STUDY ON EFFECTS OF MICROORGANISM IN DEPOLYMERIZATION PROCESS OF XENOBIOTIC POLYMERS BY MODELING AND SIMULATON

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Abstract: Effects of microorganism in biodegradation process of polyethylene glycol are studied by modeling and simulation. Dynamics of population of microorganism is taken into consideration in modeling of depolymerization process of exogenous type, and a mathematical model is described. A molecular factor of degradation rate is obtained by solving an inverse problem, and a time factor of degradation is obtained by analyzing the dynamics of population of microorganism. Once the time factor and the molecular factor of degradation rate are determined, a depolymerization process is simulated by solving an initial value problem.

1 INTRODUCTION

Biodegradation is an essential factor of environmental protection against accumulation of xenobiotic polymers. It is important not only for water soluble polymers but also for water-insoluble polymers, because they are not completely recycled nor incinerated. Microbial depolymerization processes are generally classified into exogenous type or endogenous type. In an exogenous type depolymerization process, monomer units are separated from terminals of molecules stepwise. Examples of exogenous depolymerization process include the β-oxidation of polyethylene (PE). In an endogenous type depolymerization process, molecules are split at arbitrary positions. Examples of endogenous depolymerization process include enzymatic degradation of polyvinyl alcohol PVA. Mathematical models for those depolymerization processes were proposed in previous studies. Microbial depolymerization processes of xenobiotic polymers were studied by analysis based on those models.

In this study, microbial depolymerization process of polyethylene glycol (PEG) is analyzed. PEG is one of polyethers expressed by $HO(R\text{-}O)_nH$, for example, PEG: $R = CH_2CH_2$, polypropylene glycol (PPG): $R = CH_3CHCH_2$, polytetramethylene glycol (PTMG): $R = (CH_2)_4$ (Kawai, 1993). They are utilized for constituents of products including lubricants, antifreeze agents, inks, and cosmetics. PEG is produced more than any other polyether, and the major part of the production is consumed for nonionic surfactants. PEG is depolymerized by separation of C_2 compounds, either aerobically or anaerobically (Kawai, 1995; Kawai, 2002a; Kawai, 2002b). High performance liquid chromatography (HPLC) patterns were used in analysis as the weight distribution of PEG with respect to the molecular weight before and after cultivation of a microbial consortium E1 (Figure 1).

In the previous studies (Watanabe and Kawai, 2004; Watanabe and Kawai, 2005), time independen degradation rates were assumed. Time dependent degradation rates were considered in a recent study (Watanabe and Kawai, 2007a). Cubic spline was used to take the change of microbial population into consideration (Watanabe and Kawai, 2007b). E exponential growth in a microbial population was assumed (Watanabe and Kawai, 2009b). The time factor was also determined by assuming the logistic growth in the time integral of microbial population (Watanabe and Kawai, 2009a). In this study, analysis of

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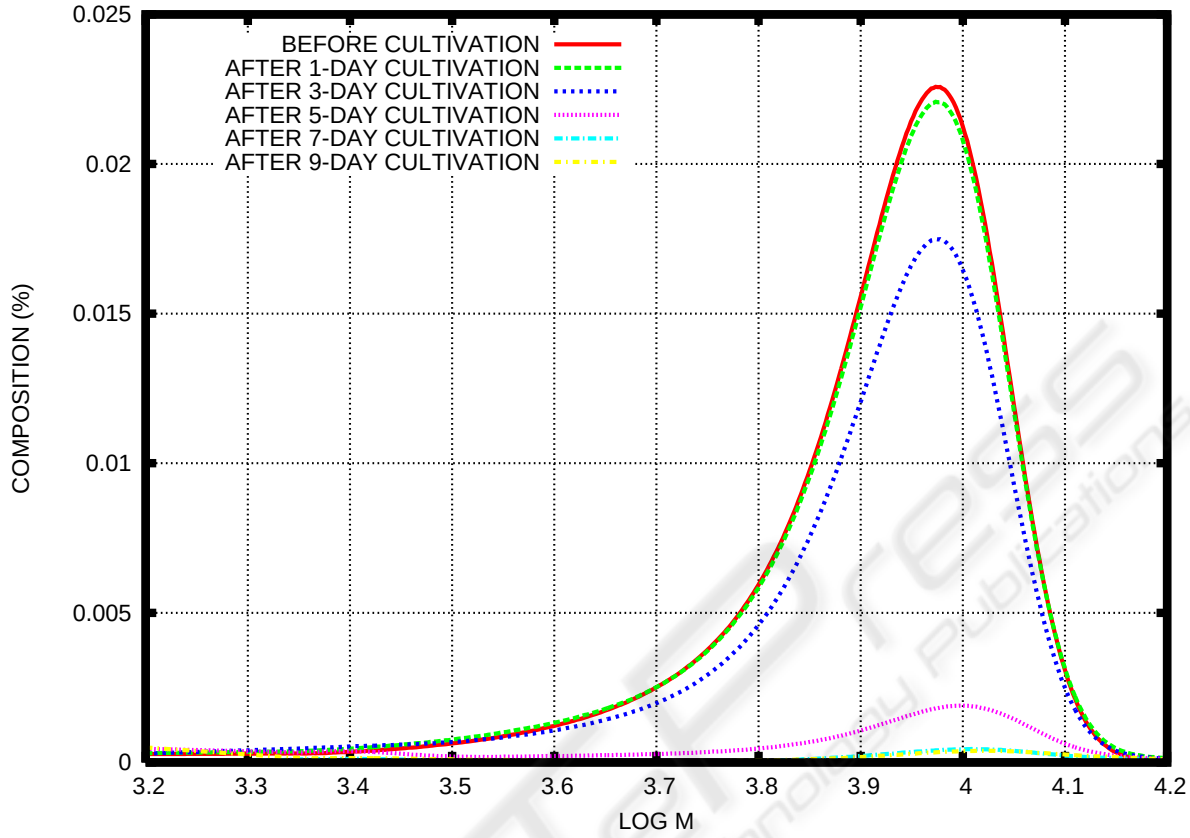

