Evaluation of Anaerobic Biofilm Reactor Kinetic Parameters Using Ant Colony Optimization

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Abstract

Fixed bed reactors with naturally attached biofilms are increasingly used for anaerobic treatment of industry wastewaters due their effective treatment performance. The complex nature of biological reactions in biofilm processes often poses difficulty in analyzing them experimentally, and mathematical models could be very useful for their design and analysis. However, effective application of biofilm reactor models to practical problems suffers due to the lack of knowledge of accurate kinetic models and uncertainty in model parameters. In this work, an inverse modeling approach based on ant colony optimization is proposed and applied to estimate the kinetic and film thickness model parameters of wastewater treatment process in an anaerobic fixed bed biofilm reactor. Experimental data of pharmaceutical industry wastewater treatment process are used to determine the model parameters as a consequence of the solution of the rigorous mathematical models of the process. Results were evaluated for different modeling configurations derived from the combination of mathematical models, kinetic expressions, and optimization algorithms. Analysis of results showed that the two-dimensional mathematical model with Haldane kinetics better represents the pharmaceutical wastewater treatment in the biofilm reactor. The mathematical and kinetic modeling of this work forms a useful basis for the design and optimization of industry wastewater treating biofilm reactors.

Key words: anaerobic biofilm reactor; ant colony optimization; inverse modeling; parameter estimation

Introduction

APPROPRIATE SELECTION of mathematical and kinetic models and accurate determination of model parameters is important in predicting and optimizing the performance of biofilm reactors. Various experimental methods have been reported for determining the kinetic parameters of anaerobic biofilm reactors (Suidan and Wang, 1985; Hsu, 1986; Jih and Huang, 1994; Hu *et al.*, 2002; Tsuneda *et al.*, 2002; Lin and Miller, 2004; Sudipta and Somnath, 2010). Numerical evaluation of kinetic parameters for biofilm processes is an attractive alternative to the experimental methods. This approach is also known as inverse modeling (IM) in which the model parameters are determined such that the behavior of the process model approximates the observed process behavior. This approach has been used to estimate the kinetic parameters of different wastewater treating biofilm processes. Towards this approach, a simplified continuous stirred tank reactor model has been considered for wastewater treatment in packed bed biofilm process, and the kinetic parameters are evaluated by using an error-in-variable algorithm under a

pseudo steady-state assumption (Zhang and Huck, 1996). Though the authors have considered recirculation, the long residence times that are usually prevalent in such reactors may not support the assumption of uniform concentration. Further, a multiple shooting technique has been used for the identification of kinetic and model parameters of second-order models based on the reported data that describe the degradation of volatile fatty acids in an anaerobic digestion of wastewater treatment process (Muller *et al.*, 2002). Most of the reported works have considered simplified models for numerical evaluation of parameters of wastewater treating biofilm reactors. However, a rigorous mathematical model with appropriate biofilm kinetics and an efficient optimization algorithm with an accurate estimation of parameters can provide an adequate representation of the biofilm process. In the recent past, a class of novel optimization algorithms such as differential evolution (DE), genetic algorithm, and simulated annealing derived from the principles of natural phenomena are gaining importance in solving complex optimization problems (Kirkpatrick *et al.*, 1983; Prince and Storn, 1997; Chen *et al.*, 2004; Faber *et al.*, 2005; Shopova and Vaklieva, 2006; Venkateswarlu and Damodar Reddy, 2008; Sumana and Venkateswarlu, 2010). These stochastic optimization algorithms are attractive because of their flexibility, ease of operation, and global perspective. Of late, the application of these algorithms has been explored for numerical evaluation of

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kinetic parameters of wastewater treatment biofilm processes. Recently, DE has been applied for numerical estimation of the kinetic parameters of a wastewater treating biofilm reactor using a set of literature reported data (Kiranmai *et al.*, 2005). The data used in that work correspond to the influent substrate with low organic loading rates (OLR). The kinetic model fitted with such data may not be valid for processes that involve reasonable or high substrate concentrations. Very recently, a hybrid modeling approach has been proposed to estimate the kinetics of an anaerobic distillery wastewater treatment process in a fixed bed reactor (Shiva kumar and Venkateswarlu, 2012). In that approach, a combined model structure that integrates a first-principles model with artificial neural networks (ANN) is employed to estimate the complex kinetics of the biofilm process as a consequence of the validation of its steady-state solution. Though this approach presents novelty toward biofilm kinetics, its implementation requires a good understanding of ANN learning mechanism in conjunction with the rigorous model of the biofilm process.

