MODELLING SIMULTANEOUS REMOVAL OF TRICHLORFON AND GLUCOSE IN A HYBRID BIOREACTOR CONTAINING MAGNETICALLY IMMOBILIZED BIOMASS

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ABSTRACT

Trichlorfon is one of the representative organophosphate insecticides widely used in agricultural and veterinary practices. Due to toxic and carcinogenic characteristics of the residues in the environment, remediation of such residues is necessary. To biodegrade trichlorfon effectively, a source of easily biodegradable substrates is needed for fulfilling the co-metabolism requirement of trichlorfon-removing bacteria. This paper focused on a simultaneous removal of trichlorfon and the glucose added as the source of the substrate. A hybrid bioreactor consisting of suspended and magnetically immobilized biomass was employed to study the removal efficiencies of both the substances. A mathematical model was developed in this paper in order to extensively evaluate the removal performance of both the biomass under various removal conditions. Comparisons between model predictions and experimental results showed that the proposed model was able to satisfactorily predict the simultaneous removal efficiency of trichlorfon and glucose in the hybrid bioreactor. This study also indicated that the suspended biomass plays a more important role in removing both the substances than the immobilized biomass when the trichlorfon- and glucose-removing bacteria completely coexist in both the biomass phases. To increase the removal contribution of the immobilized biomass, the hybrid bioreactor is recommended to deal with such complex wastewaters that contain much slowly biodegradable pollutants having a high diffusivity.

KEYWORDS

Simultaneous removal of trichlorfon and glucose; hybrid bioreactor; mathematical modelling; suspended biomass; magnetically immobilized biomass.

INTRODUCTION

Contamination of the environment by organophosphate insecticides is an important environmental issue because their residues in natural water have been found to be toxic and carcinogenic (International Agency for Research on Cancer, 1983). Due to the fast development of golf courses in some nations, this contamination problem has been greatly concerned (Primi *et al.*, 1994). To control the problem, remediation of the residues from the environment is desired. It has been found that trichlorfon, a widely used organophosphate insecticide, can be slowly biodegradable (Orus and Arco, 1991). Such biodegradation usually requires the presence of an easily biodegradable substrate in order to meet the microbial co-metabolism requirement of trichlorfon degrading bacteria (Horvath, 1972). Therefore, to obtain an effective removal of trichlorfon, addition of an easily biodegradable substrate is necessary. It is obvious that such a substrate should be simultaneously removed with trichlorfon so as to prevent any secondary pollution from addition of the substrate in a trichlorfon degradation process.

A hybrid biotreatment system consisting of both suspended and attached biomass is expected to be able to achieve a simultaneous removal of these two substances effectively (Chen, 1995). In order to extensively

evaluate the removal performance of both the biomass in the system, model simulation on the removal efficiency under various removal conditions is usually sought. A couple of mathematical models for hybrid systems have been developed for this purpose under an assumption that slowly growers mainly existed in the attached phase of biomass, that is, the slowly biodegradable substances were mainly removed by the attached biomass (Chen, 1995; Chen *et al.*, 1997). Such models may not be appropriate when a substantial amount of slowly growers are actually available in the suspended phase. Therefore, this paper is aimed at developing a more comprehensive model to improve the previous models by considering the simultaneous removal of trichlorfon and glucose in both the suspended phase and the attached phase.

Verification of the proposed model was made through comparisons between the model predictions and experimental results obtained from a hybrid bioreactor containing magnetically immobilized biomass. The introduction of such immobilized biomass is to efficiently investigate the mass ratio of the suspended biomass to the attached biomass on the simultaneous removal efficiency, which is one of the most important influencing factors in a hybrid system (Chen *et al.*, 1997).