Figure 1: Weight distribution of PEG before and after cultivation of a microbial consortium E1 (Watanabe and Kawai, 2009a).

biodegradation of PEG is continued. A change of variable transforms the time dependent model into a model for which the degradation rate is time independent. Techniques developed in previous studies are 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 is determined by assuming change in microbial population due to the amount of PEG as the sole carbon source. Once the degradation rate is found, the transition of the weight distribution was simulated by solving the initial value problem.

2 MODEL OF EXOGENOUS TYPE DEPOLYMERIZATION PROCESS WITH TIME DEPENDENT DEGRADATION RATE

In microbial depolymerization of PE, molecules lose their weight gradually by terminal separations of monomer units (β-oxidation) until they become small enough to be absorbed directly into cells. The PE biodegradation model proposed previously is based on two essential factors, the gradual weight loss of large molecules due to β-oxidation and the direct consumption of small molecules by cells. Let t and M be the time and the molecular weight respectively. Suppose tha a M-molecule denotes a molecule with molecular weight M. Let $w(t,M)$ represent the total weight of M-molecules at time t, and L be the amount of weight loss due to the β-oxidation. Let the function $\rho(M)$ represent the direct consumption rate, the function $\beta(M)$ represent the β-oxidation rate, which

is the rate of the weight conversion from the class of M-molecules to the class of $(M-L)$-molecules due to the β-oxidation, and $\alpha(M) = \rho(M) + \beta(M)$. The equation (1) was proposed to study PE biodegradation processes (F. Kawai, 2002; M. Watanabe, 2003; F. Kawai, 2004; M. Watanabe, 2004).

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

where $x = w(t,M)$, the total weight of M-molecules at time t, and $y = w(t,M+L)$, the total weight of $M+L$-molecules at time t.

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

Equation (1) is appropriate for the depolymerization processes over the period in which the microbial population has reached a stationary state. On the contrary, the change of microbial population should be taken into account for the period in which it is still in a developing stage or in a decreasing stage. Then degradation rate should be time dependent, and the exogenous depolymerization model is

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

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

$$w(0,M) = f(M), \qquad (3)$$

where $f(M)$ is the initial weight distribution. Given a presicribed degradation rate $\beta(t,M)$, 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 affect molecules regardless of sizes. Then the degradation rate should be split into the time dependent part, which we denote by $\sigma(t)$, and the molecular dependent part, which we denote by $\lambda(M)$, and the degradation rate is the product

$$\beta(t,M) = \sigma(t)\lambda(M). \qquad (4)$$

The time factor of the degradation rate can be removed by the transformation

$$\tau = \int_0^t \sigma(s)\,ds. \qquad (5)$$

Let

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

Then

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

and the equation (2) becomes

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

Given the initial weight distribution $f(M)$, solution the initial value problem is the solution of the equation (6) subject to the initial condition

$$W(0,M) = f(M). \qquad (7)$$

Given additional condition

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

solution of the inverse problem is the degradation rate $\lambda(M)$ for which the solution of the initial value problem (6), (7) also satisfies the condition (8). When the solution $W(\tau,M)$ of the initial value problem (6), (7) satisfies the condition (8), the solution $w(t,M)$ of the initial value problem (2), (3) satisfies

$$w(T,M) = g(M), \qquad (9)$$

where

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

The inverse problem (6), (7), (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 (Watanabe and Kawai, 2009a).

