# NONYLPHENOL BIODEGRADATION KINETICS ESTIMATION USING NEURAL NETWORKS

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## ABSTRACT

Many man made chemical substances are coming under the focus for environmental abuse and their impact on wild life and humans. A widely used alkylphenolethoxylates (APEs) surfactant was recently banned in Europe because scientists discovered that APE breakdown products are estrogenic and highly toxic to aquatic organisms . Nonylphenol is one such substance that has come under the focus as an environmental pollutant. However, sufficient information is not there to study the kinetic behavior of this toxic surfactant. The biodegradation process of nonylphenol is best described by Monod's model which is based on a coupled system of nonlinear differential equations. This model is based on set of kinetic parameters. It is very difficult to measure the actual biodegradation process of nonylphenol because of the unknown nature of the parameters involved and expense in measuring the states. The estimation of kinetic parameters of nonylphenol biodegradation is done by using a gradient optimization neural network estimator.

## 1. INTRODUCTION

Surfactants have been shown to be very effective in soil washing, flushing technologies and bioremediation of contaminated sites [3]. Addition of surfactants, detergents and emulsifiers has been successfully applied for cleanup of petroleum-contaminated sites. 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 [2]. Most APEs enter the aquatic environment from wastewater treatment plant discharges. Nonylphenol, one of the breakdown products of APEs, is known to be toxic. Traditionally used in the chemical industry, it is a breakdown product of surfactants and detergents widely used in cleaning industry. Nonylphenol adsorbs to soils and sludge's, tends to bioaccumulation, and has been shown to be mildly estrogenic [1]. 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. The process of nonylphenol biodegradation is 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 important for predicting the fate of pollutants. The biodegradation process of nonylphenol is best described by Monod's model [5]. Due to the expense in finding biodegradation states it has been demonstrated that it is possible to determine intrinsic kinetics of single organic compounds by using oxygen uptake data from electrolytic respirometry. This is relatively inexpensive and gives fast, accurate and reliable data. Direct nonylphenol concentration measurements require an exhaustive steam distillation extraction procedure before using high pressure liquid chromatography for analysis. This is more expensive to implement.

The purpose of this paper is to estimate the unknown intrinsic kinetic parameters and states through simulation based on the neural network concept. These estimating parameters are part of an existing mathematical biodegradation model of coupled nonlinear differential equations known as Monod's model. The model has three states, namely, oxygen uptake, substrate (or pollutant) concentration and bacterial cell mass concentration. Only the oxygen uptake is experimentally measurable by means of electrolytic respirometry [4]. This paper presents a neural network based approach for high-level performance estimation, which easily adapts to the non-linear behavior of the kinetic parameters. Through simulation the behavior of the three states can be studied using neural network test data patterns.

## 2. MONOD'S MODEL FOR NONYLPHENOL BIODEGRADATION PROCESS

The process of nonylphenol biodegradation kinetic behavior can be described by a set of nonlinear differential equations known as Monod's model of bacterial kinetics and are given by [5]

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

It 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: $\mu_m$ 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. GRADIENT OPTIMIZATION NEURAL NETWORK TECHNIQUE

In this analysis the gradient optimization neural network method [6] is used. It provides an efficient tool for estimating the unknown kinetic parameters. Through simulation using this optimization algorithm, training is performed to estimate the kinetic parameters. With these estimated kinetic parameters the states of the biodegradation process are studied.

The basic principles and concepts in estimating the parameters by using the gradient optimization algorithm using neural networks can be given as follows:

Consider $\mathcal{F}(x,\theta)$ is the approximated output where $x$ is the input data and $\theta$ is the neural network parameters vector. Given an input-output data pair $(x_i, y_i)$ where the actual output $y_i = f(x_i)$, the difference between the desired output and the approximated output is reduced by adjusting the vector $\theta$

$$e^i = y^i - \mathcal{F}(x^i,\theta)$$

The cost function $J(\theta)$ is minimized for optimization

$$J(\theta) = \sum_{j=1}^{M} e^{i\top} e^i \tag{2}$$

where $M$ is the number of input output data pairs. The approximated parameter set $\theta$ is adjusted by means of a gradient update law defined by

$$\dot{\theta} = \eta \sum_{j=1}^{M} \zeta^i e^i$$

where

$$\zeta^i = \frac{\partial \mathcal{F}(x^i,z)}{\partial z}\Big|_{z=\theta}^{\top}$$

