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Clarifying configurations of reaction rate constant for first-order and Monod-type kinetics: A comparative manner and a pursuit of parametric definition

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ABSTRACT

The mechanisms of first-order and Monod-type kinetics describes degradation in distinct manner and yet too little attention is paid on the fact that first-order kinetic was derived from pure elementary reaction while Monod-type degradation was based on microbial uptake. Both mechanisms are basic theories in developing sophisticated degradation models and there are needs to give more guidance on selection of kinetics. The objective of this study was to compare the two kinetics when used for modeling degradation and biodegradability during composting. With both experimental data, from reactor composting of swine manure/wheat straw, and simulated results, it was found that Monod-type kinetic was more capable of modeling the lag phase, while first-order kinetic could explain the fast oxygen uptake rate for the oxidation of soluble substrate. Comparison of growth rate constants, based on Monod-type equation, with maximum degradation rate constants, based on first-order kinetic, showed that the former was generally one magnitude greater, which could be explained with the fact that part of growth of cell weight was from water consumption.

1. Introduction

Understanding substrate degradation is crucial for understanding composting and the design of a successful facility (Mason, 2006; Sadef et al., 2014; Wang et al., 2014; Wang et al., 2016; Zhu et al., 2004). Biological activity can be assessed using degradation in terms of total-solid reduction or volatile-solid reduction. Heat production from substrate degradation drives the temperature rise that is important for sanitation in composting (Neves et al., 2007; Zhu et al., 2004). For an effective process, understanding degradation kinetics is key towards determining oxygen supply (Ge et al., 2015; Lin et al., 2008; Mason, 2006; Nakasaki et al., 1987), and to control thermal balance (Boniecki et al., 2013; Wang et al., 2011; Wang et al., 2014; Wang et al., 2016) or biological water production (Makan et al., 2013; Wang et al., 2015; Zhou et al., 2014). Development of degradation kinetic that can reasonably describe the biodegradation process is thus important for better predictions of mass and thermal balances during composting. Since substrate degradation is a complicated and interactive process, it is necessary to introduce systematic dynamics to understand it. Previous studies on inedible biomass biodegradation for advanced life support system (Ramirez-Perez et al., 2007; Ramírez Pérez, 2013) comprehensively addressed the physical, chemical and microbiological influences over degradation, on which the kinetics were derived to express biodegradability. A composting kinetic (Hamelers, 2001), with a strength on deploying the model to a range of particle size, was presented to gap the limitations that more or less the current models were based on empirical insights. It seems that either first-order or Monod kinetics can be used as a basic concept to express very comprehensive degradation process, but one should be very careful on variable definitions and parametrical configurations. Mathematical modeling and simulation can be a useful method to assess substrate degradation during composting.

First-order and Monod type kinetics are the most commonly used models to estimate rate of substrate degradation for composting process (Mason, 2006). First-order kinetic describes degradation as enzymatic bio-reactions, and microbial concentration is generally considered to be non-limiting (Haug, 1993). First-order kinetics was organically derived from pure enzymatic system with assumptions that enzyme concentration was not rate-limiting while substrate concentration was rate-limiting. Monod-type equation normally introduces degradation as substrate consumption

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during biological growth, and microbial concentration is considered limiting. Using these basic models, the mathematical description of degradation can be comprehensive. For complex situation like composting, one way to deal with the complexity of hundreds of substrates degrading simultaneously is to associate each type of substrate degradation with a unique first-order or Monod equation. From disintegration of particulates to uptake of VFAs, twelve Monod-type biological steps were generalized to represent the anaerobic digestion of wastes such as manure or municipal sludge (Batstone et al., 2002). Composting materials can normally be considered as a combination of various types of organics (Kaiser, 1996; Wang and Ai, 2016; Woodford, 2009). Another comprehensive degradation form is to divide the composting mixture into distinct types of organics and associate each type of organic with its own degradation kinetic. Either way, both first-order and Monod-type kinetics have proven to be practical in modeling substrate degradation (Petric and Mustafic, 2015; Shishido and Seki, 2015; Vasiliadou et al., 2015; Zhang et al., 2016; Zhang et al., 2015). However, first-order and Monod-type kinetics are both simplified mathematical forms with assumptions. There is a need to compare the two kinetic models in order to determine their effectiveness under specific degradation condition. The procedure for comparing between first-order and Monod-type kinetics has not been comprehensively addressed.

