Stability Analysis of a Model for Phenol and Cresol Mixture Degradation

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Abstract. We propose a mathematical model for phenol and p-cresol mixture degradation in a continuously stirred bioreactor. The model is described by three nonlinear ordinary differential equations. The novel idea in the model design is the biomass specific growth rate, known as sum kinetics with interaction parameters (SKIP). We establish existence and uniform boundedness of positive solutions. Then we determine the equilibrium points of the model and study their asymptotic stability. The theoretical investigations are based on the classical dynamic systems theory. Numerical simulations are included to confirm and fill out the theoretical studies.

1. Introduction
It is well known that aromatic compounds are heavy environmental pollutants. Wastewaters from petroleum refineries, coal mining and a variety of industrial chemical syntheses contain many aromatics such as phenol, cresols, nitrophenols, etc. The biodegradation of one or all components depends on the composition of the particular mixture and the used microorganisms [1], [2], [3]. The adequate analysis of interactions between the compounds and their influence on microbial growth is very important for understanding the simultaneous metabolism of phenolic mixtures. The availability of appropriate mathematical models for these biochemical processes is essential for quantification and estimation of interactions between the substrate components influencing the growth and degradation behavior of microorganisms. A few mathematical models have been developed to describe the mixed substrate biodegradation [4], [5], [6].
Recent practical experiments support the design of the so-called SKIP models (the sum kinetics with interaction parameters) for substrate mixture degradation, because they describe significantly better the microbial growth [7], [8].
Here, we perform a stability analysis of a SKIP model in a continuously stirred bioreactor, describing the mutual influence of phenol and 4-methylphenol (p-cresol).
The paper is organized as follows. The next Section 2 includes a short description of the proposed mathematical model. Section 3 is devoted to investigating the properties of the model solutions, including steady states analysis. The last Section 4 proposes numerical simulations and visualization of the model dynamics.

2. Model description
We propose the following model for phenol and p-cresol mixture degradation in a continuously stirred bioreactor...
\[
\frac{dX(t)}{dt} = (\mu(S_{ph}, S_{cr}) - D)X(t)
\]

(1)

\[
\frac{dS_{ph}(t)}{dt} = -k_{ph}\mu(S_{ph}, S_{cr})X(t) + D\left(S_{ph}^0 - S_{ph}(t)\right)
\]

(2)

\[
\frac{dS_{cr}(t)}{dt} = -k_{cr}\mu(S_{ph}, S_{cr})X(t) + D\left(S_{cr}^0 - S_{cr}(t)\right)
\]

(3)

where \(\mu(S_{ph}, S_{cr})\) is the specific growth rate, presented by

\[
\mu(S_{ph}, S_{cr}) = \frac{\mu_{\text{max}(ph)}S_{ph}}{k_{s(ph)} + S_{ph} + I_{cr/ph}S_{cr}} + \frac{\mu_{\text{max}(cr)}S_{cr}}{k_{s(cr)} + S_{cr} + I_{ph/cr}S_{ph}}
\]

(4)

The model function \(\mu(S_{ph}, S_{cr})\) accounts for the mixture effects of phenol and p-cresol compounds and is known as sum kinetics with interaction parameters (SKIP) [7], [9].

The definition of the state variables \(X, S_{ph}\) and \(S_{cr}\) as well as of the model parameters is given in Table 1. All coefficients are assumed to be positive.

As usual, the dilution rate \(D\) is considered as a control variable.

**Table 1. Model variables and parameters.**

| Definitions                        | Values       |
|------------------------------------|--------------|
| \(X\) biomass concentration [g/dm\(^3\)] | -            |
| \(S_{ph}\) phenol concentration [g/dm\(^3\)] | -            |
| \(S_{cr}\) p-cresol concentration [g/dm\(^3\)] | -            |
| \(D\) dilution rate [h\(^{-1}\)] | -            |
| \(S_{ph}^0\) influent phenol concentration [g/dm\(^3\)] | 0.7          |
| \(S_{cr}^0\) influent p-cresol concentration [g/dm\(^3\)] | 0.3          |
| \(k_{ph}\) metabolic coefficient \([S_{ph}/X]\) | 11.7         |
| \(k_{cr}\) metabolic coefficient \([S_{cr}/X]\) | 5.8          |
| \(I_{cr/ph}\) interaction coefficient indicating the degree to which phenol affects the p-cresol biodegradation | 0.3          |
| \(I_{ph/cr}\) interaction coefficient indicating the degree to which p-cresol affects the phenol biodegradation | 8.6          |
| \(\mu_{\text{max}(ph)}\) maximum specific growth rate on phenol as a single substrate [h\(^{-1}\)] | 0.23         |
| \(\mu_{\text{max}(cr)}\) maximum specific growth rate on p-cresol as a single substrate [h\(^{-1}\)] | 0.17         |
| \(k_{s(ph)}\) saturation constant for cell growth on phenol [g/dm\(^3\)] | 0.11         |
| \(k_{s(cr)}\) saturation constant for cell growth on p-cresol [g/dm\(^3\)] | 0.35         |

3. Stability analysis of the model

3.1. Basic properties of the model solutions

Define the set

\[
\Omega = \{ (X, S_{ph}, S_{cr}): X > 0, S_{ph} > 0, S_{cr} > 0 \}.
\]
Theorem 1. For any starting point \( (X(0), S_{ph}(0), S_{cr}(0)) \in \Omega \) the solution \( (X(t), S_{ph}(t), S_{cr}(t)) \) of system (1)-(3) is well defined and uniformly bounded for each \( t \geq 0 \).

