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Nonlinear Parameter Estimation of Nonylphenol Biodegradation

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Abstract— **The use of surfactants to enhance the aqueous solubilization of hydrocarbons has been investigated extensively in recent years. Researchers have indicated that solubilization followed by microbial metabolism of organic contaminants is technically feasible and has potential as a remedial technology. Addition of surfactants, detergents and emulsifiers has been successfully applied for cleanup of petroleum-contaminated sites. However, recently a certain group of widely used alkylphenolethoxylates (APEs) surfactants was banned in Europe because scientists discovered that APE breakdown products are estrogenic and highly toxic to aquatic organisms. However, very little information is available on the biodegradation kinetics of nonylphenol. Kinetic information is necessary for predicting the fate of pollutants using mathematical models. This paper presents system identification results for the nonylphenol biodegradation process using nonlinear optimization. By using non-linear regression methods such as nonlinear least squares, one can obtain the biodegradation kinetics. This kinetic description is very helpful to environmental scientists and engineers to predict the fate and transport of pollutants in the environment. The paper demonstrates the expectations and the feasibility of results from such a non-linear process.**

Keywords: Nonlinear parameter estimation, nonylphenol biodegradation, nonlinear least squares

I. Introduction

Surfactants have been shown to be very effective in soil washing, flushing technologies and bioremediation of contaminated sites. The improved effectiveness of these surfactant-amended systems is due to the solubilization of adsorbed hydrophobic compounds in soils. They have been shown to increase solubility and dispersion of poorly soluble hydrocarbons and oils thereby enhancing desorption and bioavailability. The use of surfactants to enhance the aqueous solubilization of hydrocarbons (such as, Non-aqueous phase liquid-NAPLs and polycyclic aromatic hydrocarbons etc.) has been investigated extensively in recent years by a number of investigators [1], [2], [3], [4], [5].

Researchers have indicated that solubilization followed by microbial metabolism of organic contaminants is technically feasible and has potential as a remedial technology [6]. Addition of surfactants, detergents and emulsifiers has been successfully applied for clean up of petroleum-contaminated sites [1]. However, recently 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 [7]. Throughout northern Europe a voluntary ban on APE use in household cleaning products began in 1995 and restrictions on industrial applications are set to follow by the year 2000. The city of Toronto in Canada has also banned discharges of APEs into their sewer systems.

APEs are nonionic surfactants made up of a branched chain ethylene oxide to produce an ethoxylate chain. The main alkylphenols used are nonylphenol (NP) and octylphenol (OP). Nonylphenol ethoxylates (NPEs) encompass about 80% of the world market, and octylphenol ethoxylates (OPEs) represent most of the rest [8]. They have been used extensively for their effectiveness, economy and ease of handling and formulating for more than forty years. They function as emulsifiers, wetting agents and dispersants. The primary industrial uses of APEs are for emulsion polymerization and polymer stabilization in plastics and elastomers; cleaning, spinning, weaving, and finishing of textiles; wetting agents and emulsifiers in agricultural chemicals; and pulping and deinking in the paper

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industry. Institutional use of APEs are confined to cleaning products, and most are found in commercial laundry detergents, janitorial products, and vehicle cleaners. In the household market, APEs are used mainly in laundry detergents and hard-surface cleaners. Most APEs enter the aquatic environment from wastewater treatment plant discharges.

Nonylphenol (NP), one of the breakdown products, is also approximately 10 times more toxic than its ethoxylates. The generic NPE structure is depicted in Figure 1. The average number of moles of ethylene oxide per mole of NP ranges from 1 to 100.

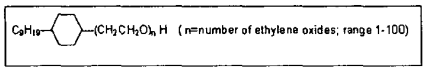

Fig. 1. Nonylphenol ethoxylate structure

The literature indicates that the metabolites of NPEs, especially nonylphenol, adsorbs to soils and sludges. Nonylphenol is persistent, lipophilic and tends to bioaccumulate. It has also been shown to be mildly estrogenic. Sewage sludge thus applied to agricultural land may contain nonyphenol. European studies indicate high concentrations of nonylphenol in treated sewage sludge thereby indicating sludge disposal as a source of aquatic contamination. Nonylphenol biodegradation has been studied by a number of researchers [9], [10], [11], [12], [13]. However very little information is available on the biodegradation kinetics of nonylphenol. Kinetic information is important for predicting the fate of pollutants using mathematical models. Studies by Grady, Dang, and Harvey [14], [15], have demonstrated that it is possible to determine intrinsic kinetics of single organic compounds by using oxygen uptake data from electrolytic respirometry.

