Weak acid/bases and pH control in anaerobic systems — A review

RE Moosbrugger, MC Wentzel*, GA Ekama and GvR Marais
Department of Civil Engineering, University of Cape Town, Rondebosch 7700, South Africa

Abstract

This paper briefly reviews the practical approaches that have been developed to evaluate and control anaerobic fermentation processes. Practical parameters considered are the H_2CO_3* alkalinity, short-chain fatty acid (SCFA) concentrations and pH. Various methods have been developed to determine either (1) the H_2CO_3* alkalinity or SCFA, (2) both the H_2CO_3* alkalinity and SCFA but approximately only, or, (3) an approximate H_2CO_3* alkalinity: SCFA ratio. None of these methods are entirely satisfactory for routine monitoring and control, being either too approximate or too elaborate in their analytical procedures. With the increased understanding of mixed weak acid/base chemistry, there is potential to develop a relatively simple acid titration procedure to give both the H_2CO_3* alkalinity and SCFA concentration reasonably accurately.

Introduction

In anaerobic fermentation a number of different microbial species contribute to the breakdown of soluble organic compounds to carbon dioxide and methane (Mosey and Fernandes, 1989; Sam-Soon et al., 1987). The main groups of bacterial species and the reactions they mediate are:

- acidogens: convert influent COD to acetic (HAc), propionic (HPr) and butyric (HBr) acid;
- acetogens: convert HPr and HBr to HAc;
- hydrogenotrophic methanogens: convert H_2 and CO_2 to CH_4; and
- acetoclastic methanogens: convert HAc to CH_4.

Each of these groups has a specific pH region for optimal growth; for acidogens a pH ~ 6, for acetogens, hydrogenotrophic and acetoclastic methanogens a pH ~ 7 (Gujer and Zehnder, 1983). The relative rates of growth of these groups change with pH. Under normal operating conditions in anaerobic digestion (see below), Mosey and Fernandes (1989) report the following average doubling times: acidogens: 30 min; acetogens: 1,4 d; hydrogenotrophic methanogens: 6 h; acetoclastic methanogens: 2,6 d. To ensure optimal breakdown one condition that must be satisfied is to provide optimal pH conditions for the slowest growing organism group. From Mosey's work, the acetoclastic methanogens are the rate limiting group; their growth rate is at its maximum at pH ~ 7,0 but falls sharply at pH < 6,6. Consequently, it is essential to maintain the pH > 6,6. Thus, information on the pH and on the factors causing/resisting change in pH is essential to ensure pH neutrality for the successful operation and control of the anaerobic system.

In anaerobic treatment systems, decline in pH would be due principally to an increase in short-chain fatty acids (SCFA). Increase in SCFA can be induced by a number of factors:

- Complete or partial phase separation of the acidogenic and methanogenic phases would result in an accumulation of SCFA in the acidogenic phase, and a decline of SCFA in the subsequent methanogenic phase. For example, in a plug flow or semi plug flow reactor like the upflow anaerobic sludge bed (UASB) reactor, along the axis of the reactor there is partial phase separation causing an increase in SCFA from the influent entry point to a maximum at some point in the reactor sludge bed, thereafter a decrease in SCFA to near zero at the top of the sludge bed.
- The hydrogen partial pressure (pH_2) also has a crucial effect on fermentation. For example, glucose is fermented first to pyruvic acid, via the Embden-Meyerhof pathway, and thereafter the pathways depend on the pH_2 conditions: Under low pH_2 conditions pyruvic acid is converted to HAc only, whereas under high pH_2 conditions HAc and the intermediate HPr are formed. Also with a high pH_2 in the reactor, the conversion of HPr to HAc by the acetogenic organisms is inhibited; these give rise to an increase in HPr and consequentially to an overall increase in SCFA.
- Toxins or inhibitory substances in the influent may act on the methanogenic phase only, causing an accumulation of SCFA.

The magnitude of the decline in pH induced by increased SCFA may be insubstantial due to the "pH buffering agents" in the reactor which would resist the pH change. However, an increase in SCFA in the effluent is in itself undesirable; it causes the effluent COD to increase, decreases gas production and the methane content of the gas. Accordingly, to manage and control an anaerobic system, information on pH, pH_2, SCFA (HAc and HPr), effluent COD, gas production rate, gas composition and "buffering agents" is desirable. The parameters pH, effluent COD, gas production rate and gas composition can be measured routinely: pH by means of a pH electrode (for plug flow systems pH profiles should be measured along the axis of the reactor, Sam-Soon et al., 1987), effluent COD by conventional wet chemical methods, gas production by gas flow meters and gas composition by Orsat-type apparatus. Measurement of pH_2 requires a rather sophisticated technique quite inappropriate for routine monitoring and hence its magnitude is inferred indirectly from the behaviour of the SCFA, HAc and HPr. Separate measurement of HAc and HPr in SCFA requires a gas chromatograph, an instrument, however, not usually available on full-scale anaerobic installations in South Africa. Monitoring and measurement of "buffering agents" are of great importance, but this aspect is complex and warrants more detailed attention.

In this paper the intention is to identify the "buffering agents" present in anaerobic treatment systems and to review the

*To whom all correspondence should be addressed.
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