Mathematical analysis of microbial depolymerization processes of xenobiotic polymers

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Abstract

Biodegradation of polyethylene glycol is studied mathematically. A mathematical model for depolymerization process of exogenous type is described, and numerical techniques based on the model are illustrated. A comparison between a numerical result and an experimental result shows that the mathematical method is appropriate for practical applications.

Contents

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1 Introduction

Biodegradation is an essential factor of the environmental protection against undesirable accumulation of xenobiotic polymers. It is important not only for water soluble polymers but also for water-insoluble polymers, so-called plastics, because they are not completely recycled nor incinerated. Microbial depolymerization processes are generally classified into either one of two types: exogenous type or endogenous type. In an exogenous depolymerization process, monomer units are separated from the terminals of molecules stepwise. Example of exogenous depolymerization process includes the β-oxidation of polyethylene (PE). On the other hand, the characteristics of endogenous depolymerization processes include the rapid breakdown of large molecules due to internal separations to yield small molecules. Examples of endogenous depolymerization process include the enzymatic degradation of polyvinyl alcohol (PVA). Mathematical models for those depolymerization processes have been proposed in previous studies, and those models are analyzed to study the biodegradation of the xenobiotic polymers.

The biodegradation of polyethylene glycol (PEG) is studied. PEG is one of the polyethers which are represented by $HO(R\text{-}O)_nH$. For examples: PEG, $R = CH_2CH_2$; polypropylene glycol (PPG), $R = CH_3CHCH_2$; polytetramethylene glycol (PTMG), $R = (CH_2)_4$ [3]. They are utilized for constituents in a number of products including lubricants, antifreeze agents, inks and cosmetics. PEG is produced more than any other polyethers, and the major part is consumed in production of nonionic surfactants. PEG is depolymer-

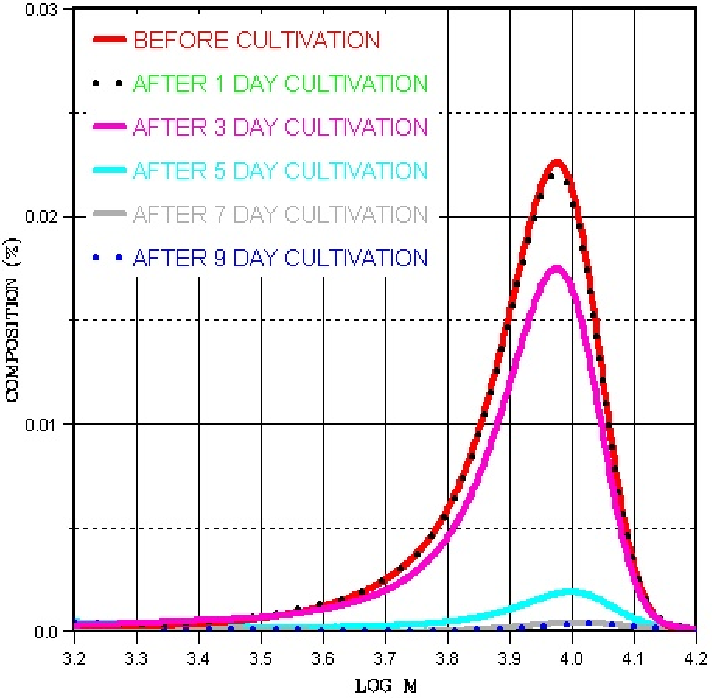

Figure 1: Weight distribution of PEG before and after cultivation of a microbial consortium E1.

ized by releasing C_2 compounds exogenously, either aerobically or anaerobically [4, 5, 10]. High performance liquid chromatography (HPLC) patterns were introduced into analysis to set the weight distribution of PEG with respect to the molecular weight before and after cultivation of a microbial consortium E1 (Figure 1).

Previous studies [9, 11], assumed degradation rates to be independent of time, although time dependent degradation rates were considered in a recent study assuming a logistic growth in a microbial population [12], and using a cubic spline to take the change of microbial population into consideration [13], and a exponential growth in a microbial population [14]. The mathematical study of biodegradation of PEG is continued with a time dependent degradation rate. A change of variable reduces the time dependent model into a model for which the degradation rate is time independent. The techniques developed in previous studies were applied to solve an inverse problem to determine the molecular factor of degradation rate for which the solution of an initial value problem satisfies not only the initial weight distribution but also the weight distribution after cultivation. The time factor was determined by assuming the logistic growth in the time integral of microbial population. Once the degradation rate was found, the transition of the weight distribution was simulated by solving the initial value problem numerically.