Most of the steady-state models used for numerical evaluation of kinetic parameters of anaerobic biofilm reactors have considered Monod kinetics. However, the type of a kinetic model representing the biofilm kinetics of a wastewater treatment process is very much dependent on the nature and characteristics of the effluent process stream. Thus, it requires studying different kinetic models in order to assess their suitability to a specific industry wastewater treatment process. Therefore, suitable selection of mathematical and kinetic models and accurate determination of their parameters is important in predicting and optimizing the performance of biofilm reactors. In this work, an IM approach based on ant colony optimization (ACO) is proposed to estimate the kinetic and film thickness model parameters of a wastewater treatment process in an anaerobic fixed bed biofilm reactor. These parameters are determined as a consequence of the solution of the rigorous mathematical models of the process using the experimental data of pharmaceutical industry waste water. The ACO is a global optimization algorithm that is derived from a heuristic ant based system, which emulates the fact that ants are capable of finding the shortest path from a food source to their nest by depositing a trail of pheromone during their walk (Dorigo and DiCaro, 1999). For comparison, a Nelder–Mead optimization (NMO) method is also employed for inverse estimation of the parameters of kinetic and film thickness models representing the biofilm reactor. The results are analyzed with regard to the rigor of the mathematical models, the appropriateness of the kinetic models, and the efficiency of the optimization algorithm.

Experimental Setup and Data Generation

A fixed bed biofilm reactor setup is employed to conduct experiments for anaerobic treatment of pharmaceutical industry waste water and to generate the data needed for the development of mathematical and kinetic models.

Reactor setup

The schematic of fixed bed biofilm reactor experimental setup is shown in Fig. 1. The reactor is a QVF glass column of 1 m height and 0.1016 m internal diameter. A Teflon perforated plate of thickness 3 mm is provided at the base of the column to support the packing material. At the bottom of the reactor, two openings fitted with valves made of Teflon are provided. One

FIG. 1. Experimental setup.

valve is used to control the flow rate of influent that is pumped into the reactor, and the other valve is used to discharge the excess sludge accumulated. At the top of the column, a provision is made to insert a thermometer for measuring temperature. The reactor consists of three sampling ports to withdraw samples at bed heights of 0.25 m, 0.5 m, and 0.75 m from the bottom. The column is insulated with 1.0 inch asbestos rope. The temperature of the column is maintained at 37°C by varying the voltage through a 0.2 kW heating tape connected to a dimmer-stat. The entire setup is supported by a 1.0 inch M.S. pipeline structure. The influent from a 2 L capacity tank enters the column from the bottom inlet connection through a peristaltic pump made of Watson Marlow. The effluent sample is collected from the top of the column. The column and the packing specifications are given in Table 1.

Experimentation and data generation

In this work, pharmaceutical waste stream is considered for anaerobic treatment in biofilm reactor. The effluent of pharmaceutical industry contains several organic solvents, acids, bases, and a variety of other organic compounds. The characteristics of the effluent collected from a typical pharmaceutical industry for its anaerobic treatment in the experimental biofilm reactor is given in Table 1. This stream is used to prepare the substrates with different chemical oxygen demand (COD) concentrations for using them as feed solutions for different experiments. The reactor is first packed with gravel stones and then seeded with 1.0 L of active anaerobic sludge brought from M/s. Alkabir, Hyderabad, India. In order to sustain the initial growth of microorganisms, the reactor is further added with 2.6 L of very dilute solution of synthetic glucose medium (1000 mg/L) with nutrients such as total nitrogen as urea (125 mg/L),

TABLE 1. BIOFILM REACTOR SPECIFICATIONS AND WASTE STREAM CHARACTERISTICS

Specifications of biofilm reactor	
Height of the column	1 m
Diameter of the column	0.1016 m (4 in)
Total volume of the reactor	8.11 L
Name of the packing material	Gravel stones
Shape	Irregular
Size	2–3 cm
Density	1.49 kg/L
Total packing weight	12.07 kg
Porosity	0.605
Wastewater characteristics	
COD	87.50 kg/m ³
BOD	44.40 kg/m ³
pH	6.8
Total alkalinity	1.900 kg/m ³ (as CaCO ₃)
Total solids	21.680 kg/m ³
Total dissolved solids	18.980 kg/m ³
Total suspended solids	2.700 kg/m ³
Total volatile acids	0.690 kg/m ³ (as CH ₃ COOH)
Chlorides	1.125 kg/m ³
Sulfates	2.300 kg/m ³
Nitrates	0.115 kg/m ³
Phosphates	0.800 kg/m ³
BOD/COD	0.507

