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재자원화기술

Evaluation of Three Feasible Biodegradation Models for Food Waste

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Abstract

Food waste is produced from food factories, food services, and home kitchens. The generated mass reached 5.4 million tons/year in 2020. The basic management technology for such waste has been biological degradation under an anaerobic environment. However, the whole process is intrinsically slow and considerably affected by the inner physicochemical properties of the waste and other surrounding conditions, which makes optimization of the process difficult. The most promising options to counter this massive generation of waste are eco-friendly treatments or recycling. As a preliminary step for these options, attempts were made to evaluate the feasibility and usability of three simulative models based on reaction kinetics. Model (A) predicted relative changes over reaction time for reactant, intermediate, and product. Overall, an increased reaction rate produced less intermediate and more product, thereby leading to a shorter total reaction time. Particle diminishing model (B) predicted reduction of the total waste mass. The smaller particles diminished faster along with the dominant effect of microbial reaction. In Model (C), long-chain cellulose was predicted to transform into reducing sugar. At a standard condition, 48% of cellulose molecules having 10^5 repeating units turned into reducing sugar after 100 h. Also it was found that the optimal enzyme concentration where the highest amount of remnant sugar was harvested was 1 mg L^{-1}.

Keywords : Biodegradation, Enzymatic reaction, Food waste, Mathematical model

1. Introduction

Food-oriented organic waste (FOW) means remnant food from kitchens and dining sites, and byproducts from food processing. This bio-waste comprises 28% of the total waste: 20% of FOW is organics, apt to decay and the other is water [1]. Since direct dump of that waste has been banned from 2005 on, some appropriate treatment plan is required [2]. One typical example is production of biogas out of municipal solid waste via MBT (mechanical biological treatment) [3]. This project evaluated feasibility of gasification of organic waste and biodegradable material in general.

Another study was made with BMP (biochemical methane potential) method [4]. In this work a variety of kitchen waste was characterized in terms of biodegradability and biodegradation rate. Specific reaction rate constants for vegetables and crops were identified. Efficient reduction of food waste is known to count on anaerobic lysis and its particle size rather than its composition. Smaller particle size provides with larger total surface area where enzymes reside to react, leading to higher reactivity [5]. Two significant works were reported recently in areas of anaerobic food waste digestion [6-7]. Fisgativa et al. [7] totally investigated mutual relationship among waste types, biochemical properties, and microbial population for better treatment of those waste. They mentioned the importance of microbial flora, i.e., *Proteobacteria* and fungus *Ascomycota* in the biological process including both of aerobic and anaerobic phases. Also, different waste types that accordingly manifest varied composition of volatile solids, fiber, density, etc. were not shown to be directly related to their biodegradability. More extensive work on the effect of waste composition was done by Li et al. [8]. Changes in amount of carbohydrates, lipids and proteins were traced through biodegradation process where higher content of lipids and proteins while lower composition of carbohydrates degraded faster significantly, thus producing more methane. Selected parameters such as lipid, C,

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N, C/N ratio, pH, CH_4, etc. were well correlated with biodegradation of a typical waste in the proposed 2nd-order polynomial model.

Mathematical modeling is regarded as a pre-requisite to reduction or treatment of FOW. It can stimulate more robust and effective process design and control that require mathematical expressions and quantification of mapping data [8]. Published technical articles may provide with valuable kinetic parameters/physical conditions for involved biological reactions, and intrinsic chemical properties of FOW. Now we present three feasible models depicting general biodegradation processes with cautiously selected literature data. Proposed models are based on kinetics, mass transfer barrier, and molecular population dynamics.

