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pH-CONTROLLED FEED-ON-DEMAND FOR HIGH-RATE ANAEROBIC SYSTEMS

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ABSTRACT

The carbonate and short chain fatty acid (SCFA) buffer subsystems govern the pH and thus the required alkalinity in high-rate anaerobic wastewater treatment systems. By controlling the SCFA concentration through a pH-controlled feed-on-demand system, the required alkalinity is only a function of the partial pressure of carbon dioxide (P_{CO2}), and for non-alkalinity producing substrates, independent of the organic loading rate. This makes the pH-controlled feed-on-demand system a simple and very effective method for minimising the start-up time and improving the reliability of high-rate anaerobic digestion. For maximum sensitivity the controlling pH was measured in a pH region near the bicarbonate equivalence point. This condition was obtained by measuring the pH in a biogas stripped side stream. The concept of pH-controlled feed-on-demand was successfully applied for the start-up and operation of an upflow anaerobic sludge bed (UASB) reactor, using SCFAs as substrate.

KEYWORDS

Bicarbonate equivalence point; feed-on-demand; high-rate anaerobic; pH-controlled; start-up.

INTRODUCTION

High-rate anaerobic digestion of soluble organic industrial wastewater has been achieved by separating the hydraulic retention time (HRT) and the biomass (sludge) retention time (SRT) (Iza *et al.*, 1991). Reactors with a variety of different biomass separation systems have been developed and each particular reactor configuration has its own method for start-up and control (Hickey *et al.*, 1991). Given the particularly complex, concentrated and fluctuating nature of anaerobic substrates as well as the multiplicity of different and often sensitive microbial groups involved (Pavlostathis and Giraldo-Gomez 1991), process control becomes very important for reliable digester operation.

Although a variety of factors can singularly or in combination cause digester failure, Ross and Louw (1987) considered metabolic overloading of the micro-organisms and the loss of biomass as principal ones. Indicators such as short chain fatty acids (SCFA) to alkalinity ratio, gas production rates and composition and pH are daily monitored for detecting gradual changes, so that corrective actions can be taken before process efficiency begins to decline (Hickey *et al.*, 1991). However, these monitoring strategies reveal little direct information concerning the metabolic activity of the biomass. Hickey *et al.* described a number of methods for on-line monitoring, but concluded that for most, the instrumentation is either complex, difficult to maintain or unavailable.

Since the organic loading rate in relation to the metabolic activity of the biomass seem to be important parameters during the start-up and subsequent operation of high-rate anaerobic digestion systems, it would be of great help if a simple method for the on-line control of these parameters could be developed.

This paper describes the use of a pH-controlled feed-on-demand system for the on-line control of organic loadings in high-rate anaerobic systems.

THEORETICAL BACKGROUND

Anaerobic step process

The anaerobic digestion of organic compounds to methane and carbon dioxide is a multistep process involving different physiological groups of micro-organisms (Pavlostathis and Giraldo-Gomez 1991). In the anaerobic digestion of soluble organic compounds, aceticlastic methanogenesis is one of the last steps and probably also the most important (McCarty and Mosey 1991). In this step acetic acid is converted to methane. All of the other SCFAs need to be converted to acetate before they can be converted to methane. The bacteria responsible for this step grow notoriously slowly and the kinetics of their growth often dominates the overall rate of the anaerobic digestion process. Their activity is often used as a measure of the activity of the anaerobic process (de Zeeuw 1984). The success or failure of a pH-controlled feed-on-demand system could thus be proved by using SCFA as substrate.

Buffers, pH and alkalinity

Moosbrugger *et al.* (1993a) reviewed the relevant buffer subsystems in anaerobic systems. Assuming that relatively low concentrations of phosphates and sulphides prevail, then only the carbonate and acetate buffer subsystems will dominate the pH range of 6.5 to 7.5, considered optimal for anaerobic digestion. The buffer index diagram for the carbonate and acetate subsystems is shown in Fig. 1.

