

SYSTEM OBSERVABILITY AND NONLINEAR PARAMETER IDENTIFICATION OF NONYLPHENOL BIODEGRADATION KINETICS

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ABSTRACT

Addition of surfactants, detergents and emulsifiers has been successfully applied for cleanup of petroleum-contaminated sites. However, a certain group of widely used alkylphenolethoxylates (APEs) surfactants was recently banned in Europe because scientists discovered that APE breakdown products are estrogenic and highly toxic to aquatic organisms. Nonylphenol is one of the very toxic breakdown products. The process of nonylphenol biodegradation is very important to many scientists because of its potential effectiveness as a treatment tool for pollution. However, very little information is available on the biodegradation kinetics of nonylphenol. Kinetic information is necessary for predicting the fate of pollutants. We start with Monod's model for nonylphenol biodegradation which is based on a coupled system of nonlinear differential equations. We prove that the states of the system and the parameters of Monod's model are locally observable. This enables us to perform a meaningful parameter estimation analysis. By using nonlinear least-squares optimization, we obtain the biodegradation kinetics and verify physical feasibility on independent datasets.

1. INTRODUCTION

Researchers have indicated that solubilization followed by microbial metabolism of organic contaminants is technically feasible and has potential as a remedial technology [1]. Addition of surfactants, detergents and emulsifiers has been successfully applied for cleanup of petroleum-contaminated sites. However, a certain group of widely used alkylphenolethoxylates (APEs) surfactants were banned in Europe because scientists discovered that APE breakdown products are highly toxic to aquatic organisms. Recent evidence that some APE breakdown products are estrogenic has intensified concern over their environmental and human health effects [2].

APEs are nonionic surfactants made up of a branched chain ethylene oxide to produce an ethoxylate chain. Most APEs enter the aquatic environment from wastewater treatment plant discharges. Nonylphenol, one of the breakdown products of APEs, is known to be extremely toxic. Nonylphenol, adsorbs to soils and sludges, tends to bioaccumulate, and has been shown to be mildly estrogenic. Sewage sludge thus applied to agricultural land may contain nonylphenol. European studies indicate high concentrations of nonylphenol in treated sewage sludge thereby indicating sludge disposal as a source of aquatic contamination. Nonylphenol biodegradation is therefore a significant environmental issue [3]. However very little information is available on the biodegradation kinetics of

nonylphenol. Kinetic information is important for predicting the fate of pollutants. It has been demonstrated that it is possible to determine intrinsic kinetics of single organic compounds by using oxygen uptake data from electrolytic respirometry [4].

The purpose of this paper is to use nonlinear least-squares optimization to obtain the intrinsic kinetic parameters of nonylphenol biodegradation from oxygen uptake data. These parameters are part of an existing mathematical biodegradation model of coupled nonlinear differential equations known as Monod's model [5]. The model has three states, namely, oxygen uptake, substrate (or pollutant) removal and bacterial cell growth. Only the oxygen uptake is experimentally measurable. We perform an analysis of Monod's model to show that its states and parameters are locally observable about the entire state space except for some isolated points. The model parameters obtained by nonlinear optimization are in agreement with the experimental measurements for all three states. This not only makes oxygen uptake data very attractive as it can eliminate monitoring of substrate removal and bacterial cell growth but also verifies the feasibility of using nonlinear optimization. The oxygen uptake data is obtained using electrolytic respirometry. This is relatively inexpensive and gives fast, accurate and reliable data.

2. MODELING OF THE NONYLPHENOL BIODEGRADATION PROCESS

The process of nonylphenol biodegradation is given by a set of nonlinear differential equations that describe its kinetic behavior. This is known as Monod's model of bacterial kinetics and is given by [5]

$$\begin{aligned}\frac{dX}{dt} &= \frac{\mu_m SX}{K_s + S} - K_d X \\ \frac{dS}{dt} &= -\frac{1}{Y} \frac{\mu_m SX}{K_s + S} \\ \frac{dO_x}{dt} &= Y_{Ox} \frac{\mu_m SX}{K_s + S} + Y_{OxD} K_d X\end{aligned}\quad (1)$$

This system has three states: S is the concentration of substrate, X is the active cell mass concentration, and O_x is the cumulative oxygen consumption in the reactor (oxygen uptake which we measure). The time evolution of the system is also determined by the several system parameters or biodegradation coefficients involved: μ_m is the specific growth rate of substrate; K_d is the endogenous decay coefficient; K_s is the substrate utilization coefficient; Y is

the cell yield coefficient (mass of cell produced divided by mass of food consumed); Y_{OX} is the oxygen consumption coefficient for substrate (mg oxygen/mg of cell mass); and Y_{OXD} is the oxygen consumption coefficient for endogenous respiration (mg oxygen/mg of cell mass).