COD, chemical oxygen demand; BOD, biological oxygen demand.

total phosphorous as KH₂PO₄ (50 mg/L), NaCl (50 mg/L), KCl (40 mg/L), CaCl₂ (15 mg/L), MgCl₂ (10 mg/L), and FeCl₃ (2 mg/L). The pH of the solution is maintained at 7.2 by adding 0.1 N NaOH. The reactor is kept undisturbed for about 20 days, thus making it biologically active. The biological activity is confirmed by measuring the gas evolution (CH₄ + CO₂), which appear as active bubbles displacing the water in the inverted level jar. The feed solutions to be treated with the biofilm reactor are prepared by diluting the industry wastewater with the COD concentrations of 4.980 g/L, 11.86 g/L, 23.46 g/L, and 40.720 g/L, respectively. On observing the biological activity of the bed, the experiment is initiated for each feed solution by displacing the column by about three bed volumes of the current solution. The duration of each experiment is kept for 13 days. The hydraulic retention time (HRT) varied from 2 to 12 days. The pH of the feeding solution is maintained at 7.2 by adding NaHCO₃. Each experiment is allowed to continue for 13 days, by which the wastewater treatment process approaches stable-state condition. Samples collected from the three sampling ports placed along the column as well as from the effluent water are analyzed for COD, biological oxygen demand (BOD), total volatile acids (TVA), total alkalinity (TA) and pH. The stable-state condition of each experiment is observed with regard to the minimal variation in reactor effluent pH, alkalinity, and COD concentrations. An average of the effluent data of the last five samples with a deviation of < 2% is considered a data point for each experiment. Thus, 13 data points resulting from the 13 experiments are used to develop the models of the biofilm reactor. The data corresponding to the influent and effluent COD concentrations, HRT, and OLR of all experiments are given in Table 2.

TABLE 2. EXPERIMENTAL DATA WITH OPERATING CONDITIONS

Data sets	OLR	HRT (days)	Influent COD (g/L)	Effluent COD (g/L)	% COD reduction
1	1.24	4	4.98	2.00	59.84
2	2.48	2	4.98	2.19	56.02
3	1.47	8	11.86	5.13	56.75
4	2.94	4	11.86	5.51	53.54
5	5.89	2	11.86	5.73	51.69
6	1.95	12	23.42	9.72	58.5
7	2.93	8	23.46	10.17	56.65
8	5.86	4	23.46	10.86	53.71
9	11.72	2	23.46	11.88	49.36
10	3.39	12	40.72	16.69	59.01
11	5.09	8	40.72	17.99	55.82
12	10.18	4	40.72	20.48	49.71
13	20.35	2	40.72	21.62	46.91

OLR, organic loading rate; HRT, hydraulic retention time.

Biofilm Reactor Models and Optimization Algorithms

Mathematical and kinetic models as well as the optimization algorithms used to evaluate the performance of the biofilm reactor involved in the treatment of pharmaceutical industry waste water are described as follows.

Mathematical models

One-dimensional model. The rate of mass transfer is considered proportional to the concentration difference between the interface and the bulk fluid. Under steady-state condition, there can be no accumulation of the component at the interface. The mass transported from the bulk liquid to the film interface moves from interface to the solid surface. The conceptual biofilm model of this work showing the substrate concentration profile in a segment of biofilm reactor is similar to that employed for wastewater treatment in fixed bed reactor by Kiranmai *et al.*, 2005.

The differential equation governing the fluid phase is given by

$$-u \frac{dc}{dz} = k_g a_v (c - c_s^s) \quad (1)$$

with the boundary condition:

$$c = c_0 \text{ at } z = 0 \quad (2)$$

In this model, the substrate concentration in the bulk fluid varies only in the axial direction.