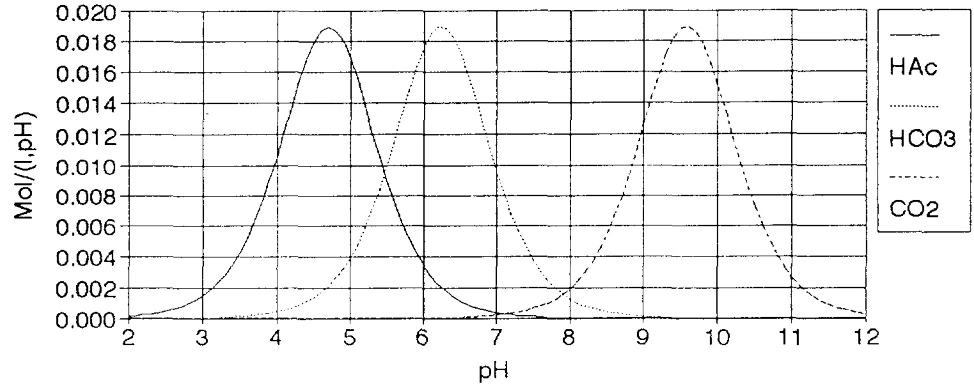

Fig. 1. Buffer index diagram for acetate and carbonate buffer subsystems.

Thus, if the SCFA in the reactor could be limited to relatively low concentrations, then the buffer capacity in the pH range optimal for anaerobic digestion is almost totally dependent on the carbonate weak acid/base buffering subsystems. This means that if the influent substrate contains no strong acids (or bases) the alkalinity needed to maintain the pH in this region is dependent on the prevailing partial pressure of carbon dioxide (P_{CO2}) in the reactor and for some substrates, independent of the COD strength of the influent. On this basis, Moosbrugger *et al.* (1993b) divides substrates into two basic categories: those that do not generate internal buffer (like carbohydrates) and hence depend completely on buffer from an external source and those that generate internal buffer, for example, proteins.

As the P_{CO2} controls the buffer action under these conditions, the amount of alkalinity required for a given P_{CO2} (whether it is externally added or internally generated) can be calculated from standard equilibrium expressions (Capri and Marais 1975, Loewenthal *et al.*, 1986). The relationship between alkalinity and pH for a few selected P_{CO2}s is shown graphically in Fig. 2.

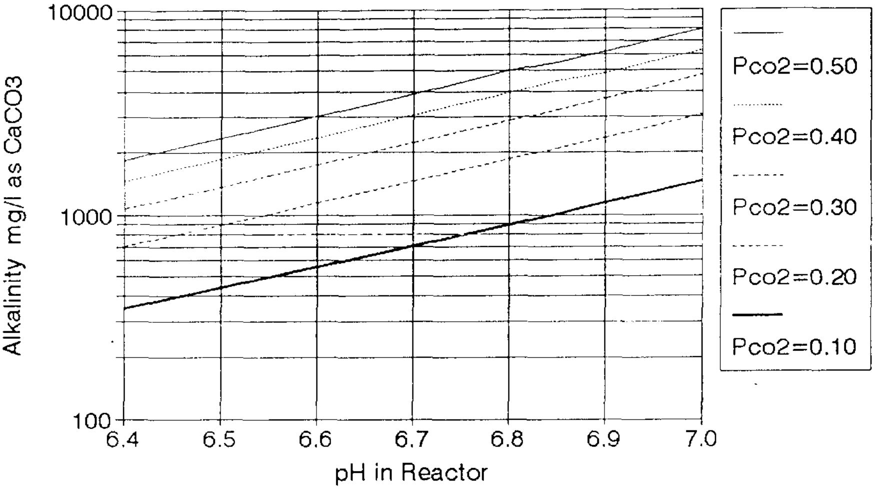

Fig. 2. pH/alkalinity relationships for different P_{CO2}s.

Buffer action and automated pH control

To produce high yields of acetate-grown methanogenic bacteria in minimum time, Sowers *et al.* (1984) kept environmental conditions optimal by feeding acetic acid to a batch culture via a pH-controlled feed-on-demand system. The pH probe was placed in the batch reactor. As the pH increased due to the metabolic conversion of acetate to neutral products and biogas, the loss of acetate was compensated for by the addition of acetic acid. This means, that in the feed-on-demand system, the organic loading rate was automatically maintained as a function of the metabolic activity of the micro-organisms.

Although the pH probe was placed in the reactor and thus measuring pH in the range where the carbonate buffer has a high buffer index (see Fig. 1), a pH change of 0.4 pH units (pH was 6.8 ± 0.2) was sufficient to maintain the acetate at a relatively constant concentration of 50 ± 5 mM.