3. OBSERVABILITY OF MONOD'S EQUATION

For convenience, we let $\mathcal{X} = [X, S, O_x]^T$ and we re-write Monod's equation (1) as

$$\dot{\mathcal{X}} = \begin{bmatrix} \dot{X} \\ \dot{S} \\ \dot{O}_x \end{bmatrix} = \begin{bmatrix} f_1(\mathcal{X}) \\ f_2(\mathcal{X}) \\ f_3(\mathcal{X}) \end{bmatrix} = f(\mathcal{X}) \quad (2)$$

We linearize (2) about some point $\bar{\mathcal{X}} = [\bar{X}, \bar{S}, \bar{O}_x]^T \in \mathbb{R}^3$ in order to study observability of the linearized system. Letting $A = \frac{\partial f}{\partial \mathcal{X}}|_{\mathcal{X}=\bar{\mathcal{X}}}$, it can be easily shown that

$$A = \begin{bmatrix} a_{1,1} & a_{1,2} & 0 \\ a_{2,1} & a_{2,2} & 0 \\ a_{3,1} & a_{3,2} & 0 \end{bmatrix} \quad (3)$$

where $a_{1,1} = \mu_m \frac{\bar{S}}{\bar{K}_s + \bar{S}} - K_d$, $a_{1,2} = K_s \mu_m \frac{\bar{X}}{(\bar{K}_s + \bar{S})^2}$, $a_{2,1} = -\frac{\mu_m}{Y} \frac{\bar{S}}{\bar{K}_s + \bar{S}}$, $a_{2,2} = -\frac{\mu_m K_s}{Y} \frac{\bar{X}}{(\bar{K}_s + \bar{S})^2}$, $a_{3,1} = Y_{OX} \mu_m \frac{\bar{S}}{\bar{K}_s + \bar{S}} + Y_{OXD} K_d$ and $a_{3,2} = Y_{OX} \mu_m K_s \frac{\bar{X}}{(\bar{K}_s + \bar{S})^2}$. For the linearized system, one can define the output equation as $y = C\mathcal{X}$ with $C = [0, 0, 1]$ (since the only measurable state is O_x). One can then build the observability matrix [9]

$$Obs = \begin{bmatrix} C \\ CA \\ CA^2 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 \\ a_{3,1} & a_{3,2} & 0 \\ a_4 & a_5 & 0 \end{bmatrix} \quad (4)$$

with $a_4 = a_{1,1}a_{3,1} + a_{2,1}a_{3,2}$ and $a_5 = a_{1,2}a_{3,1} + a_{2,2}a_{3,2}$. Clearly, Obs is invertible if and only if $a_{3,1}a_5 - a_{3,2}a_4 \neq 0$. This result shows that the linearized system is locally observable in most of the state space (except for some isolated points or regions). While this does not imply the existence of a global observability diffeomorphism for (1), it does imply that the states can be observed at least about carefully chosen operating points or possibly within a significant region.

Consider, for example, the point $\bar{\mathcal{X}} = [\bar{X}, 0, 0]^T$. Then, the parameters of the observability matrix are

$$\begin{aligned} a_{3,1} &= Y_{OXD} K_d \\ a_{3,2} &= \frac{Y_{OX} \mu_m}{K_s} \bar{X} \\ a_4 &= -Y_{OXD} K_d^2 \\ a_5 &= \frac{Y_{OXD} K_d \mu_m}{K_s} \bar{X} - \frac{Y_{OX} \mu_m^2}{Y K_s^2} \bar{X}^2 \end{aligned} \quad (5)$$

Clearly, for most combinations of values of the parameters and \bar{X} the system will be observable at this operating point. Note, moreover, that the system is *not* observable at $\bar{\mathcal{X}} = [0, 0, 0]^T$, which confirms the intuition that, without any cells or food, no reaction is possible and no information can be obtained about the system states.