Proof. It follows from (1) that if point \( X(\tau) = 0 \) for some \( \tau \geq 0 \) then \( \frac{dX}{dt}(\tau) = 0 \). The uniqueness of the solution implies \( X(t) = 0 \) for all \( t \geq \tau \). Therefore it is enough to consider only positive initial conditions implies \( X(t) > 0 \).

Using equation (1) we obtain consecutively
\[
\frac{dX}{dt} = \int_{0}^{t} (\mu(S_{ph}(\tau), S_{cr}(\tau)) - D) d\tau
\]
\[
X(t) = X(0) e^{-\int_{0}^{t}(\mu(S_{ph}(\tau), S_{cr}(\tau)) - D) d\tau} > 0 \text{ for each } t \geq 0.
\]

Equations (1) and (2) imply
\[
\frac{dS_{ph}}{dt} + k_{ph} \frac{dX}{dt} = D(S_{ph}^0 - S_{ph}) + k_{ph}X(t)
\]
Denoting \( Z_1(t) = S_{ph}(t) + k_{ph}X(t) \) we obtain
\[
\frac{dZ_1}{dt}(t) = D(S_{ph}^0 - Z_1(t))
\]
\[
Z_1(t) = S_{ph}^0 + (Z_1(0) - S_{ph}^0) e^{-D t} > 0 \text{ for all } t \geq 0.
\]

Therefore,
\[
\max\{Z_1(0), S_{ph}^0\} \geq Z_1(t) \geq \min\{Z_1(0), S_{ph}^0\} > 0 \text{ for all } t \geq 0.
\]

Similarly, using equations (1) and (3) and denoting \( Z_2(t) = S_{cr}(t) + k_{cr}X(t) \) we get
\[
\frac{dZ_2}{dt}(t) = D(S_{cr}^0 - Z_2(t)),
\]
\[
Z_2(t) = S_{cr}^0 + (Z_2(0) - S_{cr}^0) e^{-D t} > 0 \text{ for all } t \geq 0,
\]
\[
\max\{Z_2(0), S_{cr}^0\} \geq Z_2(t) \geq \min\{Z_2(0), S_{cr}^0\} > 0 \text{ for all } t \geq 0.
\]

The above presentations mean that the model solutions \( (X(t), S_{ph}(t), S_{cr}(t)) \) are uniformly bounded and thus exist for all time \( t \geq 0 \). This completes the proof of Theorem 1.

Remark 1. In the proof of Theorem 1 we didn’t use the explicit expression of \( \mu(S_{ph}, S_{cr}) \) from (4), thus the assertion is valid for any continuously differentiable and bounded specific growth rate function \( \mu(\cdot) \).

3.2. Equilibrium points of the model
The equilibrium points of (1)-(3) are solutions of the following system of algebraic equations
\[
(\mu(S_{ph}, S_{cr}) - D)X = 0 \tag{5}
\]
\[
-k_{ph}\mu(S_{ph}, S_{cr})X + D(S_{ph}^0 - S_{ph}) = 0 \tag{6}
\]
\[
-k_{cr}\mu(S_{ph}, S_{cr})X + D(S_{cr}^0 - S_{cr}) = 0. \tag{7}
\]
Obviously, the point $E_0 = (0, S_{ph}, S_{cr})$ (within $X = 0$) is always an equilibrium point of the model. We are looking now for solutions of (5)-(7) assuming that $X \neq 0$.

From (7) we obtain

$$X = \frac{D (S_{cr}^0 - S_{cr})}{k_{cr} \mu (S_{ph}, S_{cr})}.$$ 

Obviously, $X > 0$ iff $S_{cr} < S_{cr}^0$ holds. Substituting the above expression of $X$ into equation (6) implies

$$S_{ph} = S_{ph}^0 \frac{k_{ph}}{k_{cr}} (S_{cr}^0 - S_{cr}).$$ 

Denote for simplicity

$$K = \frac{k_{ph}}{k_{cr}}, \quad S^0 = S_{ph}^0 - KS_{cr}^0$$

and make the following assumption

$$S^0 > 0.$$ 

Then the presentation $S_{ph} = S^0 + KS_{cr}$ holds true and substituting the latter expression in (5) we obtain an equation with respect to $S_{ph}$ only:

$$\frac{\mu_{max(ph)}(S^0 + KS_{cr})}{k_{s(ph)} + S^0 + KS_{cr} + I_{cr/ph}S_{cr}} + \frac{\mu_{max(cr)}S_{cr}}{k_{s(cr)} + S_{cr} + I_{ph/cr}(S^0 + KS_{cr})} = D.$$ 