2. Method

2.1. Proposition of feasible models

2.1.1. Model for simple kinetics (Model A)

This model calculates the symbolized waste components with time via the first-order degradation reactions. That is, the original waste (A) is transformed to some intermediates (B) and then changed into final products (C) or can be directly changed to C. The latter case explains how some ingredients degrade easily with ammonia or carbon dioxide at an elevated temperature as fermentation proceeds. This scheme can be described as follows:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \quad (1\text{-}1)$$

$$A \xrightarrow{k_3} C \quad (1\text{-}2)$$

the kinetic parameters (k_1-k_3) are arbitrary constants that rely on temperature only (Arrhenius method). The detailed scheme is shown in Figure 1. The formulated differential equations are listed below and total mass should be conserved (Equations 1-6):

$$\dot{X}_A \quad \frac{dX_A}{dt} = -k_1 X_A - k_3 X_A \quad (1\text{-}3)$$

$$\dot{X}_B \quad \frac{dX_B}{dt} = k_1 X_A - k_2 X_B \quad (1\text{-}4)$$

$$\dot{X}_C \quad \frac{dX_C}{dt} = k_2 X_B + k_3 X_A \quad (1\text{-}5)$$

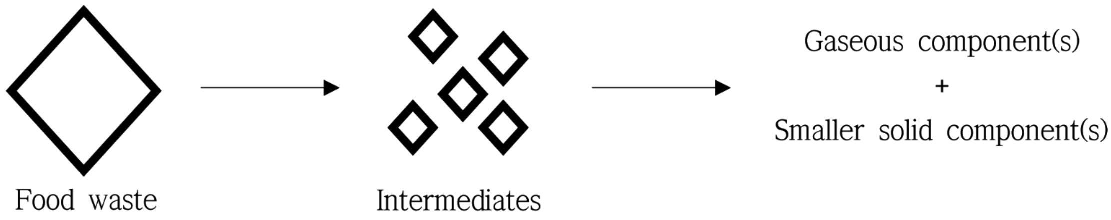

Figure 1. Scheme of the model for simple kinetics.

$$X_{A0} = X_A + X_B + X_C \quad (1\text{-}6)$$

Finally we obtained the analytical solution for those coupled kinetic equations. The answers are expressed in Equations (1-7 ~ 1-9).

$$X_A = X_{A0} e^{(-(k_1+k_3)t)} \quad (7)$$

$$X_B = \frac{k_1 X_{A0}}{k_2 - (k_1 + k_3)} \left[e^{(-(k_1+k_3)t)} - e^{(-k_2 t)} \right] \quad (8)$$

$$X_C = X_{A0} - X_B - X_A \quad (9)$$

2.1.2. Model for size-change with reactions (Model B)

This model self-explains how the waste particles-would be shredded earlier-diminish to finally disappear or into much smaller ones. The scheme for this model is represented in Figure 2. Equation (2-1) shows mass concentration of raw particles with radius R_0 decreases with time, being controlled by mass transfer barriers and a facilitated bioreaction.

$$-\frac{1}{S}\frac{dn_A}{dt} = \frac{(bn_M)}{\frac{1}{k_{air}} + \frac{1}{k_L} + \frac{R_0^2}{r_c^2}\frac{1}{k_M}} = \frac{bn_M}{\frac{1}{k_T}} \quad (2\text{-}1)$$

where $1/k_{air} \approx 0$. In spherical coordinates, surface area and mass of a sphere can be written as shown in Equations (2-2 & 2-3).

$$S = 4\pi r_c^2 \quad (2\text{-}2)$$

$$dn_A = \rho_A dV = \rho_A d(\frac{4}{3}\pi r_c^2) = \frac{4}{3}\pi \rho_A r_c^2 dr_c \quad (2\text{-}3)$$

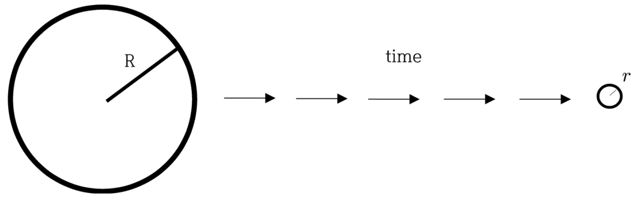

Figure 2. Scheme of the model for the size-change with reaction (R》 r).