MODEL DEVELOPMENT

It is considered in this paper that both the trichlorfon- and glucose-removing bacteria completely coexist in the suspended as well as the attached biomass phases in a hybrid bioreactor. Therefore, the bacteria species in these phases may not be necessarily divided into respective removing groups in the course of modelling. The attached biomass is assumed to be uniform with a constant density and the concentration of dissolved oxygen (DO) in the reactor to be kept in a relatively high level so that oxygen limitation can be avoided (Chen *et al.*, 1994). Under such considerations, mass balance of trichlorfon and glucose in a steady-state hybrid bioreactor can be taken as follows:

Suspended phase

$$\text{Trichlorfon} \quad Q(S_{ot} - S_t) = \frac{K_{tms} S_t}{K_{ts} + S_t} \cdot \frac{C}{K_o + C} X_m V + A J_t \quad (1)$$

$$\text{Glucose} \quad Q(S_{og} - S_g) = \frac{K_{gms} S_g}{K_{gs} + S_g} \cdot \frac{C}{K_o + C} X_m V + A J_g \quad (2)$$

where A is the surface area of the attached phase (cm^2); C is the oxygen concentration in the bulk liquid phase (mg/L); J_g and J_t are the glucose and trichlorfon removal fluxes by the attached biomass ($\text{mg/cm}^2/\text{day}$); K_{gms} and K_{tms} are the maximum specific removal rates of glucose and trichlorfon ($1/\text{day}$); K_{gs} , K_{ts} , and K_o are the saturation constants of glucose, trichlorfon, and oxygen (mg/L), respectively; Q is the flow rate (m^3/day); S_{og} and S_g are the influent and effluent glucose concentrations (mg/L); S_{ot} and S_t are the influent and effluent trichlorfon concentrations (mg/L); V is the reactor volume (m^3); X_m is the concentration of the suspended biomass (mg SS/L). In the above equations, endogenous respiration and production of secondary substrates from the lysis of dead biomass are neglected, and the values of the kinetic parameters within the attached phase are assumed to be the same as those in the suspended phase.

Attached phase

a) in the diffusion layer on the phase surface

$$\text{Trichlorfon} \quad D_{wt} \frac{\partial^2 S_{ts}}{\partial Z^2} = 0 \quad (3)$$

$$\text{Glucose} \quad D_{wg} \frac{\partial^2 S_{gs}}{\partial Z^2} = 0 \quad (4)$$

$$\text{Oxygen} \quad D_{wc} \frac{\partial^2 C_s}{\partial Z^2} = 0 \quad (5)$$

b) within the phase

$$\text{Trichlorfon} \quad D_{ft} \cdot \frac{\partial^2 S_{tf}}{\partial Z^2} = \frac{K_{tms} \cdot S_{tf}}{K_{ts} + S_{tf}} \cdot \frac{C_f}{K_o + C_f} \cdot X_f \quad (6)$$

$$\text{Glucose} \quad D_{fg} \cdot \frac{\partial^2 S_{gf}}{\partial Z^2} = \frac{K_{gms} \cdot S_{gf}}{K_{gs} + S_{gf}} \cdot \frac{C_f}{K_o + C_f} \cdot X_f \quad (7)$$

$$\text{Oxygen} \quad D_{fc} \cdot \frac{\partial^2 C_f}{\partial Z^2} = (1 - PY_g) D_{fg} \cdot \frac{\partial^2 S_{gf}}{\partial Z^2} + (1 - PY_t) D_{ft} \cdot \frac{\partial^2 S_{tf}}{\partial Z^2} \quad (8)$$

where C_f and C_s are the oxygen concentrations in the attached phase and in the diffusion layer and (mg/L); D_{fc} , D_{fg} , and D_{ft} are the diffusion coefficients of oxygen, glucose, and trichlorfon within the attached phase (cm^2/day), respectively; D_{wc} , D_{wg} , and D_{wt} are the diffusion coefficients of oxygen, glucose, and trichlorfon in the bulk liquid phase (cm^2/day), respectively; P is the conversion coefficient between COD and biomass (mg COD/mg VSS); S_{gf} and S_{tf} are the concentrations of glucose and trichlorfon within the attached phase (mg/L); S_{gs} and S_{ts} are the concentrations of glucose and trichlorfon in the diffusion layer (mg/L); X_f is the biomass density in the attached phase (mg SS/ cm^3); Y_g and Y_t are the yield coefficients of glucose and trichlorfon (mg VSS/mg COD); and Z represents two depths: 1) from the surface of the diffusion layer to the attached biomass surface (0 to L_o) and 2) from the attached phase surface to the bottom of the attached phase (L_o to $L_o + L_f$) (cm).