2 Exogenous-type depolymerization model

The PE biodegradation model proposed previously is based on two essential factors: the gradual weight loss of large molecules due to terminal separations of monomer units (β-oxidation) and the direct consumption of small molecules by cells. PE molecules lose their weight through β-oxidation processes until they become small enough to be absorbed into cells. Let t and M represent the time and the molecular weight respectively. Suppose that $x = w(t, M)$ represents the total weight of M-molecules at time t, where a M-molecule denote a molecule with molecular weight M. Suppose also that $y = w(t, M + L)$, the total weight of $(M + L)$-molecules at time t, where the parameter L represents the weight loss due to the β-oxidation. Let the function $\rho(M)$ represent the direct consumption rate, and the function $\beta(M)$ represents the rate of the weight conversion from the class of M-molecules to the class of $(M - L)$-molecules due to the β-oxidation. Let $\alpha(M) = \rho(M) + \beta(M)$. The following equation (1) was proposed as a PE biodegradation model [1, 2, 6]:

$$\frac{dx}{dt} = -\alpha\left(M\right)x + \beta\left(M+L\right)\frac{M}{M+L}y\,. \tag{1}$$

The mathematical model (1) was originally developed for PE biodegradation, and it can be viewed as a general biodegradation model involving exogenous depolymerization processes. In the exogenous depolymerization of PEG, a PEG molecule is first oxidized at its terminal, and then an ether bond is split. It follows that $L = 44$ (CH_2CH_2O) in the exogenous depolymerization of PEG. The PEG molecules studied here are large molecules that cannot be absorbed directly through membrane into cells. Then $\rho\left(M\right) = 0$ and $\alpha\left(M\right) = \beta\left(M\right)$.

Equation (1) is appropriate for a depolymerization processes over the period where the microbial population is fully developed and almost constant. However, the change of microbial population should be taken into consideration for the period in which it is still in a developing stage or in a decreasing stage, and the degradation rate should be time dependent. Then the exogenous depolymerization model is

$$\frac{dx}{dt} = -\beta\left(t,M\right)x + \beta\left(t,M+L\right)\frac{M}{M+L}y\,. \tag{2}$$

The solution $x = w\left(t,M\right)$ of (2) is associated with the initial condition

$$w\left(0,M\right) = f\left(M\right)\,, \tag{3}$$

where $f\left(M\right)$ represents the initial weight distribution. Given the degradation rate $\beta\left(t,M\right)$, equation (2) and the initial condition (3) form an initial value problem.

Time factors of the degradation rate, such as microbial population, dissolved oxygen, or temperature, should affect molecules regardless of their sizes. Then the degradation rate should be split into two parts: the time dependent part $\sigma\left(t\right)$, and the molecular dependent part $\lambda\left(M\right)$. The degradation rate is

$$\beta\left(t,M\right) = \sigma\left(t\right)\lambda\left(M\right)\,. \tag{4}$$

Let

$$\tau = \int_0^t \sigma(s)\, ds\,, \tag{5}$$

and let

$$\begin{aligned} W(\tau, M) &= w(t, M)\,, \\ X &= W(\tau, M)\,, \\ Y &= W(\tau, M+L)\,. \end{aligned}$$

Then one finds that

$$\frac{dX}{d\tau} = \frac{dx}{dt}\frac{dt}{d\tau} = \frac{1}{\sigma(t)}\frac{dx}{dt}\,,$$

and

$$\frac{dX}{d\tau} = -\lambda(M)\,X + \lambda(M+L)\,\frac{M}{M+L}Y\,. \tag{6}$$

This equation governs the transition of the weight distribution $W(t, M)$ which evolves with either the time independent or time averaged degradation rate $\lambda(M)$. Given the initial weight distribution $f(M)$, the initial value problem is a problem to find the solution of the equation (6) subject to

$$W(0, M) = f(M)\,. \tag{7}$$

The inverse problem is to find the degradation rate $\lambda(M)$ for which the solution of the initial value problem (6)–(7) also satisfies