In wastewater treatment high concentrations of SCFA in the effluent is generally not acceptable, because of the less efficient COD removal and higher external alkalinity demands for non-alkalinity producing effluents. Efforts should therefore be made to operate the high-rate anaerobic system so that the SCFA in the effluent is a minimum. This cannot readily be achieved if the feed rate controlling pH probe is placed inside the reactor because, not only is there a high buffer index (resisting pH changes), but the pH is also a function of the prevailing P_{CO2} and alkalinity concentration, which may vary. Ideally the controlling pH signal should be taken from an unbuffered region, i.e. giving a large pH change for a small increase in H^+, and where external factors (such as changes in P_{CO2} and alkalinity) have a minimum interfering effect on the pH. When the log species-pH diagram for the carbonate systems in water is examined, it is found that a bicarbonate ($HCO3^-$) equivalent solution has an equivalence point that is virtually independent of the other carbonate species concentration (Loewenthal *et al.*, 1986). In this pH region, pH buffering is a minimum and SCFA dissociates virtually completely to acetate and H^+, i.e. acts as a strong acid (Moosbrugger *et al.*, 1993a). For pH monitoring and process control purposes, the bicarbonate equivalence point of reactor contents can be achieved by reducing the P_{CO2} to atmospheric concentration. This can be done by stripping the biogas (CO_2) from a part of the reactor contents, taken from a position in the reactor which is considered important for the purpose of process control.

With this background as basis, a study was conducted where the alkalinity was fixed according to the P_{CO2} and the feed-on-demand principle was used for the start-up and operation of a high-rate anaerobic digestion system.

EXPERIMENTAL INVESTIGATION

Reactor set-up

A laboratory-scale upflow anaerobic sludge bed (UASB) reactor was constructed from a transparent 'Perspex' cylinder of 19 cm ∅, 200 cm high, with a solid/liquid gas separator at the top. The liquid volume up to the gas deflector was 41 l. Adjacent to the reactor was a biogas stripper consisting of a 5 cm ∅ x 50 cm long 'Perspex' tube, provided with an air diffusor and the necessary inlet and outlet ports. Clarified effluent was recycled through the biogas stripper followed by a pH electrode holder. The pH electrode was connected to a pH controller (Hanna Model HI8711E) which actuated the feed pump. All pumping required was by means of variable speed multi-channel peristaltic pumps. Gas production was measured with a syphon type gas meter (Veiga *et al.*, 1990). The reactor was operated in a constant temperature room at 35 °C. The reactor set-up is shown diagrammatically in Fig. 3.

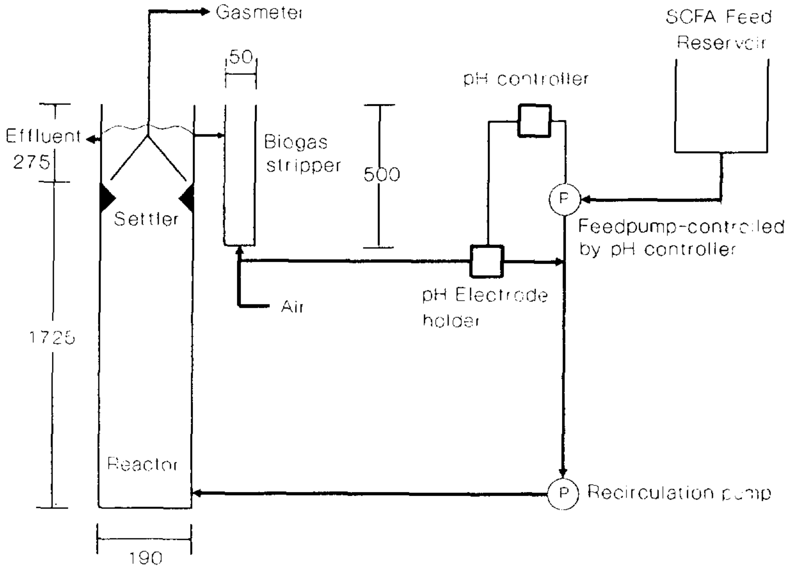

Fig. 3. UASB reactor set-up with pH controlled feed-on-demand.

Biogas stripping and recycle

The air flow to the biogas stripper was fixed at a nominal velocity of 50 $m.min^{-1}$ and the effluent recycle rate at 10 $l.h^{-1}$ giving an upflow rate of 35.27 $cm.h^{-1}$.

pH Controller

In the acid dosing mode the pH controller had a fixed on/off range of about 0.13 pH units below the set point value.

