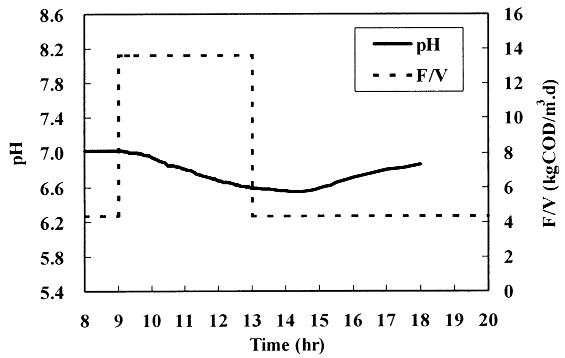

Figure 2 The variation in pH curve

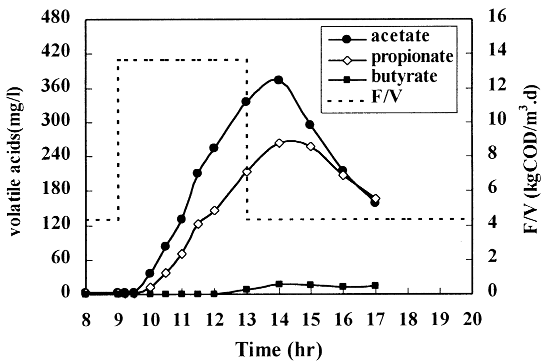

Figure 3 The variations in volatile acid curves.

Volatile acids. Figure 3 shows the variations in volatile acid (e.g. acetate, propionate and butyrate) curves. Levels of individual volatile acid accumulated significantly after shock loading. The rising tendency of the acetate curve is the most obvious, that significantly rises only one hour after starting the shock loading. The curve continually rises for about one hour and then descends after ending the shock loading. For the propionate curve, the rising tendency is similar to the acetate curve. However, the propionate concentration during the shock loading is lower than the acetate concentration. On the other hand, the butyrate is not detected in the influent as well as in the initial period of shock loading but is observed during the latter period.

Closely examining the monitoring profiles of volatile acid reveals that the accumulation rate is acetate > propionate > butyrate, furthermore, butyrate was detected under shock loading conditions even though it does not exist in the influent.

ORP (oxidation-reduction potential). A series of oxidation-reduction reactions is produced during the process of wastewater treatment. The ORP value can reflect the oxidation state under the circumstances. In this approach the variation of ORP is not relative to the shock loading time because the curve descends initially and rises later about 2 hours after starting the shock loading.

COD and TOC. Figure 4 shows the changes in COD and TOC curves. The COD concentration increased obviously (i.e. 42 % of change ratio) till about 1 hour after starting the shock loading. The rising tendency of this curve turns more significant latter. The COD continually rises about 1 ~ 2 hours after ending the shock loading and then descends smoothly. The variation in TOC curve is similar to the COD curve, but the obvious increase occurs at 1.5 hours after shock loading.

Biogas production rate. The biogas production rate has been found to be proportional to the COD removal amount (McCarty and Smith, 1986). The response of biogas production rate is more rapid than COD due to its short retention time. Figure 5 demonstrates the variation in the biogas production rate. Comparing the results between Figures 4 and 5, we discovered that the increase of the biogas production rate is more significant than that of COD.

H_2. In the anaerobic system, H_2 is produced from different reactions through various species of bacteria, and is consumed by the CO_2-reducing methanogenic bacteria. Figure 5 also depicts the variation in the H_2 curve. Results show that the H_2 concentration rapidly accumulated at the beginning of shock loading. The H_2 value increases from 123 to 296 ppm with the change ratio approximate 141% during the initial 1 hour and continuously rises to 678 ppm. The rapid rising tendency is similar to the result of H_2 variation by adding glucose, propionate and butyrate into the mesophilic digester (Whitmore *et al.*, 1985). Additionally, the accumulations of acetate, propionate and butyrate may be due to the increase of the H_2 partial pressure that may limit the degradation of volatile acid (Ferguson and Man, 1983).

The variation in H_2 concentration is rather sensitive to the shock loading. The H_2 curve rapidly decreases just 0.5 hours after stopping shock loading. Notably, the variations in other parameters such as COD and volatile acid rise continuously about 1 ~ 2 hours after stopping shock loading and then descend smoothly. Therefore, the response of H_2 concentration is different from the responses of other parameters. This result is similar to that presented by Guwy *et al*. (1997): the propionate and H_2 concentrations were not linearly correlated.

According to the above results, the biogas production parameters (H_2 and biogas production rate) are conclusively more sensitive than water quality parameters for the shock loading. Moreover, the H_2 concentration responds rapidly and varies significantly and can be adopted as an index for monitoring the strength of the influent, but is unsuitable as a standalone control variable for UASB.