We are also interested in studying parameter observability, since our main objective in this study is to perform parameter estimation

from output data. To be concise, let us concentrate on the parameter μ_m (the same analysis, with similar results, can be performed for the other parameters of interest; for brevity and clarity we concentrate only on one of the four parameters in the following). Define the augmented system

$$\begin{bmatrix} \dot{\mathcal{X}} \\ \dot{\mu}_m \end{bmatrix} = \begin{bmatrix} f(\mathcal{X}) \\ 0 \end{bmatrix} = f_{aug}(\mathcal{X}_{aug}) \quad (6)$$

where $\mathcal{X}_{aug} = [\mathcal{X}, \mu_m]^T$. The augmented system is linearized about the point $\bar{\mathcal{X}}_{aug} = [\bar{\mathcal{X}}, \bar{\mu}_m]^T$. The linearized augmented system's matrix is

$$A_{aug} = \frac{\partial f_{aug}}{\partial \mathcal{X}_{aug}} \Big|_{\mathcal{X}_{aug}=\bar{\mathcal{X}}_{aug}} = \begin{bmatrix} a_{1,1} & a_{1,2} & 0 & a_{1,4} \\ a_{2,1} & a_{2,2} & 0 & a_{2,4} \\ a_{3,1} & a_{3,2} & 0 & a_{3,4} \\ 0 & 0 & 0 & 0 \end{bmatrix} \quad (7)$$

Note that $a_{i,1}$ and $a_{i,2}$ for $1 \leq i \leq 3$ are the same as for the system without augmenting μ_m . One can show that $a_{1,4} = \frac{\bar{X}\bar{S}}{\bar{K}_s + \bar{S}}$, $a_{2,4} = -\frac{1}{Y} \frac{\bar{X}\bar{S}}{\bar{K}_s + \bar{S}} = -\frac{1}{Y} a_{1,4}$ and $a_{3,4} = Y_{OX} \frac{\bar{X}\bar{S}}{\bar{K}_s + \bar{S}} = Y_{OX} a_{1,4}$. Now, consider the output

$$y_{aug} = C_{aug} \mathcal{X}_{aug} = [0, 0, 1, 0] \mathcal{X}_{aug} \quad (8)$$

Then, the augmented systems' observability matrix is

$$Obs_{aug} = \begin{bmatrix} C_{aug} \\ C_{aug} A_{aug} \\ C_{aug} A_{aug}^2 \\ C_{aug} A_{aug}^3 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ a_{3,1} & a_{3,2} & 0 & a_{3,4} \\ a_6 & a_7 & 0 & a_8 \\ a_9 & a_{10} & 0 & a_{11} \end{bmatrix} \quad (9)$$

with $a_6 = a_{1,1}a_{3,1} + a_{2,1}a_{3,2}$, $a_7 = a_{1,2}a_{3,1} + a_{2,2}a_{3,2}$, $a_8 = a_{1,4}a_{3,1} + a_{2,4}a_{3,2}$, $a_9 = a_{1,1}a_6 + a_{2,1}a_7$, $a_{10} = a_{1,2}a_6 + a_{2,2}a_7$ and $a_{11} = a_{1,4}a_6 + a_{2,4}a_7$. One can conclude that Obs_{aug}^{-1} exists by noting that, for most combinations of values, it holds that

$$\begin{aligned} C_{aug} A_{aug}^2 &\neq c_1 C_{aug} A_{aug} \\ C_{aug} A_{aug}^3 &\neq c_2 C_{aug} A_{aug} \\ &\neq c_3 C_{aug} A_{aug}^2 \end{aligned} \quad (10)$$

for any constants c_1, c_2 and c_3 .

The fact that state observability and parameter observability can be guaranteed at least locally for most operating conditions of interest means that the problem of parameter estimation can be solved, at least in principle, by using observations of the output, O_x , the oxygen uptake in the reactor. The experiments and results that follow are then supported and shown to be feasible by this analysis.

4. NONLINEAR LEAST-SQUARES ALGORITHM

The nonlinear estimation technique seeks to identify the system parameters to minimize the mean-square error between the numerical solution for the state O_x and the experimental data obtained for O_x . Note that state O_x is the only measurable state. Since the parameters enter the model in a nonlinear fashion, the use of nonlinear search methods is appropriate. The algorithm starts with a guess of the initial parameter values, solves the differential equation in Monod's model numerically, and then adjusts the system parameters in an attempt to minimize the mean-square error between the numerical solution for O_x and the experimental data points.

