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Comparison Across Different Models for the Description of Batch Biodegradation Processes

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Experimental data related to batch biodegradation processes are here investigated. The goal is to select the most adequate mathematical model for the description of the microbial growth of a mixed microbial culture in the degradation of Caffeic Acid (a phenolic compound). To this end, different kinetic models are considered and compared by means of statistical tools. Experiments are conducted by varying the initial Caffeic Acid concentrations. It was found that the Monod model, in spite of its simplicity, provides a satisfactory agreement with the experimental data, whereas the adoption of more detailed models leads to negligible improvements of the fit.

1. Introduction

The removal of pollutant substances in contaminated environments is widespread and has been in the forefront of public and regulatory concern for the last decade. The use of microorganisms to biodegrade organic compounds present in wastewater effluents or in polluted soils represents a potential solution to such environmental problems. The modeling of biodegradation processes is often approached in terms of relatively simple, unstructured models where the pollutant species and the microbial population employed for its degradation are described, respectively, in terms of a generic substrate S and a biomass X. In spite of these simplifying assumptions, several models can be adopted to describe the biodegradation kinetics in a more appropriate way.
The selection of the proper model for the description of the biodegradation process is not a trivial task, and this aspect is often accomplished by resorting to empirical considerations and to previous experience. This aspect is further complicated when dealing with batch experimental data that can lead to large uncertainties in the kinetic parameters estimation due to their strong mutual correlation.
In this work we investigated the biodegradation of Caffeic Acid by a mixed culture of microorganisms. Caffeic Acid, whose chemical structure is reported in Figure 1, is a phenolic compound derived from cinnamic acid, which is found in many fruits, vegetables and herbs, including coffee.

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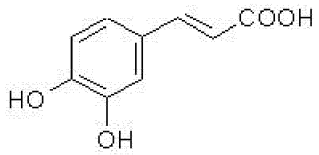

Figure 1: Chemical structure of the Caffeic Acid.

2. Materials and Methods

2.1 Materials and microorganisms

All the microbial degradation runs were carried out in a fermentor provided with control of temperature, pH and agitation (Lallai et al., 1988). The fermentor (working volume of 3 L) was operated in batch mode under constant conditions of temperature (25°C), pH (7,0) and dissolved oxygen.

A mixed culture of micro-organisms obtained from a commercial product (Bulab 5733 from Buckman Italiana, Milan, Italy) was used in this study. The composition of the mineral salt medium used is reported elsewhere (Lallai et al., 1988).

The Caffeic Acid was the only organic substrate added to the medium; so that it was the limiting growth substrate in the microbial growth kinetics tests. The batch cultures were conducted at different initial concentrations of Caffeic Acid ranging from 50–500 mg/l. For each growth experiment an inoculum acclimatized to glucose was prepared (Lallai et al. 2003). Biomass density was monitored by measuring the absorbance at a wavelength of 600 nm by using a spectrophotometer (UV-1601; Shimadzu, Kyoto, Japan) with a sampling time of 20 minutes.

2.2 Kinetic models

The degradation in the batch reactor is assumed to follow a unstructured model:

$$\begin{aligned} \frac{dS}{dt} &= -Y\mu(S,X) & S(0) &= S_0 \\ \frac{dX}{dt} &= \mu(S,X) & X(0) &= X_0 \end{aligned} \tag{1}$$

where S and X are, respectively, the substrate and the biomass concentrations, Y is the yield factor, and $\mu(S,X)$ is the specific growth rate. Most of growth models are based on the Monod model (Monod, 1942; Bailey and Ollis, 1986):

$$\mu(S) = \frac{\mu_m S}{K_S + S} \tag{2}$$

where μ_m is the maximum growth rate, and K_S is the so-called half saturation constant. There are many extensions of this growth model: Herbert corrected the Monod equation for endogenous metabolism, leading to an additional parameter m taking into account this feature (Powell, 1967). Shehata and Marr (1971) described their data with a model

consisting of two Monod terms. In this equation, the sum of μ_1 and μ_2 gives μ_m, whereas K_1 and K_2 are the corresponding saturation constants. Other models used for the description of biodegradation kinetics are the Tessier model (Powell, 1967), which is based on an exponential function, and the Contois model (Contois, 1959), where the half saturation rate is assumed to depend on the biomass concentration. Another typical extension of the Monod model is the Haldane model (Andrews, 1969), where a substrate inhibition is supposed leading to the introduction of an inhibition parameter K_i in the original Monod equation. The models considered in this study for the data evaluation are summarized in Table 1, together with the number of parameters required for their calibration. It should be noted that all the models, except the one by Tessier, can be regarded as plausible extensions of the Monod model.