3 TIME FACTOR OF DEGRADATION RATE BASED ON MICROBIAL POPULATION

Suppose that the time factor $\sigma(t)$ represents the microbial population, and that PEG is the sole carbon source. The total amount of polymer utilized by microorganisms per unit time at time t is

$$A = \int_0^\infty \sigma(t)\lambda(M)w(t,M)\,dM.$$

The microbial population increases under sufficient carbon supply when the ratio of the microbial population to the total amount is below a certain lavel

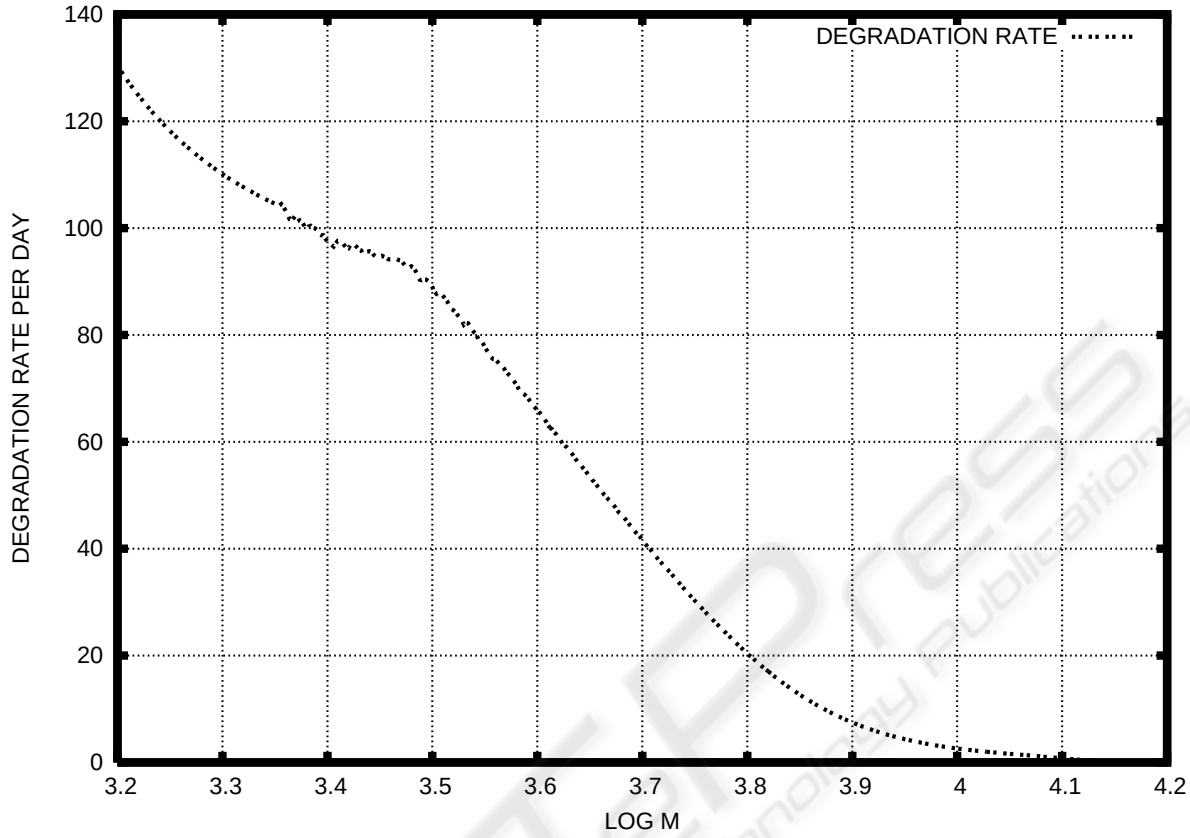

Figure 2: Degradation rate based on the weight distribution of PEG before and after cultivation of a microbial consortium E1 (Watanabe and Kawai, 2009a).