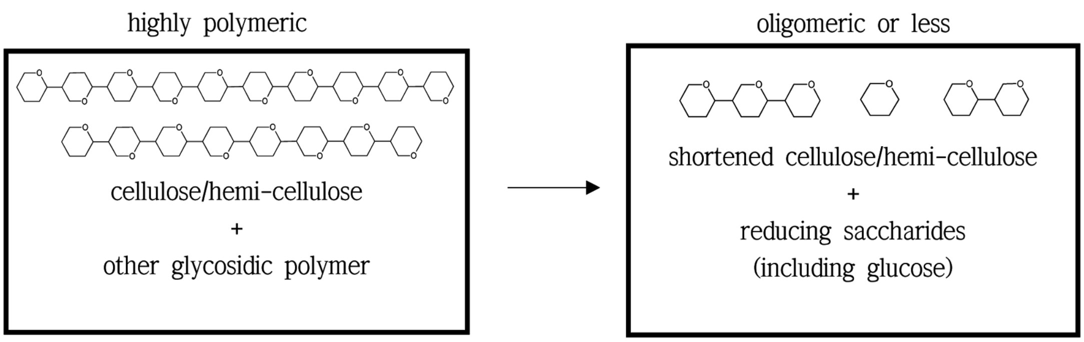

Figure 3. Scheme of the model for polymeric fission.

Generally, food-oriented organic matter degrades with ease via microbial reactions in aqueous phase (food waste normally has 80% of water content). The microbial action can be favored by the intrinsic metabolic pathways meanwhile it should be retarded by some mass transfer barriers (air & liquid-sided). Since the air-sided resistance is negligible, and it can be counted only the liquid-sided barrier. Then Equation (2-1) is to be rewritten as below.

$$-\frac{dr_c}{dt}=\frac{(bn_M/\rho_A)}{\frac{1}{k_L}+\frac{R_0^2}{r_c^2 k_M}} \quad (2\text{-}4)$$

2.1.3. Model for molecular fission of biopolymer (Model C)

Long-chained cellulose is known to be hydrolyzed by a complex of cellulases. The complex includes endoglucanase, cellobiohydrolase and β-glucosidase. The first two enzymes are reported to be identical in their functions for biodegradation [8]. Therefore, we consider two enzymes, endoglucanase and β-glucosidase in this model. The model simulates that i-length cellulose species breaks down and reducing sugar increases instead, which could be affected by reaction rate, reaction probability, and temperature. Base equation is shown in Equation (3-1). All parameters are explained fully in Nomenclature.

$$\frac{dX_i}{dt}=-k_i^{\alpha}p_i^{\alpha}X_i-k_i^{\beta}p_i^{\beta}X_i \quad (3\text{-}1)$$

where

$$k_i^j=k_i^j(i,T)\ \text{for}\ j=\alpha\ \text{or}\ \beta \quad (3\text{-}2)$$

$$p_i^j=p_i^j(X_i,i)\ \text{for}\ j=\alpha\ \text{or}\ \beta \quad (3\text{-}3)$$

Kinetic constants derived from two references [9-10] are listed in Table 1. The values of k_j^i are referenced to fungus *Trichoderma* (≥5,000 units/g) and also derived from Arrhenius formula at room temperature [11]. Maxwell-Boltzmann distribution was used to compute the reaction probability. All the calculations were performed under a constraint: total mass of all polymeric species must be conserved as shown in Equation (3-4).

Table 1. Enzyme kinetic data [7-8]

Enzyme	Degradation reaction constant (s^{-1})	Activation Energy (KJ/mol)	Gas constant ($J/K\cdot mol$)
endoglucanase	1.83×10^{-3}	182.4	8.314
β-glucosidase	2.07×10^{-3}		