While degradation kinetics generally give an idea for the quantification of degradation speed, biodegradability is an important characteristic of raw composting materials indicating the amount of substrate energy available to drive the composting process. Biodegradability was once believed to be the most important factor to the design and successful operation of a composting system in terms of temperature sanitation, oxygen demand, and the air demand for heat removal (Haug, 1993). However, degradation rates also have great effects on temperature increment or decrement, oxygen uptake rates, and determination of aeration levels. For instance, temperature will probably get higher if the respiratory heat production from degradation is faster, which relatively shortens the time for exchange of heat with ambient environment. How high the temperature will get is one issue while how long the high temperature will last is another. It seems degradation rate is more important for getting a higher peak temperature, while biodegradability has influence on maintaining high temperatures.

A number of methods are available for measuring or estimating substrate biodegradability. The mass balance approach and respiratory tests are commonly employed in composting research (Dıaz et al., 2003; Haug, 1993; Kulcu, 2014; Wang et al., 2014). Respiratory approach normally introduces BOD and COD tests. BOD testing measures oxygen concentrations in dilution water and is primarily designed for liquid sample of small volume. Sometimes, quantification of carbon dioxide produced could also be used for measurement of BOD. The method shows better consistency for homogeneous substrate, which is sometimes not the case for composting materials. Ultimate BOD is often considered to be the biological oxygen demand at a certain time, but this time range varies considerably for different composting materials. Compared to respiratory testing, mass balance approach is easier to conduct, and the method is more reliable for heterogeneous solid substrates. All these methods require a real composting operation to collect representative samples. On the other hand, degradation kinetics can be used to estimate continuous biodegradability during the whole composting process if the relationship between biodegradability and degradation kinetics can be modeled. Yet, no previous study has comprehensively looked into developing a model that relates the degradation kinetics with biodegradability.

The objectives of this study are thus two folds: (1) on an engineering perspective, compare degradation models in composting that used either the first-order kinetic or the Monod-type kinetic, serving as a guidance for selection of kinetics when much more sophisticated degradation models with sub steps of biochemical processes are about to be developed on those basic equations; (2) develop and compare simulation biodegradability models that use either the first-order kinetic or the Monod-type kinetic and validate this model with a physical composting process. Additionally, to understand these kinetic and biodegradability models in greater depths, we also explored the impact of different model inputs on the biodegradability model as well as how the different kinetics can be used to determine the rate-limiting step during composting.

2. Materials and methods

2.1. Modeling of substrate degradation

This study was trying to keep the format of those kinetics, first-order and Monod kinetics, as simple as they could be, and only adjustments of significant importance, like temperature or oxygen concentration, were outlined.

With a simple expression, first-order kinetics was introduced as one of the earliest model for the degradation of biodegradable volatile solids, which was viewed as an indicator of composting degradation. The basic equation was written, incorporating influences of temperature, moisture content and oxygen concentrations, as below:

$$\frac{dbvs}{dt} = (-1) \cdot k_0(T) \cdot k_T \cdot k_{H2O} \cdot k_{O2} \cdot \frac{bvs}{K_{bvs} + bvs} \cdot bvs \quad (1)$$

where bvs is biodegradable volatile solids (kg m^{-3}), t is time (hour), $k_0(T)$ is the maximum degradation rate constant at a certain temperature (hour^{-1}), k_T is the adjustment of temperature influence for degradation rate constant (–), k_{H2O} is the adjustment of moisture content influence for degradation rate constant (–), k_{O2} is the adjustment of oxygen concentration for degradation rate constant (–), K_{bvs} is the half velocity coefficient of biodegradable volatile solids (kg m^{-3}).

The effect of temperature on maximum rate constant likely depends on the type of substrates and microorganisms (Kaiser, 1996; Woodford, 2009). The following expression can be used to describe the factor of temperature influence in a perspective of microbial growth as:

$$k_T = C_1^{T-TR1} - C_2^{T-TR2} \quad (2)$$

where C_1 and C_2 are the temperature coefficients (–); T is the composting substrate temperature (°C); $TR1$ and $TR2$ are reference temperatures (°C). $TR1$ is normally chosen to be the measuring or lower-limit temperature of the rate constant $k_0(T)$. $TR2$ is recognized as the optimal temperature for biological degradation. Temperature T has a negative relationship with k_T when composting temperature is higher than $TR2$.

For the effect of moisture content on substrate degradation, a logistic curve was used as adjustment for the degradation rate constant as below:

$$k_{H2O} = \frac{1}{e^{a \cdot w + b} + 1} \quad (3)$$

where w is the moisture content of composting substrate (–); a, b are moisture coefficients (–). One set of typical values for the coefficients were configured to be -17.684 and 7.0622, respectively (Haug, 1993).

Just like the influence of temperature and moisture content, the influence of oxygen concentration is also complex and incorporates a group of interacting factors. Considering oxygen itself as a reaction substrate during the aerobic process is probably the most