With the use of computer simulation techniques and non-linear least squares optimization, intrinsic kinetic parameters are obtained from oxygen consumption data. The model predictions are shown to be in agreement with those obtained from traditional measurements of substrate removal and cell growth. This makes oxygen uptake data very attractive as it can eliminate monitoring of substrate removal and cell growth. Nonyphenol concentration measurements require an exhaustive steam distillation extraction procedure before using HPLC for analysis. Oxygen uptake using respirometry gives fast, accurate and reliable data. The justification for using respirometry to obtain intrinsic biodegradation kinetics lies in the concept of oxygen consumption as an energy balance. This concept states that all of the electrons available in a substrate undergoing biodegradation must either be transferred to the terminal acceptor or be incorporated into new biomass or soluble products. Since biomass growth and product formation are proportional to substrate removal, this suggests that an oxygen uptake curve can provide the same information as either a substrate removal curve or a cell growth curve. Therefore, for compounds like nonylphenol, oxygen uptake modeling for determination of biodegradation kinetics is very attractive. Kinetic coefficients help environmental scientists and engineers to predict the fate and transport of pollutants in the environment.

II. Modeling of the Nonylphenol Biodegradation Process

The nonylphenol biodegradation process is given by a system of differential equations, where parameters determine the behavior of the system. To find these parameters, our first approach has been to use a nonlinear least squares optimization method. The parameters enter the model in a nonlinear fashion, so the use of nonlinear search methods is appropriate. A comparison with linear search performance is of interest, but is not within the scope of this paper.

A. Mathematical Model

The process of nonylphenol biodegradation is given by a set of differential equations that describe its kinetic behavior. A number of models may be used, but we decided to use Monod's ordinary differential equations [16], since this is a well known model of bacterial kinetics.

$$\frac{dX}{dt} = \frac{u_m S X}{K_s + S} - K_d X$$

$$\frac{dS}{dt} = -\frac{1}{Y}\frac{u_m S X}{K_s + S}$$

$$\frac{dO_x}{dt} = Y_{OX}\frac{u_m S X}{K_s + S} + Y_{OXD} K_d X \qquad (1)$$

This system has three states: S is the concentration of substrate (M/L^3), X is the active cell mass concentration (M/L^3), and O_x is the cumulative oxygen consumption in the reactor (M/L^3). The system's time evolution is also determined by the several parameters involved: u_m

is the specific growth rate of substrate (1/T); K_d is the endogenous decay coefficient (1/T); K_s is the substrate utilization coefficient (M/L^3); Y is the dimensionless cell yield (cell produced/food consumed) coefficient (mg cell mass/mg of substrate); Y_{OX} is the dimensionless oxygen consumption coefficient for substrate (mg oxygen/mg of cell mass); and Y_{OXD} is the dimensionless oxygen consumption coefficient for endogenous respiration (mg oxygen/mg of cell mass).

B. Initial Values and Experimental Method for Data Collection

The developed nonlinear regression technique is an iterative process. The method requires some initial estimates for the parameters, which are adjusted at every iteration to improve the approximation between the numerical solution of the O_x state and the corresponding experimental measurements. The system's coefficients are constrained to lie within allowable ranges, which are dictated by the nature of the experiment (please see the results section below). The initial values for the states are taken from the experimental conditions.

The parameters that require initial values in this program are concentration of substrate (S), concentration of bacterial cells (X), oxygen uptake (O_x), and all the coefficients. The initial values for the states are taken from the experimental conditions. 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. Nutrient buffer was made according to the Watanabe media [17]. Oxygen uptake measurements were recorded with time through electrolytic respirometry (N-CON Systems Comput-OX 244, Crawford, GA). All experiments were conducted in duplicate at 20°C.

C. Algorithm - Least Squares Fit Method

Our initial approach to solving this problem was to use nonlinear least squares to find the biodegradation coefficients. The optimization is set up to minimize the sum of the squares of the vertical distances between the experimental data points and the solutions of the state O_x in Monod's equations (1). The algorithm starts with a guess of the initial parameter values, solves Monod's differential equations numerically, and then adjusts the coefficients in an attempt to minimize the sum of the squares of the error between experimental and simulated oxygen absorption.