The differential equation governing the solid phase is given by

$$\frac{D_f}{\xi^{a-1}} \frac{d}{d\xi} \left(\xi^{a-1} \frac{dc_s}{d\xi} \right) - r_s(c_s) = 0 \quad (3)$$

with the boundary conditions:

$$\frac{dc_s}{d\xi} = 0 \text{ at } \xi = 0$$

$$k_g(c_s^s - c) = -D_f \frac{dc_s}{d\xi} \text{ at } \xi = L_f \quad (4)$$

In Equation (3), the value of a is defined as 1, 2, or 3 for planar, cylindrical, or spherical geometry, respectively, and D_f is substrate diffusion coefficient in the biofilm.

Two-dimensional model. This model considers the variation of the substrate concentration in bulk fluid in both the axial and radial directions. The model accounts for inter-phase resistance to mass transfer and intra-biofilm processes. The process taking place in the biofilm is characterized by physical diffusion and reaction and is described by a second-order differential equation. Pressure losses along the length of the reactor are neglected.

The differential equation governing the bulk fluid phase is given by

$$u \frac{dc}{dz} = \frac{\varepsilon D}{r} \left[\frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) \right] - k_g a_v (c - c_s^s), \quad (5)$$

where D is substrate diffusion coefficient in the bulk fluid. This equation has to be solved subject to the boundary condition given in Equation (2). The solid phase biofilm model is same as in Equation (3) with its boundary conditions in Equation (4).

Mass transfer coefficient. The transport of substrate mass between the bulk fluid and biofilm surface depends on the dynamic properties of the fluid flowing through the reactor and the activity of the biocatalyst particle. The substrate mass transport occurring from the bulk fluid to the biofilm surface across the diffusion layer is defined by

$$j_D = \frac{k_g (sc)^{2/3}}{u} \quad (6)$$

The j_D -factor is calculated using the following correlation (Dwivedi *et al.*, 1977):

$$j_D \varepsilon = \frac{0.765}{\text{Re}^{0.82}} + \frac{0.365}{\text{Re}^{0.386}}, \quad (7)$$

$$\text{where } \text{Re} = \frac{\rho u d_p}{\mu} \text{ for } 0.01 < \text{Re} < 15,000$$

The mass transfer coefficient k_g , obtained from Equation (6), is used in the bulk fluid phase equations [Eqs. (1) and (5)].

Kinetic models

Various kinetic models can be used to represent the bioprocess kinetics.

Monod model. This model is the most popular kinetic rate expression, according to which the substrate consumption rate, r_s in biofilm is given by the following equation:

$$r_s = \left(\frac{\mu_{\max} \rho_s}{Y} \right) \frac{C_s}{K_s + C_s} \quad (8)$$

Generally, Monod kinetics are valid when growth and population density are low.

Teisser model. This model considers the substrate consumption rate to be exponentially related to concentration

(Shuler and Kargi, 2001), according to which the substrate consumption rate, r_s in biofilm is given by the following equation:

$$r_s = \left(\frac{\mu_{\max} \rho_s}{Y} \right) (1 - \exp(-KC_s)) \quad (9)$$

Moser model. This model is an extension of the Monod equation, according to which the substrate consumption rate, r_s in biofilm is given by the following equation:

$$r_s = \left(\frac{\mu_{\max} \rho_s}{Y} \right) \left(\frac{C_s^n}{K_s + C_s^n} \right) \quad (10)$$

The following models represent the bioprocess kinetics with substrate inhibition.

Haldane model. This rate expression is generally valid when the substrate concentration is high. According to this model, the substrate consumption rate, r_s in biofilm is given by the following equation:

$$r_s = \left(\frac{\mu_{\max} \rho_s}{Y} \right) \frac{C_s}{K_s + C_s + \frac{C_s^2}{K_i}} \quad (11)$$

Edward model. This model considers substrate inhibition (Edwards, 1970). According to this model, the substrate consumption rate, r_s in biofilm is given by the following equation:

$$r_s = \left(\frac{\mu_{\max} \rho_s}{Y} \right) \left(\exp\left(\frac{-C_s}{K_1}\right) - \exp\left(\frac{-C_s}{K_2}\right) \right) \quad (12)$$

Film thickness

Biofilm thickness (L_f) is an important parameter that has significant influence on the substrate conversion. Biofilm thickness primarily depends on the substrate concentration in the bulk liquid and the liquid hydraulics. Consequently, it is hypothesized that the biofilm is composed of a static portion and a variable portion in which the latter is assumed to increase with the OLR and decrease with the hydraulic loading rate. Accordingly, the expression considered for the biofilm thickness of this work is the one employed by Kiranmai *et al.*, (2005) as given by

$$L_f = a + b \text{ OLR} - c \text{ HLR} \quad (13)$$

where a , b , and c are constants to be determined.