The approximated function is given as

$$\mathcal{F}(x,\theta) = \theta^{\top}\zeta(x)$$

where, for a radial basis function neural network,

$$\zeta_i(x) = \frac{e^{-((x-c_i)/\sigma)^2}}{\sum_{i=1}^{p} e^{-((x-c_i)/\sigma)^2}}$$

where $c_i$ is the position of the radial basis function, $\sigma$ is the inverse of the width of the radial basis function and $p$ is the number of radial basis functions.

The process of function approximation not only requires a stable law be defined for $\theta$, but one must provide sufficient information before a function may be accurately approximated over all regions. The radial basis function vector $\zeta_i$ is another important factor which influences the approximator. The approximation accuracy depends critically on $\theta$ and $\zeta_i$.

Neural networks are known to be good function approximators [8]. The proposed algorithm uses a training and testing approach. Training is performed to estimate the unknown kinetic parameters. During the training phase, a large number of input output data pairs are required which are obtained through simulation. The input data is chosen in such a way that they provide sufficient information before the parameters are accurately approximated. The three kinetic parameters $K_s$, $Y$ and $Y_{ox}$ are trained and estimated separately with the proposed algorithm.

## 4. TESTING AND TRAINING OF NEURAL NETWORK ESTIMATOR

### 4.1. Training

In simulating the differential equations of Monod's model, initial conditions are required for the three states and three of the six biodegradation coefficients are to be chosen. The initial conditions are taken as [5,90,0] for the three states. The endogenous decay coefficient $K_d$, oxygen consumption coefficient $Y_{OXD}$ and specific growth rate of substrate $\mu_m$ have fixed values taken as 0.005, 0.008 and 0.5 respectively. The other three kinetic parameters are constrained to lie within the ranges given as $0.005 \leq K_s \leq 1000$, $0.1 \leq Y \leq 1.5$ and $1.5 \leq Y_{ox} \leq 3.5$.

#### *4.1.1. Estimation of $K_s$*

For the first parameter $K_s$, 100 random samples ranging from $0.005 \leq K_s \leq 1000$ were considered. The other two parameters are fixed at $Y$=1 and $Y_{ox}$=2. Considering the above three parameters, the differential equations were simulated to determine the three states. Assuming that only the oxygen uptake state $O_x$ information can be obtained experimentally, the time taken to reach the 98% of the maximum of the $O_x$ state, the time taken to reach 50% of the maximum of the $O_x$ state and the time taken to reach 20% of the maximum of the $O_x$ state were considered as the three different inputs for the neural network estimator of the $K_s$ parameter. The gradient optimization algorithm is used. The accuracy of the estimated $K_s$ parameter has been evaluated using the normalized mean square error equation given as

$$NMSE = \frac{1}{M}\frac{1}{N}\sum_{i=1}^{N}(\theta - \hat{\theta})^2 \tag{3}$$

where $N$ is the number of samples used, $M$ is the range of the parameter, $\theta$ is the actual parameter and $\hat{\theta}$ is the estimated parameter.

#### *4.1.2. Estimation of $Y$*

For the second parameter $Y$, 100 random samples ranging from $0.1 \leq Y \leq 1.5$ were considered along with the other two parameters that are fixed at $K_s$=300 and $Y_{ox}$=2. Considering the above three parameters Monod's model was simulated to determine the three states. With the assumption that only $O_x$ is available, the respective $O_x$ values and time corresponding to reach 98% of the maximum of the $O_x$ state, 50% of the maximum of the $O_x$ state and 20% of maximum of the $O_x$ state were considered as the six different inputs for the neural network estimator of the $Y$ parameter, Again, the gradient optimization algorithm is used. The accuracy of the estimated $Y$ parameter has been evaluated using the same measurement described in equation (3).