$$\sum_i M_{0,i}X_i=\sum_j M_jX_j \quad (3\text{-}4)$$

3. Result and Discussion

3.1. Model A

A few works reported on rate constants for food waste degradation. Park et al. [4] presented the values of k_i in the range of 0.0495 ~ 0.2022 d^{-1}, which were lower than those reported by Shin et al. [12]. Owens and Chynoweth [13] suggested 0.072 ~ 0.075 d^{-1} though. Some mean values like 0.072 ~ 0.137 d^{-1}, therefore, were taken for our calculations. Food waste was classified into four categories such as fruits, crops, fish and vegetables. The values of 0.0987, 0.1216, 0.072 and 0.137d^{-1}were assigned to each category in respective order. Those differences are likely to attribute to their intrinsic biological and chemical properties. The ratio of reaction rates, $k_1/k_2$was 0.514 for rural area while 1.462 for diners [10]. In our calculations, the averaged value of 0.988 for $k_1/k_2$was used. For k_3, the reaction rate assumed to be 10^{-1} of order of magnitude over the other two rates.

With the 1st order of reaction and already estimated parameters and constants, all the calculated curves are shown in Figure 4. When k_1/k_2=1, the degradation rate during the first phase was the highest for vegetables (7.3 d) and the lowest for fish (13.7 d). In 25 h, vegetables degraded by 84.8% while that of fish did by 53.6% only. After 2 days all kinds of the food waste degraded more than 86.5%. It was found that any of $k_i$accelerated the whole reactions, resulting in higher final product.

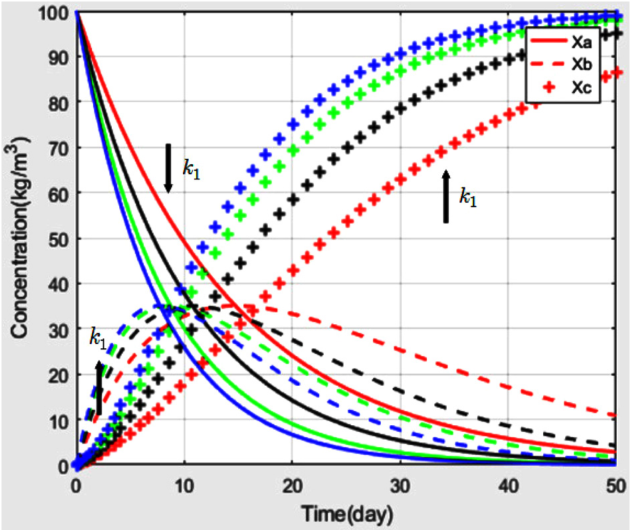

Figure 4. Biodegradation of food-oriented organic waste in model A when $k_1:k_2:k_3$=1:1:0.1 : fish, k_1=0.072d^{-1}; fruits, k_1=0.0987d^{-1}; grains, k_1=0.1216d^{-1}; vegetables, k_1=0.137d^{-1}.

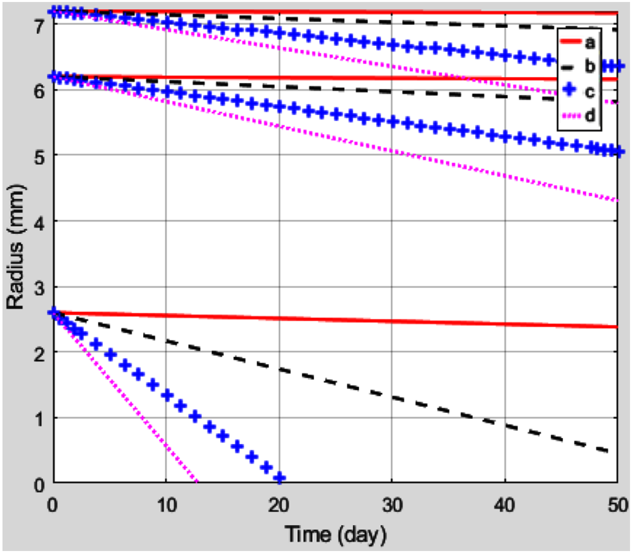

Figure 5. Diameter reduction of food-oriented organic waste particles when R=2.6 mm, R=6.2 mm, and R=7.2 mm in model B : (a) $k_L:k_M$=1:1 (b) $k_L:k_M$=1:10 (c) $k_L:k_M$=1:30 (d) $k_L:k_M$=1:50.