Ant colony optimization

The ACO introduced by (Dorigo *et al.*, 1996) is one of the most recent techniques that are used to solve optimization problems. The ACO mimics the way in which real ants find the shortest route between a food source and their nest. The ants communicate with one another by means of pheromone trails and exchange information about which path should be followed. This autocatalytic and collective behavior of ants results in the establishment of the shortest route from the nest to the food source and back. Such a pheromone-mediated intelligent ants foraging behavior is exploited by means of an ACO algorithm to solve a number of optimization problems (Dorigo and DiCaro, 1999).

In this work, the ACO algorithm with its global search features is explored for the numerical evaluation of the kinetic and film thickness parameters of fixed bed biofilm reactor involved in the treatment of pharmaceutical industry wastewater. Parameter estimation by IM needs an objective function that is formulated based on the actual process measurements and the process model predictions as given by

$$J = f(\theta) = \sum_{i=1}^l (y_i - \hat{y}_i)^2, \quad (14)$$

where J is the cost function, σ is the vector of parameters, l is the number of observations, y_i is the measured value of the i^{th} variable, and $\hat{y}_i$ is the corresponding predicted value. Iterative convergence of this equation leads to a minimization of the value of J , thus providing the optimum parameter values.

The ACO-IM problem can be stated as

$$f(\theta) : D \rightarrow R,$$

where θ is a p -dimensional parameter vector, R is of real numbers, and D is the search space of θ . The objective is to find the parameter vector θ that minimizes $f(\theta)$. The D is considered a hyper parallelepiped:

$$D = \{\theta_i | \theta_i^- \leq \theta_i \leq \theta_i^+ \}; \quad i = 1, \dots, p,$$

where θ_i^- and θ_i^+ denote the lower and upper levels, respectively, of parameter θ_i . The search space D is first divided in the interval $[\theta_i^-, \theta_i^+]$ of each parameter θ_i into a number of strata, m_i . If each stratum is represented by the value at the middle of the stratum, then there will be $M = m_1, \dots, m_p$ permutations or possible pathways through the search space of input parameters. Let $\theta_{ij} (i = 1, \dots, p \text{ and } j = 1, \dots, m_i)$ be the stratum j of parameter θ_i in the search space D . The parameters can be initially specified such that they uniformly cover the whole parameter space. Use of more strata can speed up the convergence of the optimization problem, but the increase of strata would increase the computational burden.

Let there be M ants representing M strata. The possible number of pathways, N that the ants can travel through the parameter space p are given by $N = M^p$. If $M = 3$ and $p = 6$, then there will be 729 pathways. Each ant can follow one of the pathways N pathways. The ants perform tasks such as selection of pathways that they pass through, remembering the parameter strata along the pathways, passing these parameter values to the model of the process, evaluating the value of objective function for each path way, and updating the pheromone based on the objective function values.

The computations involved in ACO implementation are as follows. The trail intensity, also called the pheromone deposit, τ_u on each pathway, u ($u = 1, \dots, N$) is computed based on the cost function values of J . The cost function J of each pathway is represented as J_u , and the minimum of the cost functions, $J_{\min}$ is found. The mean, μ_J and the standard deviation, σ_J of the objective functions are evaluated. The ratio of standard deviation to mean represents the variability in the function values and the critical cost, C which is evaluated as

$$C = J_{\min} + C_c \frac{\sigma_J}{\mu_J}, \quad (15)$$

where C_c is a constant.

The critical cost, C is used to evaluate the trail intensity, τ_u on each path according to the formula

$$\tau_u = \begin{cases} \exp \left[4.6 \left(\frac{J_u - C}{J_{\min} - C} \right) \right], & J_u \leq C \\ 0, & J_u > C \end{cases} \quad (16)$$