$\sigma/A < 1/h$ It decreases under insufficient carbon supply when $\sigma/A > 1/h$. Then the growth rate of microbial population is propotinal to

$$1 - h\frac{\sigma}{A},$$

and the microbial population $\sigma(t)$ is a solution of the equation

$$\frac{d\sigma}{dt} = k\left(1 - h\frac{\sigma}{A}\right)\sigma \qquad (11)$$

Note that equation (11) becomes

$$\frac{d\sigma}{dt} = k\left(1 - h\frac{1}{\int_0^\infty \lambda(M)\, w(t,M)\, dM}\right)\sigma. \qquad (12)$$

Equation (12) is associated with the initial condition

$$\sigma(0) = \sigma_0. \qquad (13)$$

Equations (2) and (12) are solved simultaneously to simulate the transition of weight distrubution of PEG and evolution of microbial population for $\sigma_0 \approx 0.029827$, $k \approx 51.6$, and $h = 500.0$. Figure 3 shows the resulsts of simulation for

4 CONCLUSIONS

In a depolymerization process in which microbial population is an essential factor, the dependence of the degradation rate on time becomes significant. It is appropriate to assume that the degradation rate is a product of a time factor and a molecular factor. In an environmental setting, the time factor should also depend on other factors such as temperature or dissolved oxygen. Once these essentials are taken into consideration, the exogenous depolymerization model will be applicable to assess the biodegradability of xenobiotic polymers in the environment.

Subjects in study of microbial depolymerization of xenobiotic polymers by modeling and simulation in next steps includes development of numerical techniques to identify the values of parameters which appear in the equation (11). Results of simulation should be compared with experimental results concerning the transition of weight distribution of the polymer and the microbial population to verify numerical results.

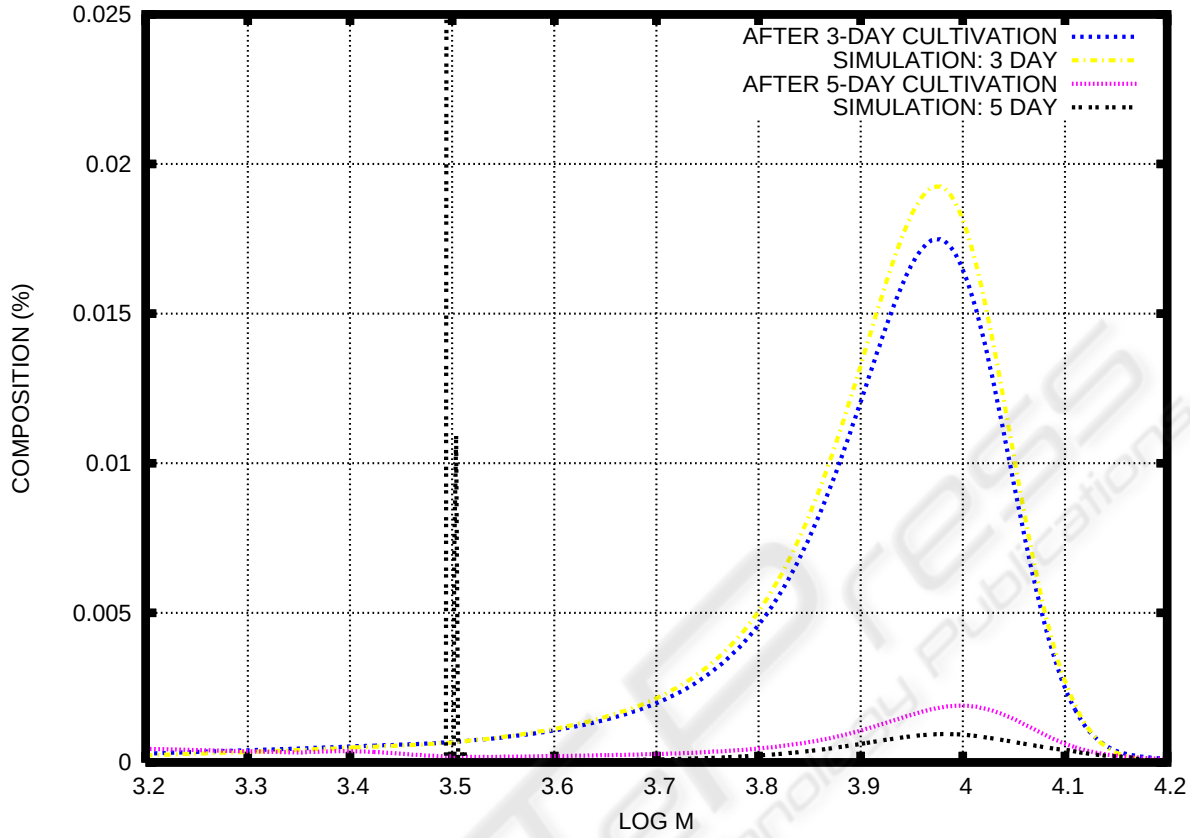

Figure 3: Numerival simulation of weight distribution and experimental results .

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