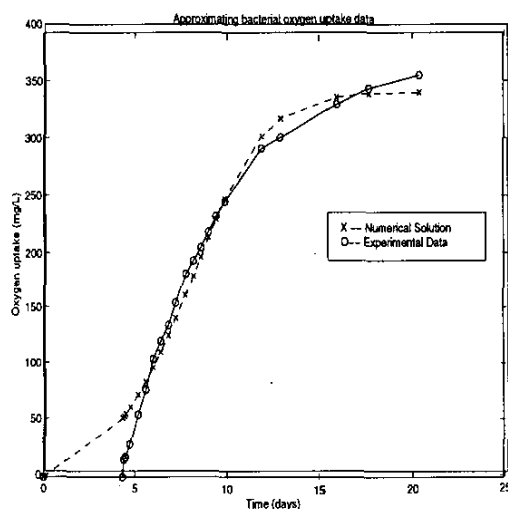


Fig. 1. Oxygen uptake

The nonlinear minimization algorithm involves a trust region approach and accommodates parameter bounds [6][7][8]. Generally, the trust region approach iteratively updates a parameter solution set by an increment that is an approximate solution to a quadratic subproblem. For the method we use [6], a quadratic model is formed and solved using the trust region method. The requirements on the parameter bounds are achieved by restricting the increments at each iteration. Second order convergence is guaranteed.

Nonylphenol (99% pure) was obtained from Fluka Chemical Corporation, Milwaukee, WI. An acclimated culture capable of degrading nonylphenol was developed from a local wastewater treatment plant. Enrichment cultures were developed in batch reactors incubated at room temperature with nonylphenol as the sole carbon source. All solutions were prepared in deionized water. Oxygen uptake measurements were recorded with time through electrolytic respirometry. All experiments were conducted in duplicate at 20°C.

Given that the optimization is performed for a nonlinear function, the initial values play a significant role in determining the parameter set to which the optimization converges. Initial conditions are required for the three states and four of the six system parameters or biodegradation coefficients. The initial values for the states are taken from the experimental conditions. The endogenous decay coefficient K_d and oxygen consumption coefficient Y_{OXD} have fixed values since they are determined by known characteristics of the experimental setup. The other four of the biodegradation coefficients of the system are experimentally constrained to lie within allowable ranges ($0.1 \leq u_m \leq 1$, $0.005 \leq K_s \leq 1000$, $0.1 \leq Y \leq 1.5$ and $1.5 \leq Y_{OX} \leq 3.5$). Different initial values within these bounds are attempted. After some trial and error, we determined that initial conditions roughly in the middle of the allowable ranges (as given above) yielded the best results. The initial conditions we use are $u_m = 0.5$, $K_s = 500$, $Y = 0.85$ and $Y_{OX} = 2.5$. After applying the algorithm, the final estimated values of Y (0.8698) and Y_{OX} (2.6353) continue to be in the middle range. The final values of u_m (0.9441) and K_s (223.5991) deviate considerably from the middle range.

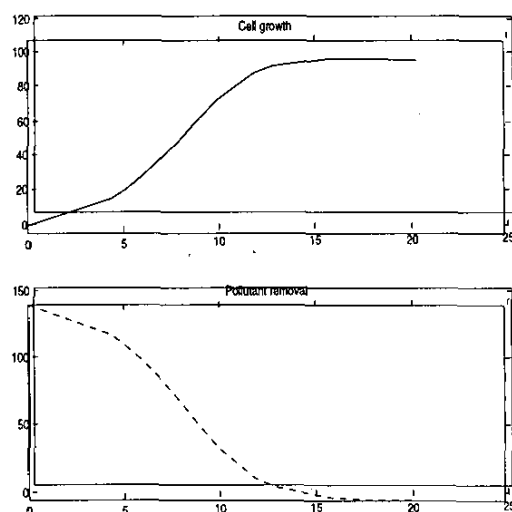


Fig. 2. Cell growth and pollutant removal

To determine the validity of the results obtained, it is necessary to determine whether the behavior of the system makes physical sense. This implies that although finding the best-fitting curve is one of our main interests, it is not the only one. We are not only interested in the oxygen uptake behavior, but also in how the cell growth and pollutant removal states evolve. It may be the case that even though the numerical method yields a good approximation for oxygen uptake, the other two states behave in a physically meaningless manner. Realistically, the graph for the pollutant removal should decay from its initial value to zero as the pollutant is utilized by the bacterial cells. On the other hand, cell growth, as time passes by, should initially increase and then decrease as the pollutant becomes less and less available for bacterial nutrition. When all the nonylphenol in the solution has been digested, the bacteria start eating each other and die out. Since only one of the three states in Monod's model can be measured, the validity of the optimized set of parameters given by the algorithm needs to be checked using these relatively subjective criteria.