According to this equation, pathways with the cost function larger than C receive no trail intensity, while those below C receive larger trail intensity values. It can be observed that any single stratum θ_{ij} in D may be the crossroad of many ant pathways. The trail share calculated with Equation (16) of each stratum θ_{ij} from each pathway can be summed to yield ϕ_{ij} as

$$\phi_{ij} = \sum_{u=1}^N \tau_u \quad u \in \text{crossing pathway}$$

Here, the crossing pathways are those that cross the stratum θ_{ij} . The mean, μ_{ij} and the standard deviation, σ_{ij} of the cost functions are used to compute the scores, S_{ij} according to the formula:

$$S_{ij} = \frac{(\phi_{ij})^A (\sigma_{ij})^B}{\sum_i \sum_j (\phi_{ij})^A (\sigma_{ij})^B} \quad (17)$$

where

$$B = C_s \frac{\sigma_{ij}}{\mu_{ij}}, \quad (18)$$

where A and C_s are constants. Equations (16) and (17) in ACO structure represent trail intensity and transition probability (Dorigo *et al.*, 2000). The scores, S_{ij} are used to eliminate the strata with lowest scores while retaining the highest score. The interval of highest retained score results in narrowing the ranges for the parameters. This strategy is subsequently re-initialized with updated parameter ranges, and the procedure is repeated until the convergence in objective defined by Equation (14) is achieved. The constant C_c in Equation (15) signifies the variability of the trail received by each stratum.

Results and Discussion

Experimental data needed for developing mathematical and kinetic models are generated by setting up a laboratory scale fixed bed biofilm reactor and performing experiments for anaerobic treatment of pharmaceutical industry waste effluent stream with varying OLR, feed rates, and HRT. These data are used to evaluate the kinetic and film thickness model parameters by applying the nonlinear optimization algorithms in association with the validation of the mathematical model of the process. On the whole, 13 experimental runs are carried out with gravel stones as packing material. The duration of each experiment is kept for 13 days. The HRT is varied from 2 to 12 days. The samples collected for each day from the effluent stream are analyzed for COD, BOD, TVA, TA, and pH. The operation attains pseudo steady state by about 8–10 days. However, perfect steady-state results cannot be observed due to variations in the data analysis. Therefore, the average data of the last five samples having a deviation of about 2% are considered steady-state data. Thus, the data corresponding to the influent and effluent COD concentrations, HRT, OLR, and percent COD reduction of all the experiments given in Table 2 are used for modeling the biofilm

reactor. The one-dimensional and two-dimensional mathematical models that govern the biofilm reactor are solved as follows. The height of the column (1 m) is divided into 50 equal steps, with each step representing 0.02 m. In the one-dimensional model, the fluid phase equation [Eq. (1)], along with its boundary condition [Eq. (2)], is solved for each height step in the axial direction by using Runge–Kutta (RK) 4th-order method. The solid-phase equation for the biofilm [Eq. (3)] is solved for each segment using orthogonal collocation on finite elements (OCFE) (Finlayson, 1980). OCFE is implemented by considering two finite elements, each with three internal collocation points. In the two-dimensional model, the fluid phase equation [Eq. (5)] is transformed to ordinary differential equation by finite difference technique, and the resulting equation along with its boundary condition [Eq. (2)] is solved by using 4th-order RK method for each height step of the axial direction. The solution for the solid-phase equation of this model is same as in the one-dimensional model. For parameter evaluation, the kinetic models are combined with the mathematical models to form different modeling configurations. The cost function J in Equation (14) is defined based on the experimental and model predicted COD conversions at the exit of the reactor. The ACO algorithm is implemented iteratively to update the parameters of kinetic and film thickness models until the convergence in the cost function is achieved. The number of strata (M) is assigned as 3. The constants involved in Equations (15), (17), and (18) are appropriately tuned as $C_c = 0.5$, $A = 1.0$, and $C_s = 0.3$, respectively. The results of ACO are compared with those of a classical NMO method (Kuester and Mize, 1973; Venkateswarlu and Gangiah, 1992). The tuning parameters involved in NMO, the reflection, contraction, and expansion coefficients are selected as 1, 2.0 and 0.5, respectively.

The combination of mathematical models, kinetic expressions, and optimization algorithms of the biofilm reactor can form a number of modeling configurations that require considerable effort for their evaluation. The analysis of the experimental results and a priori knowledge on the modeling of wastewater treating anaerobic biofilm reactors can be utilized to significantly reduce the modeling configurations to be evaluated for the biofilm reactor. The priori studies carried out for parameter estimation of pharmaceutical wastewater treatment process in biofilm reactor by IM have shown reasonably good performance of Haldane and Edward models compared with other kinetic models. Thus, these two kinetic expressions are considered along with the one-dimensional and two-dimensional mathematical models to form different modeling configurations and to evaluate the biofilm kinetics by using NMO and ACO.

