Available online at www.sciencedirect.com
ScienceDirect
Bioresource Technology 99 (2008) 882–888
BIORESOURCE TECHNOLOGY

Prediction of methane yield at optimum pH for anaerobic digestion of organic fraction of municipal solid waste

Cun-fang Liu [a], Xing-zhong Yuan [a,*], Guang-ming Zeng [a], Wen-wei Li [a], Jing Li [b]

[a] College of Environmental Science and Engineering, Hunan University, Changsha, Hunan 410082, China
[b] Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China

Received 4 October 2006; received in revised form 11 January 2007; accepted 12 January 2007
Available online 21 March 2007

Abstract

A concept of methane yield at optimum pH was advanced and subsequently a mathematical model that simulates the optimal pH of a batch process for anaerobic digestion of organic fraction of municipal solid waste (MSW) was developed and validated. The model was developed on the basis of the microbial growth kinetics and was divided into three processes: hydrolysis of substrates by hydrolytic bacteria, consumption of soluble substrate by acidogenic bacteria, and finally consumption of acetate and methane generated by methanogenic bacteria. Material balance and liquid phase equilibrium chemistry were used in this study. A series of experiments were conducted to validate the model. The model simulation results agreed reasonably with experimental data in different temperatures and total solid (TS) concentrations under uncontrolled pH. A computer circulation program was used to predict the optimal pH in different conditions. Experiments in different temperatures and TS were run under optimal pH which predicted by the model. The model was succeeded in increasing the methane production and the cumulative methane production had an average increment about 35% in optimal pH of different temperatures and TS.

Keywords: Anaerobic process; Methane yield at optimum pH; Mathematical model; Municipal solid waste; Anaerobic batch reactor

1. Introduction

Anaerobic digestion is a natural process in which bacteria existing in oxygen-free environments decompose organic matter (Keshtkar et al., 2001). This has been proven as a sound technology for treatment of the organic fraction of municipal solid waste (MSW) which could generate renewable energy in the form of methane (Baere, 2000; Parawira et al., 2004).

Since the establishment of the first dynamic model for anaerobic process by Andrews (1969), mathematical models of anaerobic digestion process have been developed expeditiously with the ever-deepening understanding and widening application of anaerobic treatment. However, almost all these models are process description models and the influence of pH on the digestion process was not sufficiently considered. In Masse and Droste's (2000) model which simulated anaerobic digestion of swine manure sludge, the effects of pH variation on microbial kinetics were neglected. The studies of Keshtkar et al. (2001) and Siegrist et al. (2002) involved pH inhibition in the anaerobic digestion of cattle manure and sewage sludge, respectively, yet the pH was a factor other than a protagonist and the optimization of pH–methane yield relationships was not involved. The methane production efficiency is the most important evaluation yardstick in anaerobic digestion, there are several factors affecting methane production efficiency such as pH, temperature, type and quality of substrate, mixing etc. (Molnar and Bartha, 1989), and the value of pH is the pivotal factor. Although it has been proven that the optimal range of pH to obtain maximal biogas yield in anaerobic digestion is 6.5–7.5, the range

* Corresponding author. Tel.: +86 731 8823413; fax: +86 731 8823701.
E-mail address: yxz@hnu.cn (X.-z. Yuan).

0960-8524/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2007.01.013

is relative wide in the plant scale and the optimal value of pH varies with substrate and digestion technique.

In 2002, the ADM1 model was developed by the IWA Task Group for Mathematical Modeling of Anaerobic Digestion Processes. The model reflects the major processes that are involved in the conversion of complex organic substrates into methane and carbon dioxide and inert byproducts. In this model, all microbial mediated substrate conversion processes are subject to inhibition by extremes of pH. And an empirical correlation is employed as a process rate multiplier to reflect the effects of extreme pH (IWA, 2002). However, the ADM1 model employs a large number of constants and coefficients. Given the model complexity it was impossible to calibrate the model parameters with any of the data sets that were available (Parker, 2005).

The objective of this study was to develop a mathematical model which can describe the relationship between the pH and methane production for anaerobic digestion of organic fraction of municipal solid waste (MSW) in a batch process. A computer circulation program was used for obtaining the optimal pH and a maximal cumulative CH_4 production at this optimal pH. Therefore, the maximal recover energy of MSW can be obtained by using optimization control of pH.