$$W(\mathcal{T}, M) = g(M)\,. \tag{8}$$

When the solution $W(\tau, M)$ of the initial value problem (6)–(7) satisfies this condition, the solution $w(t, M)$ of the initial value problem (2)–(3) satisfies

$$w(T, M) = g(M)\,, \tag{9}$$

where

$$\mathcal{T} = \int_0^T \sigma(s)\, ds\,. \tag{10}$$

The inverse problem consisting of the equation (6) and the conditions (7) and (8) was solved numerically with techniques developed in previous studies. Figures 2 shows the degradation rates based on the weight distribution before and after cultivation for three days ($\lambda_1(M)$) and five days ($\lambda_2(M)$). The degradation rate $\lambda_2(M)$ is approximately six times as large as $\lambda_1(M)$ in their common interval, which shows the increase of microbial population over five days. The figures also show the graph of the function $\lambda(M)$ based on $\lambda_1(M)$ and $\lambda_2(M)$

$$\lambda(M) = \begin{cases} \lambda_1(M)\,, & M \leqslant 10^{4.1}\,, \\ \lambda_2(M)\,, & M > 10^{4.1}\,. \end{cases}$$

The initial value problem (6)–(7) was solved numerically using the degradation rate $\lambda(M)$. The numerical results shows that the experimental results for $t = 3$, $t = 5$, $t = 7$ match the numerical results for $\tau = 3$, $\tau = 30$, $\tau = 50$ (Figure 3). Section 3 uses this result to determine the time factor of the degradation rate.

3 Logistic growth in time integral of microbial population and numerical simulation

A microbial population grows exponentially in a developing stage. The time integral of the population τ increases monotonically to a constant value due to the limited supply of carbon source. A function with such properties was proposed by Murray [7] to be

$$\tau = \frac{N_0 K e^{rt}}{K + \tau_0\left(e^{rt} - 1\right)}\,. \tag{11}$$

Section 2 shows numerically that $t_1 = 3$, $t_2 = 5$, $t_3 = 7$ correspond to $\tau_1 = 3$, $\tau_2 = 30$, $\tau_3 = 50$. The values of parameters N_0, K and r were determined numerically using the result.

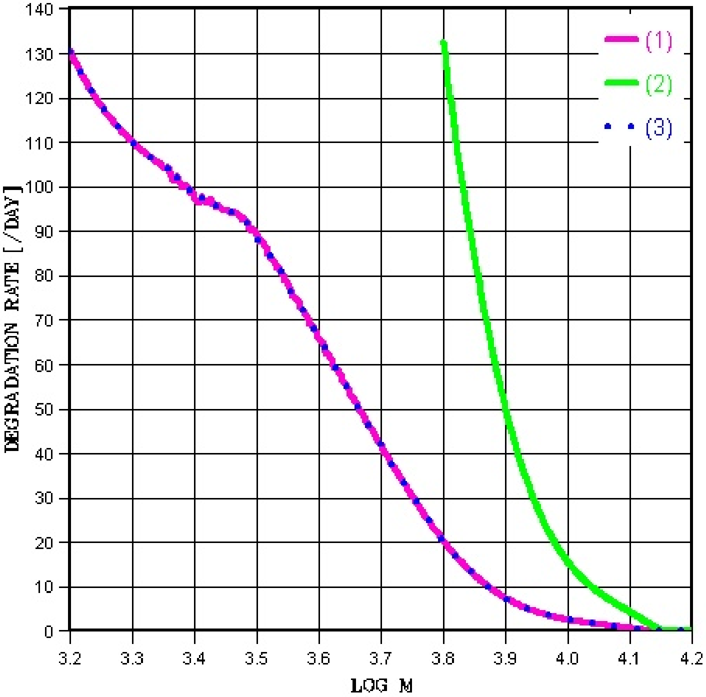

FIGURE 2: Degradation rate based on the weight distribution of PEG before and after cultivation of a microbial consortium E1: (1) $\lambda_1(M)$, (2) $\lambda_2(M)$, (3) $\lambda(M)$.