Results of different modeling configurations of the biofilm reactor with gravel stones packing are shown in Table 3. Each of the kinetic models in Equations (11) and (12), along with the film thickness expression in Equation (13), involves the estimation of six parameters. The results of various modeling configurations are analyzed with regard to the rigorousness of the mathematical models, the optimization methods, and the kinetic expressions. The statistical significance of these results is evaluated using the coefficient of determination (R^2), relative root mean square error (RRMSE), and model efficiency (ME). The R^2 is computed as

$$R^2 = \frac{\left[\sum_{i=1}^N (X_i - \bar{X})(Y_i - \bar{Y}) \right]^2}{\sum_{i=1}^N (X_i - \bar{X})^2 \sum_{i=1}^N (Y_i - \bar{Y})^2} \quad (19)$$

TABLE 3. BIOFILM KINETICS AND THICKNESS MODEL PARAMETERS AS WELL AS PERFORMANCE MEASURES

Parameter	1D-ACO	1D-NMO	2D-ACO	2D-NMO
Haldane kinetics				
$\mu_{\max} \rho_s/Y$	2.063e+001	2.0e+001	29.39	20
K_s	1.999536	5.75e-001	2.00	0.34
A	5.50e-005	2.757e-005	9.63e-005	1.38e-005
b	4.75e-004	2.55e-004	5.00e-004	2.55e-004
c	3.749e-004	1.250e-004	9.39e-005	6.26e-005
K_I	1.499e+002	7.5e+001	1.5e+002	1.13e+002
Cost	0.026157	0.1019	0.010633	0.1453
R^2	0.8956	0.67	0.9568	0.643
RRMSE	0.000045	0.1961	0.000054	0.2088
ME	0.0101779	-3.1905	0.145262	-2.1513
Edward kinetics				
$\mu_{\max} \rho_s/Y$	2.329e+001	5.565793e+001	26.27	40.805
K_s	9.996e+001	2.064660	249.78	2.007
a	5.510e-005	1.330e-006	5.52e-005	0.193
b	1.939e-004	1.041e-005	1.61e-004	0.155
c	3.439e-005	1.36e-006	5e-005	1.07
K_I	1.257e+001	1.11e-001	7.86e-001	14.2
Cost	1.092e-01	0.043272	0.015469	0.19353
R^2	0.843206	0.654	0.9035	0.7958
RRMSE	0.0891	0.19161	0.07156	0.1747
ME	-0.1028	-3.2905	0.6308	-2.6313

1D and 2D, one- and two-dimensional; ACO, ant colony optimization; NMO, Nelder–Mead optimization; RRMSE, relative root mean square error; ME, model efficiency.

where X_i refers to measured values of N observations of a single variable and Y_i refers to the corresponding prediction values of the same variable.

The RRMSE for a data set is evaluated as

$$\text{RRMSE} = \sqrt{\frac{(1/N) \sum_{i=1}^N (Y_i - \hat{Y}_i)^2}{\bar{Y}}} \quad (20)$$

The ME for a data set is calculated according to the formula

$$\text{ME} = 1 - \frac{\sum_{i=1}^N (Y_i - \hat{Y}_i)^2}{\sum_{i=1}^N (Y_i - \bar{Y})^2} \quad (21)$$

In the preceding equations, X_i , Y_i =two sets of data, $\bar{X}$, $\bar{Y}$ =mean values of X , Y data series, Y_i =observed value, and $\hat{Y}_i$ =predicted value.

The upper part of Table 3 refers to the results of different modeling configurations based on Haldane kinetics, and the results in the lower part of the table correspond to Edward kinetics. The comparison of the cost function values and the

statistical results (R^2 , RRMSE, and ME) of 1D and 2D models with the estimated parameters involved in Haldane or Edward kinetics by ACO as well as NMO in Table 3 show that the 2D model offers improved performance over 1D model. Further, the results of different modeling configurations are evaluated with regard to the effectiveness of optimization algorithms. The comparison of the cost function values and the statistical measures (R^2 , RRMSE, and ME) evaluated for 1D and 2D models by ACO and NMO in Table 3 indicate the better suitability of ACO compared with NMO. The cost function values and the statistical results of 1D and 2D models with Haldane and Edward kinetics evaluated by ACO in Table 3 show the better suitability of Haldane kinetics compared with Edward kinetics. The comparison of experimental substrate conversions at the exit of the reactor with the predicted conversions of 1D and 2D models involving Edward and Haldane kinetics along with the three parameter film thickness expression based on ACO are shown in Fig. 2. The results of this work, thus, present the better suitability of the 2D model with Haldane kinetics to represent the biofilm reactor treating pharmaceutical industry wastewater. The simulation data of this model are found to adhere well to the experimental data obtained from the operation of the biofilm reactor. The parameters of Haldane kinetics and the film