2. Mathematical model

2.1. Model description

The process optimization mathematical model presented here is based on models developed by Moletta et al. (1986), Kiely et al. (1996) and Keshtkar et al. (2001). This model includes three processes: hydrolysis of substrates by hydrolytic bacteria, consumption of soluble substrate by acidogenic bacteria, and finally consumption of acetate and methane generation by methanogenic bacteria. This model is described as a set of algebraic equations that have been formulated based on mass balances for substrates, products and microbial components, and physico-chemical equilibrium relationships among ionized/unionized species. Harper and Pohland (1986) and Mosey (1983) indicated the dissolved hydrogen concentration in the digester controls the course of substrate utilization. A digester that is functioning well has a very low dissolved hydrogen concentration, so the influence of hydrogen concentration in digester is not considered in this model. Bacterial cell mass is represented by the empirical molecular formula $C_5H_7O_2N$. The growth of anaerobic microorganisms is expressed by Monod-type kinetics, the consumption of substrates and acids as well as the biomass decay is described by first-order reactions.

2.2. Model development

2.2.1. Hydrolysis kinetics

Complicated biodegradable organic substrate is hydrolyzed by hydrolytic bacteria and converted to soluble substrate in hydrolysis process. The variation of concentration of complicated biodegradable organic substrates with time can be expressed by

$$\frac{dS_h}{dt} = -\frac{\mu_h X_h}{Y_h} \tag{1}$$

where X_h is hydrolytic biomass (g/L); μ_h, the specific growth rate of hydrolytic bacteria (d^{-1}); S_h, glucose equivalent concentration of complicated biodegradable organic substrates (g/L); Y_h, the degradation coefficient of S_h ($g(X_h)/g(S_h)$). The hydrolytic biomass with time is

$$\frac{dX_h}{dt} = \mu_h X_h - K_{dh} X_h \tag{2}$$

where K_{dh} is the death rate of hydrolytic bacteria (d^{-1}). Suppose the inhibition factors have no influence on the hydrolytic bacteria basically (Vavilin et al., 1996). The specific growth rate of hydrolytic bacteria can be expresses as follows:

$$\mu_h = \frac{\mu_{hmax} S_h}{K_{sh} + S_h} \tag{3}$$

where μ_{hmax} is the maximum specific growth rate of hydrolytic bacteria (d^{-1}); K_{sh}, the half-velocity constant for hydrolytic bacteria growth (g/L).

2.2.2. Acidification kinetics

In acidification process, the soluble substrate is metabolized by acid-producing bacteria to provide carbon dioxide and organic acids. Then the long chain organic acids are converted into acetates by acidogenic bacteria (Nopharatana et al., 2003). The variation of concentration of soluble substrates with time is

$$\frac{dS_a}{dt} = \frac{\mu_h X_h}{Y_{vh}} - \frac{\mu_a X_a}{Y_a} \tag{4}$$

where X_a is the acidogenic biomass (g/L); μ_a, the specific growth rate of acidogenic bacteria (d^{-1}); S_a, glucose equivalent concentration of soluble substrates (g/L); Y_a, the degradation coefficient of S_a ($g(X_h)/g(S_a)$); Y_{vh}, the yield coefficient for S_a ($g(X_a)/g(S_a)$). The variation of acidogenic biomass with time is

$$\frac{dX_a}{dt} = \mu_a X_a - K_{da} X_a \tag{5}$$

where K_{da} is the death rate of acidogenic bacteria (d^{-1}). The unionized acetate will influence acidogenic bacteria which are sensitive to pH. So the growth of acidogenic bacteria is obeyed by modified Monod-type kinetics as follows:

$$\mu_a = \frac{\mu_{amax}}{1 + \frac{K_{sa}}{S_a} + \frac{A_u}{K_{ia}}} \tag{6}$$

where μ_{amax} is the maximum specific growth rate of acidogenic bacteria (d^{-1}); K_{sa}, the half-velocity constant for acidogenic bacteria growth (g/L); A_u, the concentration of unionized acetate (g/L); K_{ia}, the inhibition coefficient of unionized acetate (g/L).