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Fractal-like kinetics of the solid-state anaerobic digestion

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ABSTRACT

Total solid content (TS) negatively impacts the methane production efficiency (MPE) of solid-state anaerobic digestion (SS-AD), to which the classic mass action-based kinetics failed to provide a unified explanation. This study revealed that SS-AD reactions actually follow the fractal-like kinetics in light of the surface reactions in crowded SS-AD environment packed with heterogeneous media. The fractal characteristics of the SS-AD kinetics were found increasingly pronounced as TS increased. This study represents the first attempt to resolve the dilemma in SS-AD kinetics with the application of fractal theory. Employing this new concept allows explaining the reduced MPE at high TS and offers an easy assessment of the fractal characteristics of the SS-AD media.

1. Introduction

Anaerobic digestion (AD) enables biological conversion of organic matter into bioenergy in the form of methane gas in an oxygen-free environment (Karthikeyan and Visvanathan, 2013). This popular technique can be categorized into either liquid AD (L-AD) or solid-state AD (SS-AD) based on the total solid content (TS) in reactors (Li et al., 2011). Traditionally, AD processes operating with diluted TS ranging from 0.5% to 15% are categorized as L-AD; while, SS-AD should be capable of handling solid waste with TS greater than 15% (Li et al., 2011). With less water in reactors, SS-AD demonstrated a variety of advantages over L-AD including compact reactor size, simple design, high loading capacity, reduced heating demand, less leachate production, easy digestate handling, and reduced nutrient runoff during the digestate storage and distribution (Jha et al., 2011). For these advantages, SS-AD has gained increased attention and application in recent years along with the growing market demand for solid organic wastes treatment (Karthikeyan and Visvanathan, 2013).

Yet, accumulated experimental evidence also revealed that the methane production efficiency (MPE) (ml methane g^{-1} initial volatile solids (VS)) out of SS-AD tends to decrease with the increase in TS. This phenomenon was particularly prominent in the later stage of SS-AD when MPE profiles plateaued at levels inversely related to the initial TS employed (Figs. 1 and 2), leaving large fractions of organics undigested in spite of prolonged reaction time (Fernandez et al., 2010; Fujishima et al., 2000; Le Hyaric et al., 2012; Li and Wang, 2011; Motte et al., 2013a). For instance, even with 300 days of digestion, MPEs in SS-AD with high TS were still found far below their theoretical methane yield values (Abbassi-Guendouz et al., 2012; Pommier et al., 2007), indicating the peculiarity of SS-AD kinetics. Product inhibition as a result of high organic loading is usually used as a convenient explanation (Karthikeyan and Visvanathan, 2013). However, the reduced MPE at increased TS was also frequently reported in SS-AD with neither volatile fatty acid accumulation nor pH decline (Abbassi-Guendouz et al., 2012; Motte et al., 2013b; Xu et al., 2014). This is especially true when lignocellulosic biomass was used as the feedstock in SS-AD, because in this case hydrolysis is usually the rate-limited step, which is bound to minimize intermediate product accumulation (Table 1). Many studies attempted to shed light on this peculiarity of the SS-AD through kinetic modeling (Table 1), which has prompted researchers to inversely correlate the negative effect of TS to various kinetic parameters such as the hydrolysis rate coefficient, mass diffusion or transfer coefficients, maximum specific growth rate, half-saturation coefficient, etc. (Table 1). Interestingly, all these approaches, even though with different kinetic parameters adjusted, were all originated from the same modeling framework, namely anaerobic digestion model No. 1 (ADM1) (Batstone et al., 2001), implying the incompetence of ADM1 in providing a consistent explanation for the negative TS effect on SS-AD. It should be also noted that ADM1 is a very difficult to use modeling system for its structural complexity (Donoso-Bravo et al., 2011).

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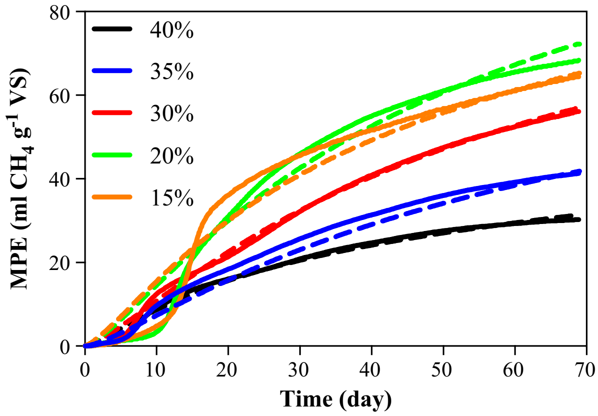

Fig. 1. MPE profiles from the SS-AD of corn stover at various TS percentages; solid line – respirometer data logged at two-hour interval (one of the two replicate data set is presented); dashed line – Eq. (10) simulated data with parameters in Table 2.