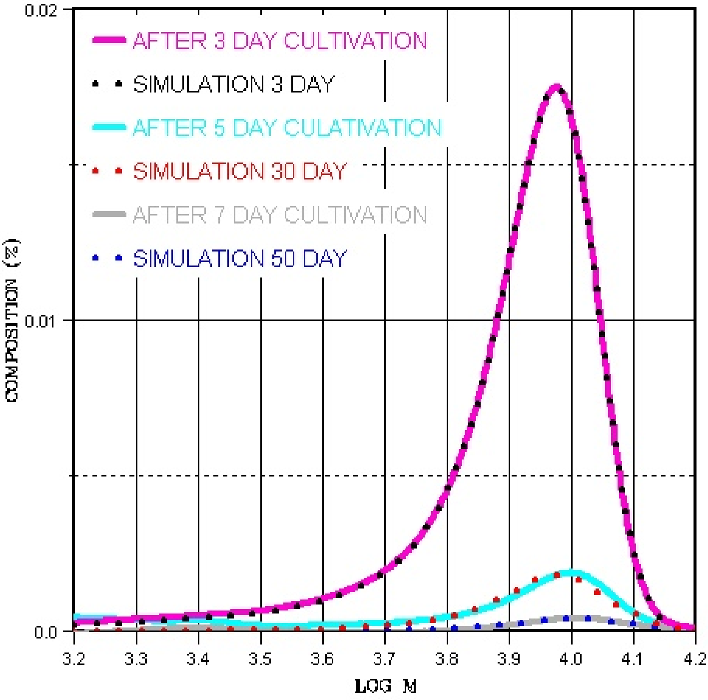

FIGURE 3: Numerical results based on the initial value problem (6), (7) for $\tau = 3$, $\tau = 30$, $\tau = 50$, and the experimental results for $t = 3$, $t = 5$, $t = 7$.

Solving Equation (11) for N_0 and substituting t_1 and τ_1 for t and τ,

$$N_0 = \frac{\tau_1 K}{Ke^{rt_1} - \tau_1 \left(e^{rt_1} - 1\right)}. \tag{12}$$

Solving Equation (11) for K and substituting t_2 and τ_2 for t and τ,

$$K = \frac{\tau_2 N_0 \left(e^{rt_2} - 1\right)}{N_0 e^{rt_2} - \tau_2}. \tag{13}$$

Substituting the right hand side of Equation (12) for N_0 in Equation (13) and solving for K gives

$$K = \frac{\tau_1 \tau_2 \left(e^{rt_2} - e^{rt_1}\right)}{\tau_1 e^{rt_2} - \tau_2 e^{rt_1}}. \tag{14}$$

Substituting the right hand side of Equation (14) for K in Equation (12),

$$N_0 = \frac{\tau_1 \tau_2 \left(e^{rt_2} - e^{rt_1}\right)}{\tau_2 e^{rt_1} \left(e^{rt_2} - 1\right) - \tau_1 e^{rt_2} \left(e^{rt_1} - 1\right)}. \tag{15}$$

Let

$$f\left(r\right) = \tau_3 - \frac{N_0 K e^{rt_3}}{K + \tau_0 \left(e^{rt_3} - 1\right)},$$

where K and N_0 are given in terms of t_1, τ_1, t_2, and τ_2 by Equations (14) and (15). The equation

$$f\left(r\right) = 0$$

was solved numerically by Newton's method, and found

$$r \approx 1.556758. \tag{16}$$

Once the degradation rate $\sigma\left(t\right)\lambda\left(M\right)$ are given, the initial value problem (2)–(3) can be solved directly to see how the numerical results and the experimental results agree. Here the initial value problem (2)–(3) was solved numerically with techniques base on previous results [2, 6, 8, 14]. Figure 4 shows