#### *4.1.3. Estimation of $Y_{ox}$*

The $Y_{ox}$ parameter with 100 random samples ranging from $1.5 \leq Y_{OX} \leq 3.5$ is estimated following a similar procedure as in the estimation of the $Y$ parameter with the other two parameters values fixed at $K_s$=300 and $Y$=1. The accuracy of the estimated $Y_{ox}$ is determined as in equation (3).

#### 4.1.4. Estimation of States

The estimated parameters, $K_s$, $Y$, $Y_{ox}$, (see the above sections (4.1.1), (4.1.2) and (4.1.3)) have been used in the simulation of Monod's model to estimate the behavior of the three states (cell concentration, substrate and oxygen consumption). Monod's model is again simulated to determine the behavior of the states with the parameter values (some estimated and some fixed). The normalized mean square error is calculated using the equation (4) to quantify the accuracy of the above estimated states. The development of Equation (4) is as follows:

$$X_{min} = \min_{0 \le t \le t_f, 1 \le i \le p} (X_i(t))$$

$$X_{max} = \max_{0 \le t \le t_f, 1 \le i \le p} (X_i(t))$$

where $t_f$ is the simulation time and $p$ is number of sample points

$$M_X = X_{max} - X_{min}$$

$$MSE_{X_i} = \frac{1}{N} \sum_{j=0}^{N} (X_i(j) - \hat{X}_i(j))^2$$

where $N$ is length of $X_i(j)$

$$MSE_X = \frac{1}{M} \sum_{i=1}^{p} MSE_{X_i}$$

$$NMSE_X = \frac{1}{M_X} MSE_X \quad (4)$$

### 4.2. Testing

To test the neural network, test set patterns of 100 random sample values for the parameters $K_s$, $Y$, $Y_o x$ are used in the testing stage. The test patterns are chosen within the respective ranges ($0.005 \le K_s \le 1000$, $0.1 \le Y \le 1.5$ and $1.5 \le Y_{OX} \le 3.5$) but are obviously different from the patterns used in training. Monod's model is simulated with the test set patterns to determine the states.

#### 4.2.1. Estimation of Kinetic Parameters in Testing

Using the estimated $O_x$ state (oxygen consumption) from the procedure given in Section (4.2), the parameters $K_s$, $Y$ and $Y_{ox}$ are estimated following the procedures discussed in Sections (4.1.1), (4.1.2) and (4.1.3) respectively. Now, the sets of parameters ($K_s$, $Y$, $Y_{ox}$) thus obtained are used in Monod's model to simulate and determine the behavior of the three states. The performance of the approximator is evaluated by taking the normalized mean square error of the states determined using actual testing data samples and states determined using the estimated testing data set values (see equation (4)). The results of normalized mean square error in training and testing for three kinetic parameters are shown in Table 1 and the normalized mean square error for three states are shown in Table 2.

To determine the validity of the results obtained, it is necessary to determine whether the behavior of the system approaches a practically meaningful solution. This implies that along with the estimation of the parameters we would like to know the behavior of the states too. Theoretically, 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.

| | $K_s$ | Y | $Y_{ox}$ |
|---|---|---|---|
| error in training | 1.8225 | 0.2982 | 0.508 |
| error in testing | 42.997 | 0.1047 | 0.2032 |

**Table 1**. Normalized mean square error for parameter estimation

| | cell conc | substrate conc | oxygen rate |
|---|---|---|---|
| error in training | 0.1975 | 0.0213 | 3.6726 |
| error in testing | 0.0481 | 00077 | 0.3184 |

**Table 2**. Normalized mean square error for state estimation

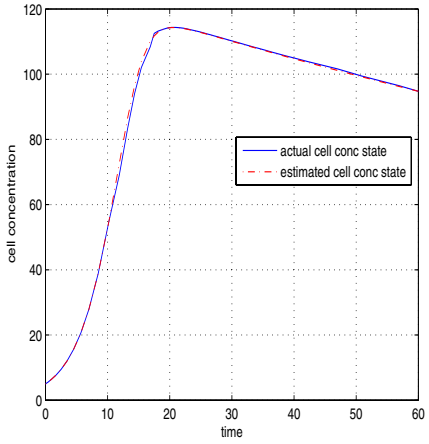
By considering one of the testing pattern values for the three parameters as $K_s$=82.2195, $Y$=1.2946, $Y_{ox}$=2.6866 the validity of the optimized set of parameters and three states obtained through simulation is studied. Figure 1 and Figure 2 show the behavior of the three states.

