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Anaerobic fermentation of cattle manure: Modeling of hydrolysis and acidogenesis

M. Myint[a], N. Nirmalakhandan[b,*], R.E. Speece[c]

[a]Civil Engineering Department, MSC 3CE, New Mexico State University, Las Cruces, NM 88003, USA
[b]Civil Engineering Department, MSC 3CE, New Mexico State University, Las Cruces, NM 88003, USA
[c]Civil Engineering Department, Vanderbilt University, Nashville, TN 37235, USA

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ABSTRACT

A mathematical model for the hydrolysis and acidogenesis reactions in anaerobic digestion of cattle manure is presented. This model is based on the premise that particulate hydrolysable fraction of cattle manure is composed of cellulose and hemicellulose that are hydrolyzed at different rates according to a surface-limiting reaction; and, that the respective soluble products of hydrolysis are utilized by acidogens at different rates, according to a two-substrate, single-biomass model. Batch experimental results were used to identify the sensitive parameters and to calibrate and validate the model. Results predicted by the model agreed well with the experimentally measured data not used in the calibration process, with correlation coefficient exceeding 0.91. These results indicate that the most significant parameter in the hydrolysis–acidogenesis phase is the hydrolysis rate constant for the cellulose fraction.

1. Introduction

Manure residues from livestock industries have been identified as a major source of environmental pollution. Traditionally, these wastes have been disposed of, directly or after composting, as soil amendments in the agricultural industry (van Horn et al., 1994; USDA, 1995). Since this practice has resulted in the degradation of air, soil, and water resources, new regulations for protecting the environment have been promulgated to control land application of animal manure (US EPA, 1995). As such, livestock industries and regulatory agencies are seeking alternate technologies to manage manure residues in environment-friendly manner (Sims, 1995; van Horn et al., 1994; USDA, 1995).

Biotechnologies have the potential to manage this problem in a cost-effective and sustainable manner. Even though cattle manure residues are complex and naturally polymeric (Palmisano and Barlaz, 1996; Ong et al., 2000), anaerobic digestion has been recognized as a preferred process for stabilizing such complex wastes and at the same time regenerating useful chemicals, generating energy, and reducing the volume for disposal (Ghosh, 1987; Speece, 1996; Lettinga, 2001).

1.1. *Anaerobic technology*

Anaerobic digestion of complex wastes in the *liquid form* (<5% total solids) is a mature technology that has been well studied and successfully implemented at full-scale (Speece, 1996; Munch et al., 1999). Several studies have adapted this technology to digest particulate wastes in *slurry form* (5–15% total solids). More recently, feasibility of anaerobic digestion of *high-solid substrates* (>20% total solids content), referred to as "dry digestion", has been demonstrated (Mata-Alvarez,

*Corresponding author. Tel.: +1 505 646 5378; fax: +1 505 646 6049.
E-mail address: nkhandan@nmsu.edu (N. Nirmalakhandan).
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1989; Kayhanian et al., 1996; Vavilin et al., 2002). Examples of dry digestion studies include: municipal solid wastes in a leach-bed reactor (Ghosh, 1987); fruit and vegetable wastes in a plug flow reactor (Negri et al., 1993); organic fraction of municipal solid wastes in a solid phase reactor (Veeken et al., 2000) and with leachate recycling (Vavilin et al., 2002); and food wastes by a hybrid solid–liquid reactor (Hai-Lou et al., 2002).

In the case of animal wastes, anaerobic digestion in *slurry form* has been reported previously (Hill and Barth, 1977; Eastman and Ferguson, 1981; Hashimoto et al., 1981; Bryers, 1985; Munch et al., 1999; Masse and Droste, 2000; Miron et al., 2000; Ruel et al., 2002; Noykova et al., 2002; Sung and Santha, 2003; Mahmoud et al., 2004). However, dry-digestion of animal wastes has not been investigated.

The anaerobic conversion of particulate substrates to biogases has been regarded as taking place in two distinct phases—an acid-production phase and an acid-consumption phase (Munch et al., 1999). The conversion process involves at least six independent, parallel, and sequential reactions, mediated by different groups of biomass under different environments (Gujer and Zehnder, 1983; Mata-Alvarez, 1987; Noykova et al., 2002). These reactions include: (1) *anaerobic hydrolysis* where, hydrolysable complex particulate organics such as insoluble cellulose and hemicellulose, are converted into monomers such as amino acids, sugars, and long-chain fatty acids; (2) *fermentation* where, amino acids and sugars are converted to volatile fatty acids; (3) *acetogenesis* where, long-chained fatty acids are converted to acetate and hydrogen; (4) *anaerobic oxidation* where, intermediate products such as volatile fatty acids are converted to acetate and hydrogen; (5) *aceticlastic methanogenesis* where, acetate is converted to methane by acid-utilizing methanogens ; and (6) *hydrogenotrophic methanogenesis* where, hydrogen is converted to methane by hydrogen-utilizing methanogens.