FIG. 2. Comparison of experimental and model predicted substrate conversions: (a) Edward kinetics and (b) Haldane kinetics. 1D and 2D, one- and two-dimensional; ACO, ant colony optimization; Exp, experimental.

thickness expression evaluated by DE using the IM approach have been reported for the data of the tannery waste water treatment process in a fixed bed biofilm reactor (Kiranmai *et al.*, 2005). The optimally configured parameters of the kinetic and film thickness expressions for pharmaceutical wastewater treatment process of our study are found to be in the range of the reported parameters. Any change in the estimated parameters can be attributed to the nature and characteristics of the industry effluent stream. Thus, the better suitability of ACO is justified for parameter estimation in the pharmaceutical industry wastewater treatment biofilm process.

Conclusions

The complex nature of biological reactions in biofilm reactors often poses difficulty in analyzing them experimentally, and mathematical models could be very useful for their design and analysis. However, the application of biofilm reactor models to real practical problems suffers due to the lack of knowledge of accurate kinetic models and uncertainty in model parameters. Effective modeling of biofilm reactors, therefore, requires the selection of appropriate kinetic models and an accurate estimation of model parameters. In this work, ACO, a global optimization method, is presented for inverse estimation of the parameters of kinetic and film thickness models as a consequence of the solution of the process models with the aid of measured data. The results evaluated for different modeling configurations using the experimental data of pharmaceutical industry wastewater treatment in fixed bed anaerobic biofilm reactor show the better suitability of 2D model with Haldane kinetics. The results also explain the efficacy of ACO in determining the kinetic and film thickness model parameters of the biofilm reactor. The mathematical and kinetic modeling of this work forms a useful basis for predicting and optimizing the performance of biofilm reactors.

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Author Disclosure Statement

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Nomenclature

COD=chemical oxygen demand (kg/m^3)
 HLR=hydraulic loading rate (m/day)
 HRT=hydraulic retention time (days)
 OLR=organic loading rate ($\text{kg}/\text{m}^3/\text{day}$)
 c =substrate concentration in the bulk fluid (kg/m^3)
 c_s =substrate concentration in the bio-film (kg/m^3)
 c_s^s =substrate concentration on the bio-film surface (kg/m^3)
 k_g =mass transfer coefficient (m/s)
 D =substrate diffusion coefficient in the bulk fluid (m^2/day)
 D_f =substrate diffusion coefficient in the bio-film (m^2/day)
 d_p =equivalent particle diameter (m)
 a_v =specific surface area of particle (m^{-1})

K_I =substrate inhibition constant (m^3/kg)
 K_s =half velocity constant (kg/m^3)
 L_f =thickness of the bio-film (m)
 r =radial coordinate (m)
 Re =Reynolds number ($Du\rho/\mu$)
 Sc =Schmidt number ($\mu/\rho D$)
 r_s =reaction rate ($\text{kg}/\text{m}^3/\text{day}$)
 u =superficial velocity (m/s)
 y =measured substrate conversion
 $\hat{y}$ =predicted substrate conversion
 Y =yield coefficient
 z =axial coordinate (m)
 $C_{e,m}$ =measured substrate concentration at the outlet of the reactor (kg/m^3)
 C_e =model predicted substrate concentration at the outlet of the reactor (kg/m^3)
 $X_{e,m}$ =measured fractional conversion of the substrate at the outlet of the reactor
 X_e =model predicted fractional conversion of the substrate at the outlet of the reactor

Greek symbols

ε =porosity of bed
 α =vector of parameters
 μ =viscosity ($\text{kg}/\text{m}/\text{day}$)
 μ_{max} =maximum specific growth rate (day^{-1})
 ξ =space coordinate in the bio-film (m)
 ρ =density of fluid (kg/m^3)
 ρ_s =density of biomass (kg/m^3)

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