MODEL ANALYSIS

Approach for model simulation

To simplify a numerical analysis of the proposed model, it is assumed that the oxygen concentration profile within the attached phase was mainly controlled by glucose oxidation because the concentration of glucose was significantly higher than trichlorfon in this study. Thus, calculation of the glucose and oxygen concentration profile in the diffusion layer and within the attached phase can be separated from the calculation of trichlorfon which is conducted lately based on the oxygen profile obtained in the glucose profile calculation. It is also assumed that a TOC unit could be used to quantify glucose as the glucose concentration in this study was about five times higher than that of trichlorfon and 1 trichlorfon is only equal to 0.19 TOC while 1 glucose gives 0.4 TOC. Based on these assumptions, the following numerical analysis procedure was developed for solving the model: 1) A value of the S_g is given by the rule of golden section

that is applied to Eq. (2); 2) With the given values of C and S_g , the $J_g (= D_{wg} \frac{\partial S_{gs}}{\partial Z} \big|_{z=0})$ can be

calculated from the S_g profile in the diffusion layer. The profile calculation starts from the surface of the diffusion layer to the bottom of the attached phase under a boundary condition that the fluxes of oxygen and glucose at the bottom are zero. In this calculation discretization of Eqs. (4), (5), (7), and Eq. (8) neglecting the last term of its right hand side are proceeded to form coupled ordinary differential equations from which the concentration profiles of glucose and oxygen can be calculated; 3) An iteration of the S_g and C_f is introduced in step 2) for obtaining a stable result of the profile because of the non-linearity of Eqs. (7) and (8); 4) If the J_g and the S_g do not satisfy Eq. (2), step 1), 2), and 3) will be repeated until acceptable values of the S_g and J_g for Eq. (2) is identified; 5) Following the above steps the S_t can also be calculated from the Eqs. (1), (3) and (6) after the oxygen profile has been determined in the glucose calculation.

Determination of Parameter Value

To conduct the numerical simulation of the model, the values of the parameters employed in the model should be determined. There are three types of parameters included in this model: 1) substances removal related kinetic parameters such as K_{gms} , K_{tms} , K_{gs} , K_o , and K_{ts} ; 2) physical, chemical, and biochemical properties related parameters such as D_w , D_f , Y , and P ; and 3) bioreactor configuration and operational conditions related parameters such as A , Q , V , S_o , C , X_m , X_f , L_f , and L_o . The first group parameters are the most important ones that directly govern the removal capacity of the system. Therefore, those parameters

were identified through a batch test using cultivated biomass with trichlorfon and glucose. The cultivation of biomass started with seeding material taken from a sewage treatment plant in Kyoto city of Japan. A fill and draw batch cultivation was carried out for at least two months with the artificial wastewater composed of 25 mg/L trichlorfon, 1000 mg/L glucose, and sufficient trace nutrients.

The batch test was conducted with initial concentrations of glucose at 120 mg TOC/L, measured by a TOC analyzer (Shimadsu), and of trichlorfon at 25 mg/L, measured by a HPLC instrument (Yanagimoto) adapted from Samuelsen (1987). The DO level in the test was controlled above 5 mg/L. Thus, oxygen limitation was not considered (Chen *et al.*, 1994). Figure 1 shows the experimental results of the test. The kinetic parameters, except for the saturation constant of oxygen which was assumed to be 0.1 mg/L in this paper (Chen *et al.*, 1988), were identified from the batch test data and the following Eqs (9) and (10), as shown in Fig. 1

$$\text{Trichlorfon} \quad \frac{dS_t}{dt} = \frac{K_{tms} \cdot S_t}{K_{ts} + S_t} X_m \quad (9)$$

$$\text{Glucose} \quad \frac{dS_g}{dt} = \frac{K_{gms} \cdot S_g}{K_{gs} + S_g} X_m \quad (10)$$

where t is the reaction time (hr).