In Figure 1 one can observe the approximated oxygen uptake trajectory and compare it with the experimental data. The circled data points are obtained from the experiment, while the other data points are obtained from the numerical solution. A better approximation is indeed obtained in the middle portion of the curve, rather than at the extremes. The discrepancy is due to errors caused by the experimental data. The bacterial process involved in this experiment for times less than five days may have been initially idle, thus causing the observed behavior.

Figure 2 shows that both cell growth and pollutant removal behavior meet our expectations as described before. Pollutant removal decreases over time as bacteria consume the available nonylphenol, while cell growth initially increases and then starts to decrease at a slow rate.

5. VERIFICATION OF THE RESULTS

In order to verify the usefulness of the parameters obtained, we applied the parameter values to a set of data points that is not used

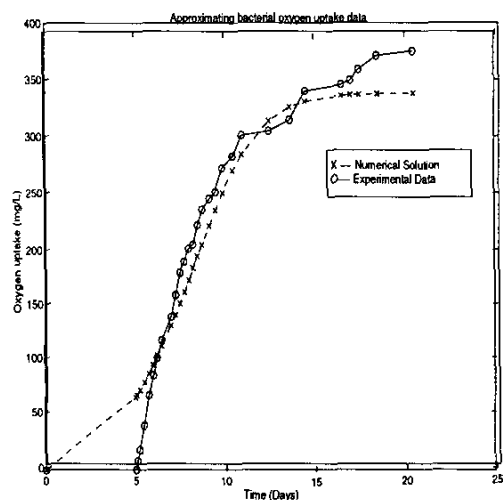


Fig. 3. Oxygen uptake using the test data set

for training. The data set was obtained using the same initial experimental conditions as the data set used to obtain the preliminary results. For this new data set, the resulting oxygen uptake trajectory does indeed resemble the evolution of the experimental measurements, as shown in Figure 3. Moreover, in Figure 4, one can observe the evolution of the other two states. It is important to note that, to obtain these results, we did not use the least squares optimization algorithm. Rather, we simply used the obtained biodegradation coefficients to solve the differential equations in Monod's model numerically, using the experimental initial conditions for the states.

The oxygen uptake graph for the new data set shows that the obtained analytical solution does approximate the experimental data points quite well. The cell growth and pollutant removal states behave in a physically consistent manner, as shown in Figure 4. The pollutant decreases over time, while cell growth increases until there is no more pollutant (food) available. At this point cell growth starts to decrease as cell begin to die out. Robustness to a varying data set is established.

6. CONCLUSIONS

The purpose of this study was to model the influence of nonionic surfactants on biodegradation of nonylphenol. To model this nonlinear biodegradation process requires knowledge of the intrinsic parameters of the system, which is generally difficult to obtain through only experimental measurements. We first prove that the states of the system and the parameters of Monod's model are locally observable. By using nonlinear least squares optimization, we have shown that it is possible to obtain the biodegradation kinetic information. Overall, the proposed algorithm provides a good approximation of the experimental data and is based on Monod's model. The results obtained are also shown to be physically meaningful in that the behavior of the unobservable states, cell growth and pollutant removal, was well modeled. Robustness to data sets not used for training was also verified.

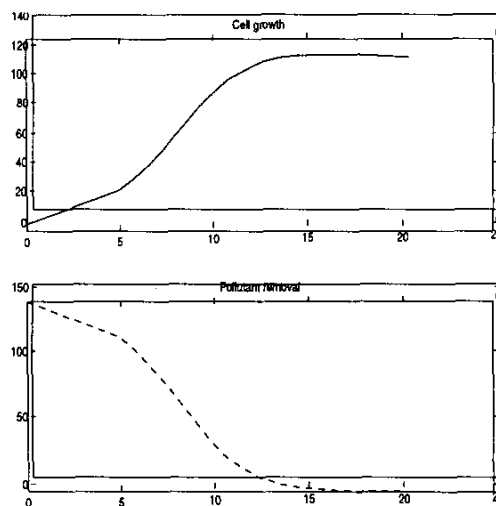


Fig. 4. Cell growth and pollutant removal using the test data set

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