In Figure 1 the dashed lines represent the state behavior considering the estimated kinetic parameters and the solid lines represents the state behavior with the actual kinetic parameters. We can observe both estimated cell growth and pollutant removal states behave close to the actual states. The simulation process shows a realistic time evolution. Indeed, the graph of the pollutant removal is decaying from its initial value and goes to zero, while the cell concentration grows initially and then starts to decrease at a slow rate.

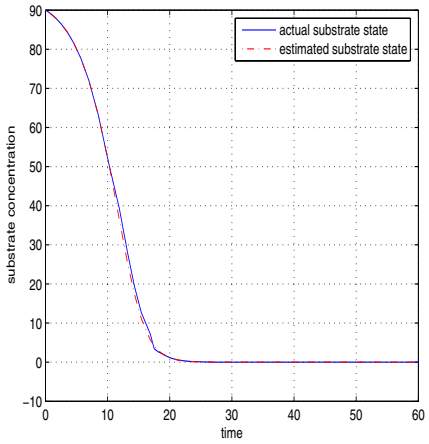
In Figure 2, one can see that the estimated oxygen uptake trajectory approximates the actual state evolution very well. It grows along with the cell mass concentration indicating that as cell concentration increases, the oxygen consumption also increases.

## 5. RESULTS

In this section, we present the potential behavior of the states obtained through simulation which can be studied from the figures 1 and 2. Simulation is performed on the testing data patterns and validity of the results has been studied by estimating the mean square error for the states estimated. The consistency of the behavior of all three states shows that the mean square error obtained for the estimated kinetic parameters as $K_s$=42.997, $Y$=0.1047 and $Y_{ox}$=0.2032 are considerably acceptable. It is shown that the obtained results from the simulation approximate the true behavior very well. All the simulations were performed under the basic assumption that only oxygen uptake information is available experimentally. The results under this basic assumption shows a well modeled behavior of the nonylphenol biodegradation kinetics. The cell growth and pollutant removal states behave in a physically consistent manner, as shown in Figure 1. 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. The oxygen uptake state also behaves in a realistic way. All the graphs show that the obtained simulated solution does approximate the actual data quite well.




(a)




(b)

**Fig. 1**. a) Showing cell concentration for test data value. (b) Showing substrate concentration for test data value

## 6. CONCLUSION

The purpose of this study is to estimate the behavior of nonylphenol biodegradation kinetics. This requires the information about the intrinsic kinetic parameters, which is generally difficult and expensive through experimental analysis. This paper shows the applicability of neural networks in parameter estimation via simulation. In this analysis, the gradient optimization neural network algorithm is used which provides an efficient tool for estimating the unknown kinetic parameters. Based on oxygen consumption, simulation results show that this method is very precise for estimation of the nonlinear behavior of the parameters. The kinetic behavior of the states are shown to be physically meaningful and consistent.

## 7. REFERENCES

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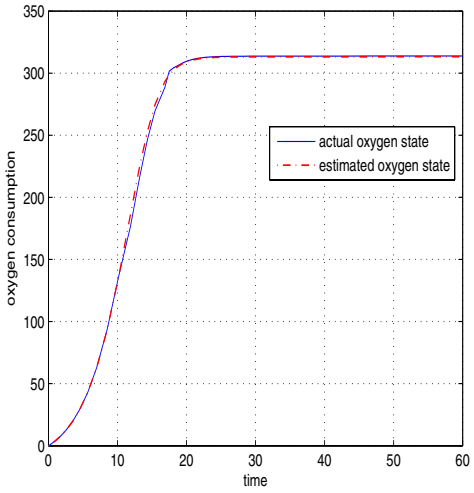


**Fig. 2**. Showing oxygen consumption for test data value

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