Feedstock and nutrients

A petrochemical effluent containing a mixture of SCFA (Kühn and Pretorius 1989) at a concentration of about 17 g COD l^{-1} was used as carbon and energy source. Ammonia and K_2HPO_4 were added to give a final COD : N : P of 600 : 4.8 : 1 respectively. Trace elements (Series II at half strength, Nel *et al.*, 1985) and NaOH to give 1500 $mg.l^{-1}$ alkalinity as $CaCO_3$ were added. The final pH of the feedstock was about 4.0. Feedstock was prepared in 100 l quantities and stored at room temperature.

Reactor preparation

Active digesting sewage sludge was screened through a BS Mesh No. 6 screen. The reactor was charged with 15 l of the screened sludge and filled to the working volume with tap water supplemented with ± 1000 $mg.l^{-1}$ sodium acetate. After 24 hours, recycling and biogas stripping were commenced and the pH-controller was set in 'start-up' mode.

Automatic operation

Two modes of operation were chosen: start-up mode and operational mode. During the start-up mode, substrate concentration in the reactor had to be kept at an optimum to allow maximum growth rates of the methanogenic bacteria. For the start-up period the pH-controller was arbitrarily set at pH 7.48 (on at pH 7.48 and off at 7.35). In operational mode, the main function of the pH controller was to protect the biomass from uncontrolled organic overload while at the same time achieving maximum COD reduction. This was done by setting the feed pump at a fixed rate giving an average volumetric loading rate of 5 kg $COD.(m^3.d)^{-1}$ and the pH controller set at pH 7.90.

ANALYSIS

Daily:
- Effluent samples for suspended solids (SS) and COD according to Standard Methods (1989).
- Cleaning the pH probe and recalibrate the pH controller.
- Measuring biogas and effluent volume.

Periodically:
- Microscopical observations of wet mounts of effluent using phase contrast illumination.
- Electron micrographs.
- Biogas composition using a Mariotte type gas meter filled with 5 N NaOH solution in tandem with syphon type gas meter. The volume difference registered being taken as CO2 absorbed.

RESULTS

Start-up

The initial pH in the biogas stripped recycle line was 8.6. The pH-controller was turned on, the feed pump was activated until a pH of 7.35 was reached when it was automatically turned off. The pH dropped further until it established at about 6.5. This pH overshoot was due to the time it took the substrate fed at the bottom of the reactor to reach the pH control point. To lessen the effect of pH overshoot, the feed pump rate setting was arbitrarily reduced to a point just slightly higher than the expected feed demand. The pH in the reactor was 6.00. The pH increased gradually for about 8 days while the gas production rate remained more or less constant at 650 ml.h^{-1}. After 8 days the pH of 7.48 was again reached in the biogas stripped effluent and subsequent the feed was automatically added in accordance with demand. The gas production rate during start-up is shown in Fig. 4.

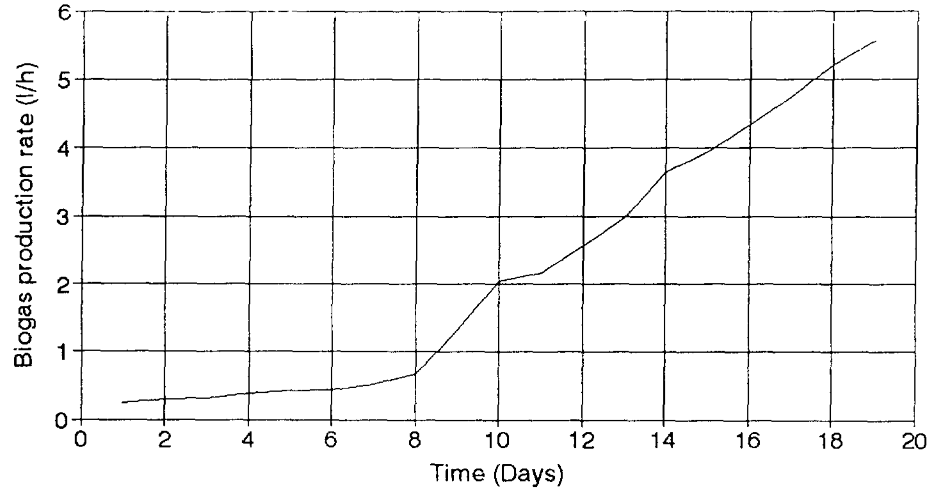

Fig. 4. Gas production rate (l.h^{-1}) during the start-up phase.

The SS, and COD in the effluent and the biogas COD produced are shown in Table 1.