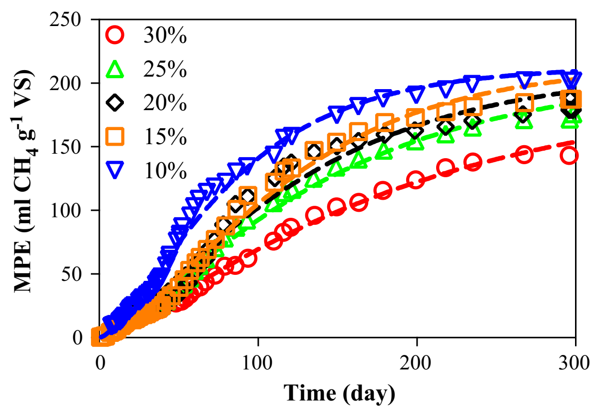

Fig. 2. MPE profiles from the SS-AD of cardboard at various TS percentages; symbol – experimental data from the study by Abbassi-Guendouz et al. (2012); dashed line – Eq. (10) simulated data with parameters in Table 3.

Besides, ADM1 was originally developed based on the classic mass-action law for completely mixed system such as L-AD. Implicit in this is the assumption that the reaction should have occurred in dilute solutions that are spatially homogeneous. On the contrary, the media environment inside SS-AD reactors is characterized by particle crowding, heterogeneous characteristics, and non-uniform distribution (Li et al., 2011), in which the reaction kinetics can be quite different from its homogeneous counterpart in L-AD.

About two decades ago, a fractal kinetic theory was introduced for describing the reaction dynamics in heterogeneous environment (Kopelman, 1988). This theory provided explanation for heterogeneous reactions in crowded environments spatially constrained on the microscopic level by pore channels or phase boundaries, which is similar to the media environment in SS-AD. Moreover, this fractal kinetic approach is dependent on averaging a large number of probabilistic events to capture the essence of complex phenomena such as those in SS-AD, which may allow for a simplistic modeling structure beyond the capacity of the ADM1 (Xu and Ding, 2007). So far, this fractal theory has been broadly applied for kinetic modeling of reactions such as those occurring in crowded environment (Neff et al., 2011), on solid surface (Haerifar and Azizian, 2014), controlled by mass diffusion (Park, 2001), spatially segregated (Berry, 2002), with lignocellulosic biomass as substrate (Yao et al., 2011) and so on. Although these types of kinetics are closely relevant to the actual situations in SS-AD reactions, unfortunately, this fractal kinetics has yet to be introduced to the SS-AD study. In this work, we firstly presented the evidence that the mass action kinetics is not suitable for SS-AD. Then, we presented fractal-like simulations of SS-AD performance with varying TS. It is our intention to investigate the SS-AD kinetics under crowded, heterogeneous conditions with the aid of fractal theory. The present work represents the first attempt to introduce fractal-like kinetics in SS-AD modeling to provide a solution to one of the major challenges baffling those interested in the understanding of SS-AD.

2. Experimental section

2.1. Experimental procedure

2.1.1. Substrate and inoculum

Corn stover was collected from a farm operated by the Ohio Agriculture Research and Development Center (Wooster, Ohio, USA). Before use, the corn stover was dried at 40 °C in a drying oven (VWR/Sheldon Manufacture Inc., Cornelius, OR, USA) for 24 h to a moisture content of less than 10% and then ground to pass a 12.7 mm sieve (Mighty Mac, MacKissic Inc., Parker Ford, PA, USA). L-AD effluent obtained from a mesophilic anaerobic digester (Akron, OH, USA) fed with municipal wastewater sewage sludge was used as inoculum. The L-AD effluent was incubated at 37 ± 1 °C for 2 days to activate inoculum prior to use.

2.1.2. Batch mode anaerobic digestion

Anaerobic bottles (250 mL) were loaded with mixtures of corn stover and inoculum at a fixed F/M ratio = 2 (VS basis). Pretreated digester leachate was added into each bottle to adjust the TS content from 15% to 40%. The leachate was obtained from a commercial centrifuge in the same aforementioned L-AD digester located in Akron, OH, with the TS less than 0.2%. The detailed characteristics of the leachate can be found in a previously published paper (Sheets et al., 2014). The leachate was stabilized at 37 °C for 7 days

Table 1
A summary of the existing kinetic approaches for explaining the negative TS effect on SS-AD performance.

Parameter adjusted	Mechanism	Rate-limiting	Feedstock	TS range	Model	Literature
Decreased hydrolysis rate coefficient	Diffusion limitation	Hydrolysis	Corn stover	1–28%	ADM1	Xu et al. (2014)
			Wheat straw	15–25%		
			Cardboard	10–35%		
Decreased disintegration coefficient	Unspecified	Disintegration	Rice straw & food waste	4.5–23%	ADM1	Liotta et al. (2014a)
		Unspecified	Carrot waste	5–11.3%	ADM1	Liotta et al. (2014b)
Increased half-saturation coefficient	Diffusion limitation	Hydrolysis	Municipal solid waste with acetate addition	18–25%	ADM1	Bollon et al. (2011)
Decreased maximum specific growth rate	Unspecified	Unspecified	Rice straw and food waste	4.5–23%	ADM1	Liotta et al. (2014a)
Decreased mass transfer coefficient	Mass transfer limitation	Hydrolysis	Cardboard	10–30%	ADM1	Abbassi-Guendouz et al. (2012)
Decreased maximum specific growth rate & accessibility coefficient	Substrate accessibility limitation	Hydrolysis	Paper, cardboard	6–60%	Logistic	Pommier et al. (2007)