Table 1: Growth models considered for the data evaluation.

	Model	$\mu = f(S,X)$	**Number of parameters** p	**Parameters**
(1)	Monod	$\mu = \frac{\mu_m S}{K_S + S}$	3	$\boldsymbol{\theta} = [\ln \mu_m, K_S, Y]$
(2)	Contois	$\mu = \frac{\mu_m S}{B X + S}$	3	$\boldsymbol{\theta} = [\ln \mu_m, B, Y]$
(3)	Herbert	$\mu = (\mu_m + m)\frac{S}{K_S + S} - m$	4	$\boldsymbol{\theta} = [\ln \mu_m, K_S, Y, m]$
(4)	Shehata and Marr	$\mu = \mu_1 \frac{S}{K_1 + S} + (\mu_m - \mu_1)\frac{S}{K_2 + S}$	5	$\boldsymbol{\theta} = [\ln \mu_m, \mu_1, K_1, K_2, Y]$
(5)	Tessier	$\mu = \mu_m (1 - \exp(-S/T))$	3	$\boldsymbol{\theta} = [\ln \mu_m, T, Y]$
(6)	Haldane	$\mu = \frac{\mu_m S}{K_S + S + K_i S^2}$	4	$\boldsymbol{\theta} = [\ln \mu_m, K_S, K_i, Y]$

The parameters $\boldsymbol{\theta}$ are estimated by using the least square criterion, thus searching the minimum of the objective function:

$$\phi(\boldsymbol{\theta}) = \sum_{i=1}^{a} \sum_{j=1}^{N_i} \left(X_{\text{exp}}^{ij} - X_{\text{mod}}(t_{ij}; \boldsymbol{\theta}) \right)^2 \tag{3}$$

In Equation 3, a is the number of experiments performed at different initial substrate concentrations S_0, N_i is the number of experimental points collected for every different initial condition at time t_{ij}, $X_{mod}(t_{ij};\boldsymbol{\theta})$ is the biomass concentration evaluated through numerical integration of Equation 2 at time t_{ij}, while X_{exp}^{ij} is the experimental observation of the biomass at time t_{ij}. The minimum search is carried out by the Levenberg-Marquardt method (Bates and Watts, 1988). The performance of the models is evaluated by calculating the adjusted determination coefficient R^2 (R-squared):

$$R_a^2 = 1 - \frac{N_T - 1}{N_T - p - 1}\left(1 - \frac{\sum_{i=1}^{N_T}\left(X_{\exp}^i - X_{\mathrm{mod}}\left(t_i;\hat{\boldsymbol{\theta}}\right)\right)^2}{\sum_{i=1}^{N_T}\left(X_{\exp}^i - \overline{X}_{\exp}\right)^2}\right) \tag{4}$$

In Eq. 4, $\hat{\boldsymbol{\theta}}$ is the point estimation of the parameters obtained through minimization of the objective function in Eq. 3, N_T is the total number of experimental points collected in the experiments, and $\overline{X}_{\exp} = \sum_{i=1}^{N_T} X_{\exp}^i \Big/ N_T$ is the mean of the experimental points.

3. Results and Discussion

The point estimations of the parameters, together with their confidence intervals and the adjusted determination coefficient, are reported in Table 2. The model performances (at least in terms of the adjusted R^2 scalar) are similar, regardless the number of parameters involved in the model. The estimation of the maximum growth rate μ_m and the half-saturation rate K_s are quite similar for all the models: $\mu_m \sim 0.105 \div 0.13$ h^{-1} and $K_S \sim 1.2 \div 1.9$ $mg\ l^{-1}$. A further investigation on the confidence intervals for the additional parameters shows that none of them is significantly different from zero. These considerations support the choice of the most parsimonious model, i.e. the Monod model.