Fig.1 Determination of the kinetic parameters from batch test data and Eqs. (9) and (10) ($K_{gms} = 0.245/\text{day}$; $K_{tms}=0.228/\text{day}$; $K_{gs}=5 \text{ mg/L}$; $K_{ts}=15 \text{ mg/L}$; and $X_m=2000 \text{ mg/L}$)

Some parameters in other two groups could be either estimated or taken from literature: the diffusivities of glucose and oxygen in the bulk liquid phase were taken from literature (Perry *et al.*, 1963) while that of trichlorfon was estimated from its molecular size (Perry *et al.*, 1963); the diffusivities of the substances within the attached phase were assumed to be 80 % of those in the bulk liquid phase (Williamson and McCarty, 1976); the thickness of the diffusion layer and the yield coefficients of glucose and trichlorfon were assumed to be 100 μm (Williamson and McCarty, 1976), 0.5 (Idei, 1990), and 0.1 , respectively. The rest of the parameters in these two groups were measured directly, such as the concentrations of the suspended biomass, and the biomass density and the thickness of the attached phase (Ozaki *et al.*, 1991, 1993) or are given in the simulation, such as the A , Q , V , bulk DO level, and the influent concentrations of the pollutants. A summary of the values of the parameters used for the model simulation is shown in Table 1.

Example of Model Simulation Results

Figure 2 shows an example of the model simulation results, which demonstrates that the proposed model and the analysis approach in this paper can give reasonable simulations on the simultaneous removal of trichlorfon and glucose in the hybrid bioreactor. By this model, effluent concentrations of both trichlorfon and glucose

can be predicted under a specific removal condition, the model is, therefore, able to quantitatively evaluate the removal performance of both the biomass in a hybrid bioreactor under various removal conditions.

Table 1 The values of the parameters used in the model simulation

Parameter	Value	Parameter	Value
A	609 cm^2	D_{wc}	2.16 cm^2/day
C	5.0 $\text{mg O}_2/\text{L}$	D_{wg}	0.60 cm^2/day
L_f	3 mm	D_{wt}	0.42 cm^2/day
Lo	100 μm	K_{gms}	0.245 /day
Q	12.8 L/day	K_{tms}	0.228 /day
S_{og}	150 mg TOC/L	K_{sg}	5.0 mg TOC/L
S_{ot}	25 mg/L	K_{st}	15.0 mg/L
V	2.2 L	K_o	0.1 $\text{mg O}_2/\text{L}$
X_m	2000 mg SS/L	P	1.42 mg COD/mg VSS
X_f	11 mg SS/cm^3	Y_g	0.5 mg VSS/mg COD
		Y_t	0.1 mg VSS/mg COD

Fig. 2 An example of the model simulation results

MODEL VERIFICATION

To verify the proposed model, a hybrid bioreactor consisting of the suspended biomass and magnetically immobilized biomass, as shown in Fig. 3, was used in this study. By using such immobilized biomass, it is easier to alter the thickness and density of the attached biomass, and the weight ratio of the suspended biomass to the attached biomass (Sakai, *et. al.*, 1992), which are extremely difficult to be regulated with a naturally attached growth. Therefore, extensive experiments for the model verification can be conducted under a variety of removal conditions in this study.

In this hybrid bioreactor, 147 pieces of a small permanent magnetic block possessing a magnetic strength of 3200 gauss were installed around the wall of the reactor as the magnetic support media. The media can effectively attract the biomass carrying magnetic powders (Fe_3O_4) onto the surface of reactor wall. Thus, an immobilized biomass layer or a “magnetic biofilm”, was formed by the “magnetic” biomass and the magnetic support media. Prior to the formation of such a biofilm, the magnetic biomass was prepared by a vigorous mixing between original suspended biomass and the magnetic powders in the reactor. The magnetic biomass was composed of 50% magnetic powders and 50 % biomass in a dried basis. A continuous attachment of the magnetic biomass was then initiated by a gently mixing. Within a short period of time, a uniform attachment

of the biomass was developed on the inner wall surface of the reactor, as shown in Fig. 3. After the development of such magnetic biofilm, a certain amount of non-magnetic suspended biomass was added into this reactor to establish tow phases of biomass in the system.