3.2. Model B

According to Choi et al. [14] preprocessed particle size and anaerobic conditions affected more on efficient reduction of food waste than composition of the organics. Accordingly, Radius of a spherical particle and its decay over time were introduced in Model B. Also, mass transfer resistance and microbial reaction factor to evaluate the performance of the model were considered. Earlier work classified food waste into three groups where crops have 2-9 mm of size while meat or vegetable has 2-25 mm in common. Under literature review the averaged values of crops, meat, and vegetables were 2.6 mm, 6.2 mm, and 7.2 mm, respectively. Resulting time-course graphs are shown in Figure 5.

Standard value of k_M was set to 0.1073 d^{-1}. Density of the particle was found to be 1.093 cm^3/g by considering water content and the largest portion of vegetables among the particulate waste. Tentatively, the microbial reaction rate contant (k_M) was found to affect greatly on shrinkage of the particle meanwhile the mass transfer barrier (k_L) did not influence much on the reduction of waste mass. With an enhanced microbial activity (if better microbial ability or larger population of the microbes were to be applied), the average radius of the waste particles shrank more rapidly with higher ratio of k_M/k_L(see Figure 5). Crops diminished faster than vegetables, on the other hand, due to their smaller initial radii.

3.3. Model C

This model hypothesizes food waste is solely made of one component, cellulosic polymer. Cellulose, one type of molecular biopolymer is a starting material for biodegradation. Figures 6-8 explain how a longer chain polymer breaks down to give oligomers or glucose (so-called as reducing sugar) when different doses of

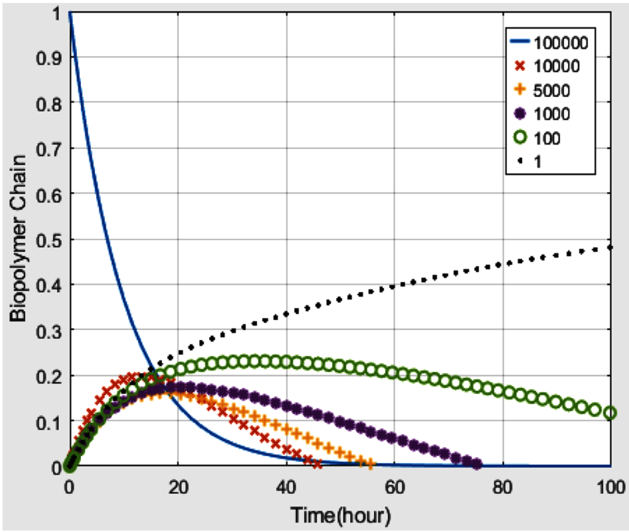

Figure 6. Reduced chain length when biodegraded at 25 ℃ in model C.

corresponding enzymes are applied. Under a standard condition raw cellulose turned into 48% of reducing sugar and others in 100 h. With higher doses of the enzymes degradation proceeded further, eventually to almost half of the raw polymer. However, overdoses (more than 15 mg/L of enzymes) actually produced less reducing sugar in real tests than in calculations, which implied that there would be an optimal dose of enzyme for maximal degradation of the biopolymer. In both of test and simulation, 10 mg/L of enzymes was found to optimal (Figure 8).