On the other hand, Haldane model has a slightly better performance with respect to the other models, thus suggesting that substrate induced inhibition phenomena could occur in the biodegradation process. This result is somehow expected since phenolic compounds often show inhibition phenomena when subjected to biodegradation processes. However, it should be remarked that the confidence interval for the inhibition parameter K_i is relatively large, including also the zero value (i.e., absence of the inhibition term). Some further statistical tests on the extra sum of the squares (not reported in detail for sake of space) also showed that there is no significant information to reject the null hypothesis that K_i is, in fact, zero with a p-value equal to $p = 0.2$.

The models are also compared with by exploiting the residual analysis, i.e. the distance between theoretical prediction and experimental observations:

$$e\left(t_{ij}\right) = X_{\exp}^{ij} - X_{\mathrm{mod}}\left(t_{ij};\hat{\boldsymbol{\theta}}\right), \qquad i = 1,\ldots,a \qquad j = 1,\ldots,N_i \tag{5}$$

Residuals theory establishes that these deviations are expected to be independent with respect to the time, provided the model adequately captures the dynamics of the time series (e.g. Bates and Watts, 1988). Conversely, the occurrence of structure in the residuals (when reported with respect to time) can reveal the non-independence or the correlation of the disturbances. Thus, this scenario can be related to the failure of the model to completely detect the hidden determinism in the time series.

Table 2: Point estimation and confidence intervals for the model parameters.

Model	Parameter estimation	Adjusted R-squared
1 (Monod)	$\ln \mu_m = -2.11 \pm 0.0034$ $K_S = 1.2 \pm 0.1$ $Y = 1.86 \pm 0.12$	0.848
2 (Contois)	$\ln \mu_m = -2.12 \pm 0.068$ $B = 5.6 \pm 33$ $Y = 1.86 \pm 0.55$	0.851
3 (Herbert)	$\ln \mu_m = -2.12 \pm 0.043$ $K_S = 1.3 \pm 51$ $m = 0.036 \pm 3.12$ $Y = 1.86 \pm 0.29$	0.850
4 (Shehata and Marr)	$\ln \mu_m = -2.25 \pm 0.64$ $\mu_1 = 0.5213 \pm 1.04$ $K_1 = 11.7 \pm 72.0$ $K_2 = 25.9 \pm 125.0$ $Y = 1.86 \pm 0.23$	0.855
5 (Tessier)	$\ln \mu_m = -2.12 \pm 0.035$ $T = 8.0 \pm 16.0$ $Y = 1.86 \pm 0.30$	0.852
6 (Haldane)	$\ln \mu_m = -2.00 \pm 0.40$ $K_S = 1.9 \pm 35.1$ $K_i = 0.4162 \pm 1.027$ $Y = 1.85 \pm 0.40$	0.859

Figure 2 shows the lag plots of the residuals for Monod, Contois and Haldane models. Similar results are observed also with the Herbert, Tessier and Shehata & Marr models (here not reported for sake of space). A strong correlation among the residuals is evident, thus suggesting that all the models fail to take fully into account a quantitative description of the process dynamics.

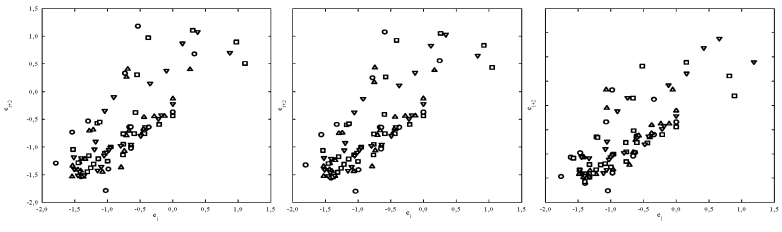

Figure 2: Lag-plots of the residuals for the Monod, Contois and Haldane models.

4. Conclusions

The Caffeic Acid biodegradation in a batch reactor was studied by using a mixed culture of microorganisms. Different growth models were investigated in order to establish the most adequate one to describe the current process dynamics. It was found that Monod model gives fair results. In fact, inhibition phenomena are not easily discerned, although they are usually observed when dealing with phenolic compounds biodegradation. The estimated parameters are reasonable and they are similar to the ones observed for other phenolic compounds reported by other researchers in literature.

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