III. Parameter Estimation

To determine the validity of the results obtained, it is necessary to determine whether the behavior of the system makes physical sense. It is indeed possible that the analytical solution may not approximate the experimental data to the extent we would desire. Therefore, after obtaining a set of coefficients, we measure the goodness of the approximation by computing the mean square error,

$$e = \frac{1}{N}\sum_{i=1}^{N} e_i^2 \tag{2}$$

where N is the number of data points, and e_i is the error between the numerical solution for O_X and the experimental data points.

Although finding the best-fitting curve is one of our main interests, it is not the only one. The coefficients must satisfy the constraints described below. Moreover, 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. For example, 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 equation can be measured, the validity of the optimized set of coefficients given by the algorithm needs to be checked using these relatively subjective criteria. One of the main goals of this research is to figure our how to get around this limitation: on one end, better and cheaper measurement techniques may be used; on the other hand, as will be outlined below, a tool like a nonlinear observer may eliminate the need for costly measurement and improve our estimation capabilities.

Two of the six system coefficients (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: their values depend upon the cell type used in the experiment and the cells' oxygen consumption rate. The other four parameters, however, are unknown, and we attempt to determine them using the algorithm described above. They are constrained to lie within the ranges of lower and upper bounds given in Table I.

Range	u_m	K_s	Y	Y_{ox}
Lower	0.1	0.005	0.1	1.5
Upper	1	1000	1.5	3.5

TABLE I

LOWER AND UPPER COEFFICIENT BOUNDS

Given that the optimization is performed over a nonlinear function, the initial values play a significant role in determining the parameter set to which the optimization converges. After some trial and error, we determined that initial conditions in the mid-range yielded the best results (Table II).

Initial Values	Lower Bound	Lower than Mid Range	Mid Range
MSE	446.5501	423.8438	382.7506

Initial Values	Higher than Mid Range	Upper Bound
MSE	384.9916	387.9703

TABLE II

MEAN SQUARE ERROR (MSE) FOR VARIOUS INITIAL CONDITIONS

The coefficient set we obtained in this manner is given in Table III, where the initial values chosen and the final values given by the algorithm are shown.

	u_m	K_s	Y	Y_{OX}
Initial Values	0.55	500	0.85	2.5
Obtained Values	0.9441	223.5991	0.8698	2.6353

TABLE III

INITIAL AND FINAL COEFFICIENT VALUES

In Figure 2 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 form the numerical solution. Good approximation is obtained in the middle portion of the curve, while at the extremes approximation is unsatisfactory. The discrepancy is due to a considerable length in the acclimation period (approximately five days).

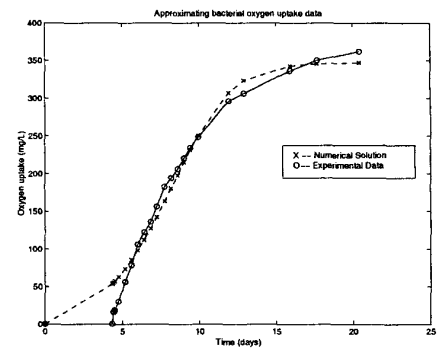

Fig. 2. Oxygen uptake

The last portion of the oxygen uptake graph, as shown in Figure 2, also exhibits a dissatisfying approximation of the experimental data points. This problem is not yet well understood, but we speculate that it could be due to error in the experiment, or due to the nature of Monod's differential equation. It may be possible that for the given parameter ranges, these differential equations do not model the oxygen uptake process accurately. Moreover, this process may be better identified using different methods, including neural network-based estimators or nonlinear observers. This, however, is the subject of future work.

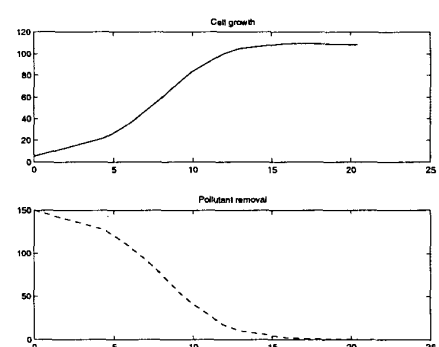

Fig. 3. Cell growth and pollutant removal

Figure 3 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 nonlyphenol, while cell growth initially increases and then starts to decrease at a slow rate.