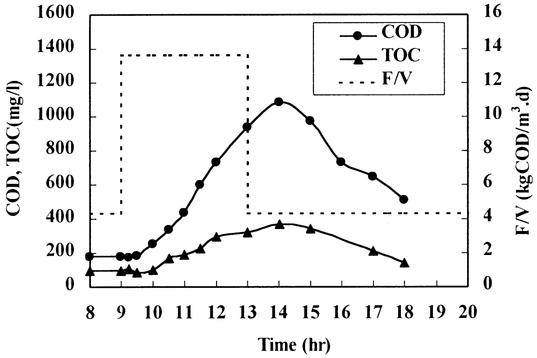

Figure 4 The variations in COD and TOC curves

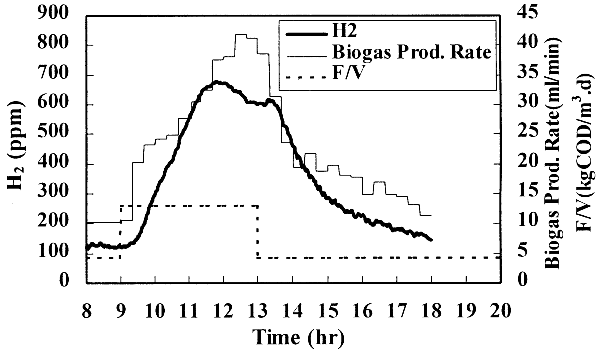

Figure 5 The variations in H_2 and biogas production rate curves for the continuous-flow mode

Batch mode with a pulse input of shock loading

H_2 curve. In Figure 6, the H_2 curves for three feeding formulas: (A) acetaldehyde, (B) EG and (C) raw wastewater are shown. The H_2 gas of these three different feedings significantly accumulated,which resulted in the rapid increase of the H_2 concentrations about 20 minutes after feeding acetaldehyde, EG and raw wastewater in pulse.

Among these three groups, the variation in the acetaldehyde feeding is the most obvious, as shown in Figure 6(A). The curve tendency of the raw wastewater feeding involving EG and acetaldehyde is smoother than the other two individual feedings that contain only one component separately. Therefore, we found that the variation in H_2 curve is correlated with the COD concentration and affected by the compositions of the feeding. The feeding using only one component causes a more significant increase of H_2 partial pressure and a steeper rise of the H_2 curve than the feeding using the raw wastewater with different components.

The H_2 production per unit COD. To further understand the effects of short-duration shock loading on the H_2 production, the H_2 production per unit COD was calculated. Figure 7 shows the relationship between the H_2 production per unit COD and the fed COD concentration. The H_2 production per unit COD varies dramatically for these three different feedings. The H_2 production per unit COD (Y) is linear to the fed COD concentration (X). Three equations for the (1) acetaldehyde, (2) EG and (3) raw wastewater feedings are shown as follows.

$$Y=1716X-216 \quad R^2=0.985 \text{———} (1)$$
$$Y=1394X-611 \quad R^2=0.991 \text{———} (2)$$
$$Y=1098X-706 \quad R^2=0.983 \text{———} (3)$$

Among these three feedings, the acetaldehyde feeding has the largest H_2 production with the maximum slope value, and the raw wastewater feeding has the smallest H_2 production.

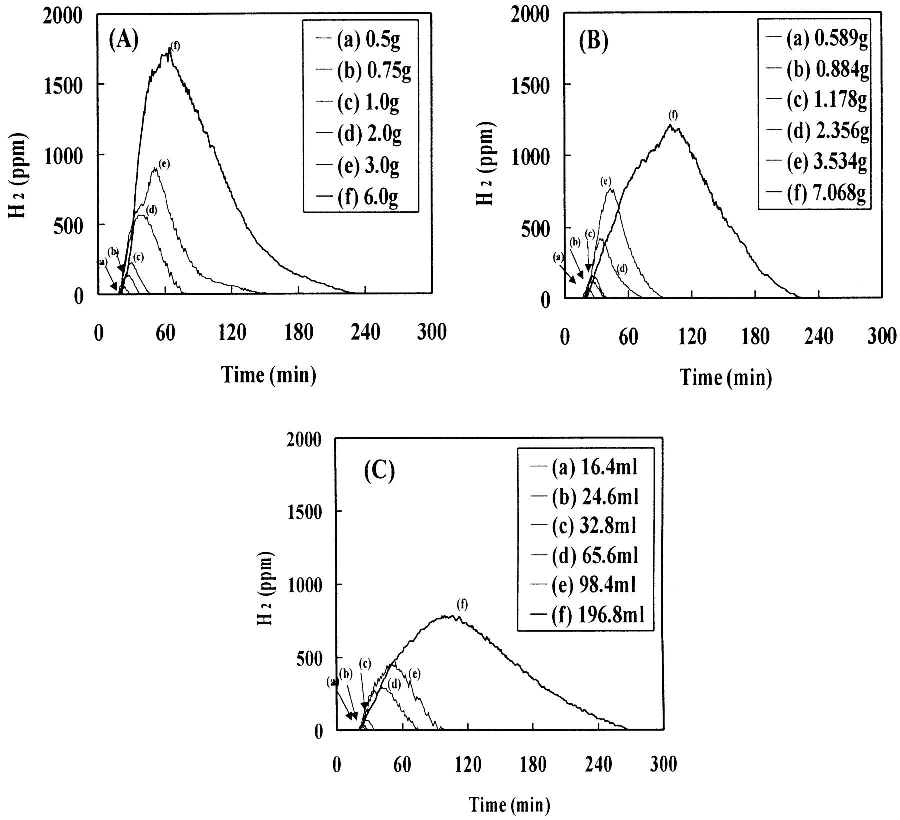

Figure 6 The H_2 curves for different feeding formulas: (A) acetaldehyde, (B) EG and (C) raw wastewater