Fig 3. Experimental setup for continuous experiment

A set of continuous experiments using the above experimental setup was conducted in a temperature constant room (20°C) under various removal conditions. Each experiment continued for around 90 hours to obtain a stable effluent. DO level and the suspended biomass concentration were controlled at 5-6 mg/L and a fixed level, respectively. The actual reactor volume and the biofilm surface area were measured to be 2.13 L and 609 cm². The hydraulic retention time was fixed at 4 hours for each experiment. The detail of the experimental conditions is shown in Table 2.

Table 2 Removal conditions in the continuous experiment

Run No.	Influent Glucose (mg TOC/L)	Influent Trichlorfon (mg/L)	Suspended Biomass (mg SS/L)	Biofilm Density (mg SS/cm ³)	Biofilm Thickness (mm)
1	141	25.9	4000	0	0
2	159	25.1	2000	11	3
3	146	25.2	2000	13	5
4	153	25.4	2000	18	7
5	140	110.7	2000	11	3
6	159	24.1	250*	13	5

*: estimated value.

In this table, the densities were calculated from the amount of biomass used for forming the magnetic biofilm, the surface area of the biofilm formed, and the thickness measured. Based on these measurements and the values of other necessary parameters indicated in Table 1, the model predicted the simultaneous removal efficiencies of trichlorfon and glucose under each condition. The comparisons between the experimental results and the model predictions are shown in Fig. 4. The model predictions for each test run were well close to the experimental results. It can then be said that the proposed model is able to satisfactorily predict such removal efficiency in the hybrid bioreactor. This figure also shows that in this hybrid system, the simultaneous removal of trichlorfon and TOC is mainly due to the suspended biomass. This implies that an increase of a total biomass amount by introducing an attached biomass phase may not be very effective as both the suspended and attached biomass in this system contain the same pollutants removing microorganisms, and the advantage of the biofilm in removing slowly biodegradable substances cannot be utilized. However, when a substance having either a small maximum specific removal rate (K_{tms}) or a high diffusivity is introduced, the contribution of the biofilm can be maximized, as shown in Fig. 5.

Fig. 4 Comparison of the experimental results with the model prediction

Fig. 5 Simulation on the effects of biodegradability and diffusivity of trichlorfon on its removal rate

This can be explained that a very slowly biodegradable substance usually requires a long contact time which can be achieved by a penetration of the substance in the biofilm (Chen, *et al.*, 1997). On the other hand, since such a penetration is also influenced by the diffusivity of the substance, a high diffusivity is in favor of the removal rate in the biofilm. As a result, an overall removal of such a substance in a hybrid bioreactor is controlled by the biodegradability as well as the diffusivity. It can be seen from this figure that the biodegradability effects the removal rate more significantly than the diffusivity does. To effectively apply such a hybrid system in treating a complex wastewater containing both easily and slowly biodegradable pollutants, it is recommended to apply it to treat such complex wastewaters that contain very slowly biodegradable and highly diffusitive substances.

CONCLUSION

This paper has developed a mathematical model for predicting the simultaneous removal of trichlorfon and glucose in the hybrid bioreactor that contained a magnetically immobilized biomass phase.

The model has been verified well by the comparisons of the model predictions with the experimental results under various removal conditions.

The suspended biomass has also been found to play a more important role in such simultaneous removal than the attached biomass does if both the biomass have the same pollutant removing microorganisms.

To maximize the removal capacity of the attached biomass, it is recommended to apply such a hybrid bioreactor to deal with a complex wastewater that contains much slowly biodegradable pollutants with a high diffusivity.

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