IV. Verification of the Results

In order to verify the coefficients obtained, we applied the parameter values obtained in Table III to a set of data points (that is, data points not used for training). This test data set was obtained using the same initial experimental conditions as the data set used to obtain the preliminary results. For this data set, the resulting oxygen uptake trajectory does indeed resemble the evolution of the experimental measurements, as shown in Figure 4. Moreover, in Figure 5 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 coefficients in Table III to solve Monod's Differential Equations numerically, using the experimental initial conditions for the states.

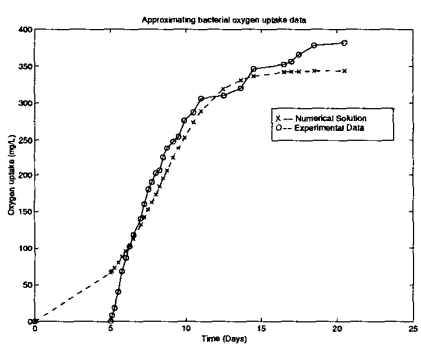

Fig. 4. Oxygen uptake using the test data set

The oxygen uptake graph for the new data set shows that the obtained analytical solution does approximate reasonably well the experimental data points. The first portion of the graph indicates that the error between analytical and experimental data is large. Again, this is probably caused by the initial idling of the process, which is not captured by Monod's equations (1). The error also increases in the last portion of the plot. There could be many reasons behind this discrepancy, but we suspect that Monod's model itself may be insufficient to accurately describe this system. Further testing and research are necessary to reach more definite conclusions.

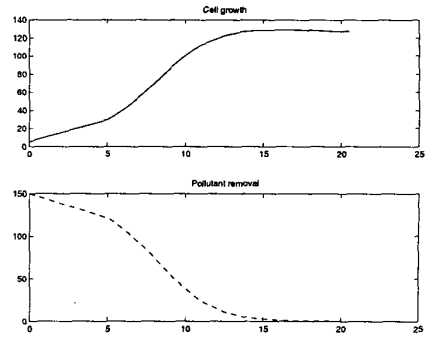

Fig. 5. Cell growth and pollutant removal using the test data set

The cell growth and pollutant removal states behave in a physically consistent manner, as shown in Figure 5. 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.

V. Impact of Research

The results of this research will be significant in shaping the future of regulations on surfactant production, use and disposal. The wastewater treatment plant community will also benefit tremendously from this study as they are impacted significantly by discharges of nonionic surfactants in their wastewaters. The results of this research will also have a major impact on engineering technology related to in situ bioremediation in the hazardous waste treatment and management field. Engineers must have a thorough understanding of the fate and transport of surfactants and their metabolites for successfully implementing a surfactant based treatment technology. The results of this study will also have a major impact on the disposal of nonionic surfactants by industries involved in manufacturing or utilizing these surfactants in processing plants.

VI. Conclusion

We deal with many non-linear processes in our day to day life and the task of obtaining results from these type of systems is generally nontrivial. The purpose of this study was to model the biodegradation kinetics of nonylphenol. To model this non-linear biodegradation process requires intrinsic parameters of the system, which is generally difficult to obtain through experimental measurements. By using nonlinear least squares, we have

shown that it is possible to obtain the information to some reasonable extent.

Overall, the proposed algorithm provides a reasonable approximation of the experimental data. However, this method depends heavily on the initial parameter values. In addition to the effect of the initial values, the developed mathematical model plays a key role in the success of this process. Without the proper model the validity of the results is questionable.

The results obtained suggest that it is in fact possible to obtain a physically meaningful kinetic description of nonylphenol biodegradation with the nonlinear least squares optimization method. The numerical approximation of the oxygen uptake data was found to be reasonable within experimental limits for some data sets. At the same time, the behavior of the other two states, cell growth and pollutant removal, was as expected and nicely modeled. To improve the results, the current mathematical model may need to be revised, and other nonlinear system identification techniques (e.g., neural network-based estimator or nonlinear observers) may prove more effective in estimating the coefficients of nonylphenol biodegradation.

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