Most of the studies on anaerobic digestion of organic particulates in slurry form have concluded that hydrolysis is the rate-controlling step in the overall process (Eastman and Ferguson, 1981; Gossett and Belser, 1982; Pavlostathis and Giraldo-Gomez, 1991; Veeken et al., 2000; Vavilin et al., 2002). Therefore, attempts to improve the overall process have to focus on the hydrolysis reaction.

1.2. *Anaerobic hydrolysis*

Even though Bryers (1985) and Mata-Alvarez (1989), among others, had pointed out that the mechanisms, stoichiometry, kinetics, and modeling of biological particulate hydrolysis had not been adequately studied, recent reports have addressed many of those areas. Most of the early studies, including the first anaerobic digestion model (ADM1) proposed by IWA, had focused mainly on fermentation and methane production (Ruel et al., 2002; Batstone et al., 2002).

In one of the early studies of anaerobic hydrolysis of animal waste slurries, the kinetics of the process was assumed first-order in acidogenic biomass (Hill and Barth, 1977). In a study of digestion of primary sludge, Eastman and Ferguson (1981) assumed first-order hydrolysis kinetics in the remaining particulate concentration. Recognizing the limited knowledge about the mechanisms and kinetics of this phase, Bryers (1985) followed the same assumption as Eastman and Ferguson (1981). Mahmoud et al. (2004) have used a similar approach in their study of anaerobic stabilization of primary sludge. Noykova et al. (2002) assumed second-order kinetics in acidogenic biomass concentration and volatile solids concentration.

Munch et al. (1999) have proposed a kinetic expression based on the observation from the Contois kinetic model that the hydrolysis rate is reduced when the biomass concentration is high, probably due to limited surface area causing mass transfer limitations. Their work proposed the hydrolysis rate to be proportional to the ratio of (particulate concentration $\times$ hydrolytic enzymes concentration) to acidogenic biomass concentration. This model is similar to that proposed in the IWA Activated sludge Model No. 2. Ruel et al. (2002) followed a similar approach, incorporating the concept of surface-limited reaction, with a maximum rate for anaerobic hydrolysis and a saturation coefficient, limited by the ratio of particulate concentration to acidogenic biomass concentration.

In a review of the relevant literature up to 1990, Pavlostathis and Giraldo-Gomez (1991) found that most studies had used the first-order model to describe anaerobic hydrolysis of particulate wastes. Subsequent studies have affirmed this conclusion, but using different models for the hydrolysis process (Munch et al., 1999; Veeken et al., 2000; Ruel et al., 2002; and Mahmoud et al., 2004). We have evaluated three of the more common hydrolysis models—the first-order model; the second-order model; and the surface-limiting reaction model, for their suitability in describing hydrolysis-acidogenesis of cattle manure residues. We found that the two-parameter, surface-limiting reaction model followed the trend of the measured data more closely and fitted the measured data slightly better than the other two models (Myint and Nirmalakhandan, 2006).

1.3. *Objectives of this study*

Our ongoing study builds upon the literature reports to develop a 2-phase leach-bed reactor system for dry digestion of cattle manure residues. One of the goals of our study is to optimize chemical oxygen demand (COD) generation by enhancing hydrolysis and acidogenesis and minimizing methanogenic activity by maintaining pH below 5.5 (Eastman and Ferguson, 1981; Yu et al., 2003) and heat treatment of seed sludge (Oh et al., 2003). The objectives of this paper are to develop a two-substrate, single-biomass model for the hydrolysis/acidogenesis phase and to validate it using batch experimental data. Also included in this paper are a sensitivity analysis of the model parameters, and a comparison of the parameters with values from the literature.

2. Modeling approach

In our preliminary studies of dry digestion of cattle manure residues in a leach-bed reactor, substrate degradation curves typically exhibited two distinct segments. Based on the reports by Frigon et al. (2002), Ong et al. (2000), Orhon et al. (1999), Chandler and Jewell (1980) and Robbins et al. (1979), we