The experiment of the raw wastewater feeding can be regarded as a toxicity bioassay of chemical mixtures. The relatively low H_2 production can be explained by the toxicity antagonism, that is, the mixture toxicity is less than that expected from a simple summation of the toxicities of the individual chemicals (Rand and Petrocelli, 1985). Therefore, the feeding with only one component has larger H_2 production per unit COD.

The negative value at X=0 of the intercept of the equations (1)~(3) is due to the response time of the H_2 detector and the time lag of the anaerobic bioreaction system. Furthermore, for the three equations, the respective X values are 0.13, 0.44 and 0.64 gCOD at Y=0. The X intercept of equation (1) is the smallest, and that of the equation (3) is the largest. It means that the COD removal by this anaerobic system may be limited seriously by acetaldehyde with just a little dosage. This phenomenon may be related to the higher toxicity of acetaldehyde. The acetaldehyde concentration that inhibited the activity by 50% (IC50) for the anaerobic bacteria is only 10 mM (LinChou *et al.*, 1978).

The maximum H_2 concentration ($[H_2]_{max}$). Figure 8 shows the changes in $[H_2]_{max}$ with the feeding COD concentration. The $[H_2]_{max}$ increases with the increasing fed COD concentration; the former is almost linear to the latter. Among these three groups, the largest $[H_2]_{max}$ value appears in the acetaldehyde feeding; the next in order is the EG feeding at the same dosage. Notably, the $[H_2]_{max}$ value obtained in the continuous-flow mode with a step change of raw wastewater concentration was 678 ppm for 22 g COD of long-duration shock loading. Comparing results between the continuous-flow mode (long-duration, feeding 22 gCOD during 4 hours) and the batch mode (short-duration, feeding 0.77~9.18 gCOD in pulse) shock loading, we discover that the wastewater quality is an important factor for affecting the H_2 production. Furthermore, the effect of shock loading for the short-duration

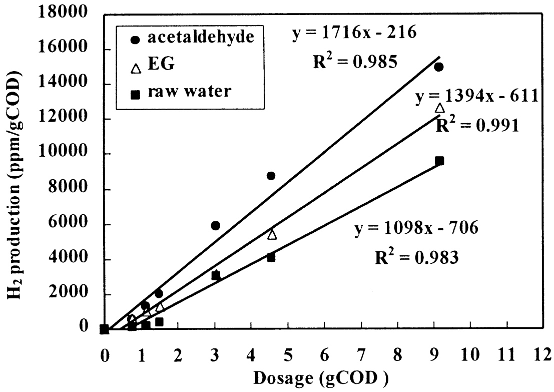

Figure 7 The H_2 production per unit COD for different feeding formulas

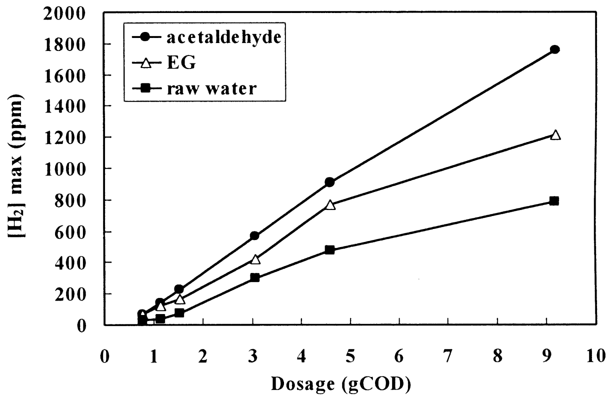

Figure 8 The $[H_2]$max per unit COD for different feeding formulas

shock loading is more prominent than for the long-duration shock loading, and the former leads to the larger rise of H_2 partial pressure. Rand and Petrocelli (1985) pointed out that an acute exposure to a single high concentration of a chemical may have an immediate adverse effect on the microorganisms, while continuous exposures with the same cumulative dosage as the single acute exposure may have less effect.

Conclusions

Based on the results presented herein, we can conclude the following. For treating the esterification wastewater with UASB, the index of biogas production parameters is more sensitive than that of water quality parameters for shock loading. The H_2 concentration responds rapidly and varies significantly. The factors such as COD, TOC and volatile acids increase with an increase of H_2 concentration, but no linear relationships between these factors and H_2 concentration are observed. Furthermore, butyrate can be detected under shock loading conditions even though it does not exist in the raw wastewater. Acetaldehyde is more toxic than EG for leading the H_2 partial pressure to accumulation. The H_2 concentration can be adopted as an index for monitoring the fluctuation of the influent loading.

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