TABLE 1. Effluent SS and COD Concentrations and COD Conversion to Biogas During Start-Up Phase

Parameter	n	x	σ
SS (mg ℓ$^{-1}$)	6	188	45
COD (mg.ℓ$^{-1}$)	9	2541	113
g biogas COD.(g feed COD)$^{-1}$	8	0.640	0.0157

n = number of samples x = average σ = standard deviation

Operational phase

The data obtained during operational phase are shown in Table 2

TABLE 2. Gas Production, Effluent Concentration and Biogas COD Produced During Operational Phase

Parameter	n	x	σ
ℓ biogas.h^{-1}	8	4.434	0.215
COD mg ℓ$^{-1}$	8	783	177
g biogas COD.(g feed COD)$^{-1}$	8	0.892	0.03

The approximate composition of the biogas was 77% CH_4:23% CO_2 during start-up and 85% CH_4:15% CO_2 during operational phase.

The dominant species of micro-organisms changed from a micrococcus type during the start-up phase to a filamentous type during the operational phase as shown in Fig. 5.

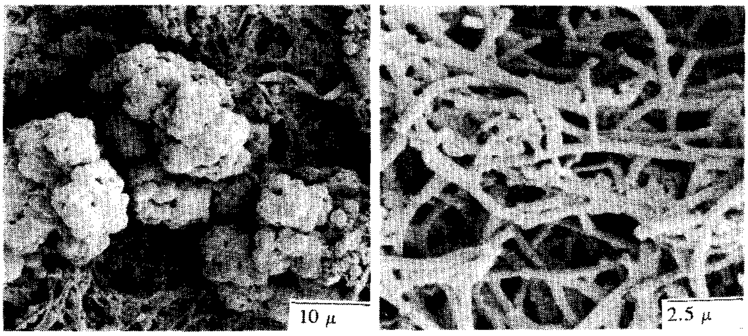

Fig. 5. (a) Micrococcus type bacteria dominating during start-up phase. (b) Filament type bacteria dominating during operational phase.

DISCUSSION AND CONCLUSIONS

After the addition of 1500 mg l^{-1} alkalinity to the feedstock the resultant pH was 4.00. This pH increased in the reactor to 6.57 due to methanogenesis. The pH of 6.57 corresponds very well with the calculated pH of 6.6 shown in Fig. 2 for a P_{CO2} of 0.23. This observation confirms the work of Moosbrugger *et al.* (1993b) that for substrates that do not generate interal buffer, the alkalinity required to maintain a particular pH in the reactor is a function of the P_{CO2} and not the COD concentration of the substrate. This means that once the P_{CO2}, digested effluent alkalinity and pH of a particular wastewater have been determined, the requirement of external alkalinity (if required) is only a function of the flow volume and independent of the COD strength of the wastewater. From Fig. 2 it can be seen that there is a logarithmic relationship between P_{CO2} and alkalinity required to maintain a particular pH in the reactor. This means that if the P_{CO2} in the reactor can be reduced by means of stripping CO_2 from the recycle stream or by recycling biogas from which the CO_2 has been absorbed, it would logarithmically reduce the alkalinity required from an external source.

After an initial acclimatisation period of 8 days biogas production rate increased linearly to reach the predetermined loading rate of 10 kg COD.$(m^3.d)^{-1}$ as shown in Fig. 4. Although the biogas production rate increased linearly, the effluent COD and biogas/feed did not vary much as shown in Table 1, indicating that the pH-controlled feed-on-demand automatically compensate for the increase in bioactivity.

Design operation

By increasing the fixed point pH to 7.90 the high rate anaerobic system re-adjusts, reducing the COD in the effluent to 783 mg l^{-1} with a corresponding increase in biogas/feed as shown in Table 2. Because the pH-controller keeps the conditions in the reactor within close limits, it is possible with the necessary influent flow equalisation to constantly produce a fixed quality effluent. With such a controlled system, organic overload and pH shocks are eliminated.

The prevailing COD (SCFA) concentration has a marked effect on the microbial population selected. When the average COD was 2541 mg l^{-1} during the start-up phase, Methanococcus type bacteria dominated, while, when the COD was reduced to 783 mg l^{-1}, Methanothrix bacteria dominated as shown in Fig. 5. This confirms the findings of other researchers (Harper and Suidan, 1991). From the information presented here it is clear that with rather simple instrumentation, good control can be exerted on high-rate anaerobic digestion systems, thereby not only shortening the start-up period, but also improving reliability by prevention of organic overloading with the resultant pH shock.

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