4. Conclusion

This work presents kinetics based biodegradation models for

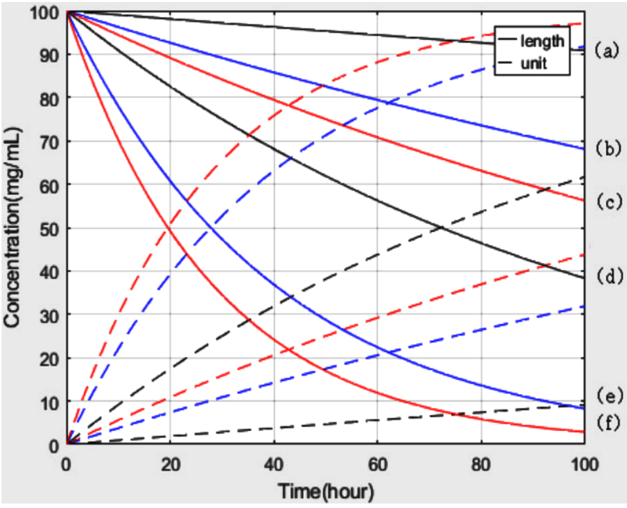

Figure 7. Change in the amount of enzyme added at 25 ℃ in model C : (a) 1 mg/L (b) 5 mg/L (c) 10 mg/L (d) 15 mg/L (e) 30 mg/L (f) 50 mg/L.

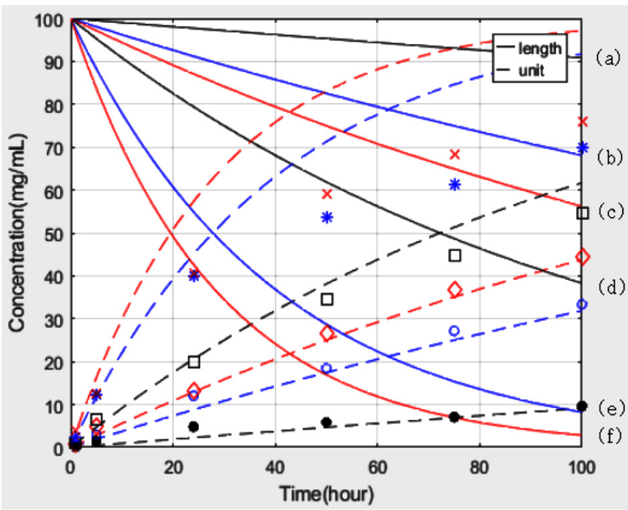

Figure 8. Change in cellulosic species with increasing enzyme addition at 25 ℃ in model C : (a) 1 mg/L (b) 5 mg/L (c) 10 mg/L (d) 15 mg/L (e) 30 mg/L (f) 50 mg/L for simulation; ● 1 mg/L, ○ 5 mg/L, ◇ 10 mg/L, □ 15 mg/L, ✱ 30 mg/L, × 50 mg/L for test.

efficient reduction of food-oriented waste. Three different models derived from unique views of their own to evaluate their performances were established. What was found in this study are: 1) Model (A) predicted relative changes over reaction time for reactant, intermediate and product. Overall increased reaction rate produced less intermediate but more product, thus led to the shorter total reaction time. 2) Particle diminishing model (B) predicted reduction of the total waste mass. The smaller particles diminished faster along with dominant effect of microbial reaction. 3) Long-chained cellulose was predicted to transform into reducing sugar (Model C). At a standard condition a cellulose molecule having 10^5 repeating units turned into 48% of reducing sugar in 100 h. Also it was found that optimal enzyme concentration was 10 mg/L, where the highest remnant sugar was harvested.

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Nomenclature

A : original waste

B : intermediates

C : final products

k_1 : reaction rate constant when converting from original waste to intermediates

k_2 : reaction rate constant when converting from intermediates to final products

k_3 : reaction rate constant when converting from original waste to final products

R_0 : the initial radius of the particle

r_c : final radius of the particle

k_{air} : gaseous resistance

k_L^{-1} : liquid mass transfer resistance

k_M : surface biochemical reaction

b : organic concentration

n_M : total microbial population

ρ_A : density

$1/k_T$: total transfer resistance

S : sphere surface area

n_A : mass of waste particles

$M_{0,i}$: i-species' (raw) molecular weight

M_i : i-species' molecular weight

X_i : concentration of cellulose of length i

k : decomposition reaction rate of each enzyme

p : reaction probability of cellulose molecules

α : endoglucanase

β : β-glucosidase

k_i^{α} : rate constant of endoglucanase

k_i^{β} : rate constant of β-glucosidase

R : gas constant

E_a : activation energy of cellulose

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