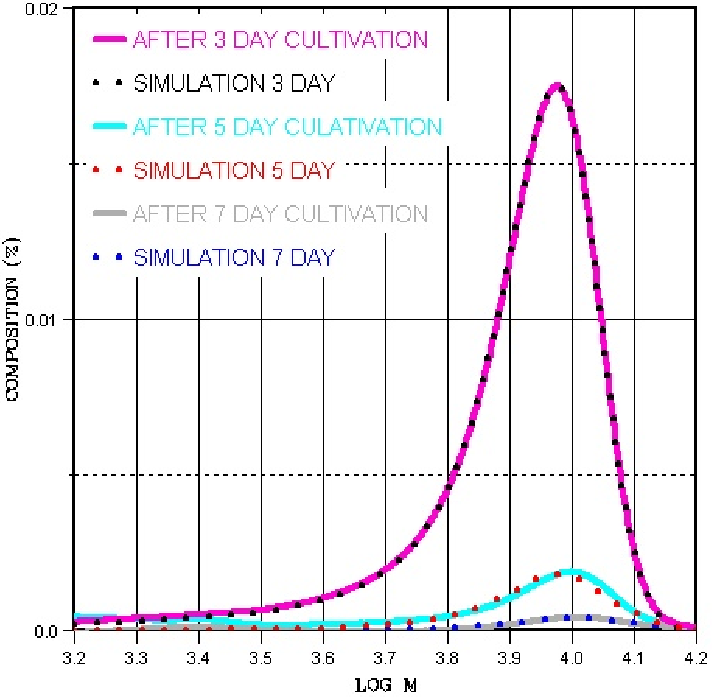

Figure 4: The weight distribution of peg before and after cultivation for three, five, and seven days, and the transition of the weight distribution based on the initial value problem (2)–(3).

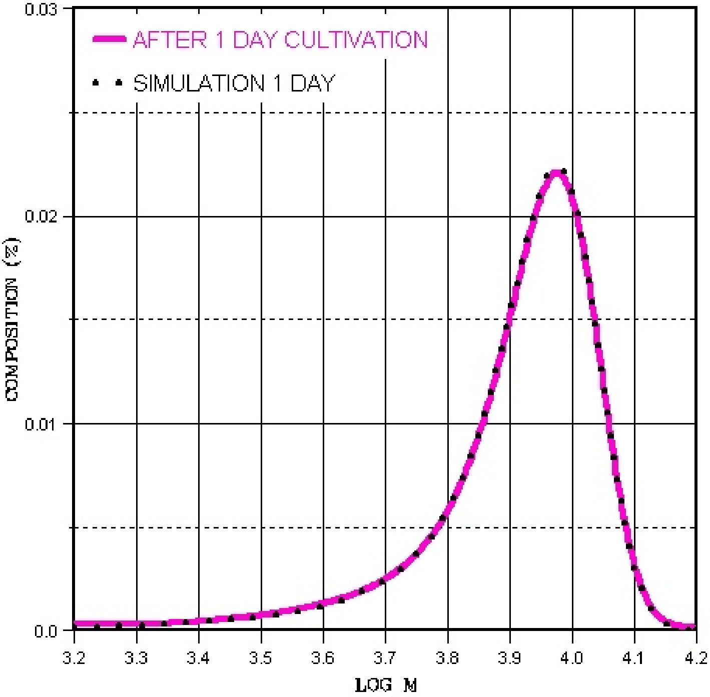

Figure 5: The weight distribution of PEG after cultivation for one day, and the weight distribution based on the initial value problem (2)–(3).

the transition of the weight distribution during cultivation of the microbial consortium E1 for five days. Figure 5 shows the numerical result and the experimental results for the weight distribution after one day cultivation of the microbial consortium E1.

The numerical results shown in Figure 4 were obtained by solving the initial value problem (2)–(3). The figure shows a fair agreement between the experimental results and the numerical results, which validate the exogenous depolymerization model with time dependent degradation rate. Note that no information concerning the weight distribution after cultivation for one day was introduced into the analysis to determine the time factor $\sigma(t)$. Nevertheless, Figure 5 shows an acceptable agreement between the experimental result and the numerical result.

4 Discussion

In a depolymerization process where the microbial population becomes an essential factor, it is important to consider the dependence of the degradation rate on time. The numerical results based on the exogenous depolymerization model show reasonable agreement with the experimental results. Those results show that it is appropriate to assume that the degradation rate is a product of a time factor and a molecular factor, and that the integral of the time factor increases as a logistic growth. In the environment, the time factor should also depend on other factors such as temperature or dissolved oxygen. Once these essentials are incorporated into the time dependent factor, the exogenous depolymerization model should be applicable to assess the biodegradability of xenobiotic polymers in the environment.

Mathematical models for endogenous depolymerization processes have also been proposed, and depolymerization processes of PVA and polylactic acid (PLA) have been studied by analysis and simulation based on those models [20, 21, 22, 23, 24]. Mathematical models similar to the endogenous depolymerization models have also been introduced by other authors [15, 16, 17, 18, 19].

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