Let us introduce the notations

$$A_1 = 1 + K I_{ph/cr}, \quad A_2 = K + I_{cr/ph}, \quad A_3 = k_{s(cr)} + I_{cr/ph}S^0, \quad A_4 = k_{s(ph)} + S^0$$

and further

$$A = \mu_{max(ph)}KA_1 + \mu_{max(cr)}A_2 - DA_1 A_2$$

$$B = \mu_{max(ph)} (S^0 A_1 + KA_3)\mu_{max(cr)}A_4 - D (A_1 A_4 + A_2 A_3)$$

$$C = (\mu_{max(ph)} S^0 - DA_4)A_3.$$ 

Then the $S_{cr}$-component of the equilibrium point should satisfy the quadratic equation

$$AS_{cr}^2 + BS_{cr} + C = 0,$$ 

which coefficients $A, B, C$ depend on the model parameter $D$. To check the existence of real (and positive) roots of (9), we need to calculate its discriminant $\Delta(D) = B^2 - 4AC$. Straightforward calculations lead to the following expression for $\Delta(D)$.

$$\Delta(D) = aD^2 + bD + c,$$ 

where

$$a = (A_1 A_4 - A_2 A_3)^2 > 0,$$ 

$$b = 2\mu_{max(ph)} (A_1 A_2 A_3 S^0 - A_2^2 A_4 S^0 - A_3 (A_1 A_4 + A_2 A_3) K + 2 A_1 A_2 A_4 K) +$$

$$+ 2\mu_{max(cr)} A_4 (A_2 A_3 - A_1 A_4),$$

$$c = (A_1 A_4 - A_2 A_3)^2 - 4A_1 A_3 A_4 K (2 A_1 A_4 + A_2 A_3).$$
\[ c = \left( \mu_{\text{max}(p)} A_1 S^0 + \mu_{\text{max}(cr)} A_4 \right)^2 + \mu_{\text{max}(p)}^2 K A_3 (KA_3 - 2A_3 S^0) + 2\mu_{\text{max}(p)} \mu_{\text{max}(cr)} A_3 (KA_4 - 2A_2 S^0). \]

Obviously, the model can possess up to two internal (with positive components) equilibrium points. Their existence depends on the coefficient values as well as on values of \( \mu \). More precisely, we have to solve the inequality \( aD^2 + bD + c \geq 0 \) with respect to \( D \) to determine bounds of \( D \), for which one or two positive equilibria do exist. This will be done numerically in the next section, using the values of the model coefficients, given in the last column in Table 1. It is worth to note that these values are determined by real-life laboratory experiments [9].

Before that we shall study some important properties of the model solutions.

In what follows we shall use the notation

\[ D^+ = \mu(S^0_{\text{ph}}, S^0_{\text{cr}}). \]

**Theorem 2.** The dynamic system (1)-(3) undergoes a transcritical bifurcation at the equilibrium point \( E_0 = (0, S^0_{\text{ph}}, S^0_{\text{cr}}) \) for \( D = D^+ \).

**Proof.** Let \( J = (E_0; D^+) \) be the Jacobian of the model equations (1)-(3) evaluated at \( E_0 = (0, S^0_{\text{ph}}, S^0_{\text{cr}}) \) and \( D = D^+ \). It is straightforward to see that the eigenvalues of \( J = (E_0; D^+) \) are the roots of the following characteristic equation \( \lambda(\lambda^2 + k_{cr}D^+\lambda - k_{ph}D^+) = 0 \); the latter obviously possesses one root \( \lambda = 0 \) and two more real roots with opposite signs. This means that \( E_0 \) is a nonhyperbolic equilibrium, and a transcritical bifurcation occurs at \( D = D^+ \) [10].

**Remark 2.** It is known [10] that the occurrence of a bifurcation for some parameter values (in our case for \( D = D^+ \)) leads to destabilization of the model dynamics. It is not difficult to see that if \( D > D^+ \) then \( E_0 \) remains the unique equilibrium of (1)-(3) and it is necessarily the global attractor. This means that for any initial conditions \((X(0), S_{\text{ph}}(0), S_{\text{cr}}(0)) \in \Omega \), the relations \( X(t) \to 0 \) and \( S_{\text{ph}}(t) \to S^0_{\text{ph}}, S_{\text{cr}}(t) \to S^0_{\text{cr}} \) hold as \( t \to +\infty \). The practical interpretation of this fact is that the organisms are washed-out and the environment is not detoxified, which is the worst possible case.

For the practical applications, the most important equilibrium point is that one with positive components, i.e. the internal equilibrium. The existence of such an equilibrium, and especially when it is asymptotically stable, means that the organisms remain in the system and detoxification is carried out.

**Theorem 3.** If \( D < D^+ \) and there exists at least one internal equilibrium \( E^* = (X^*, S^*_{\text{ph}}, S^*_{\text{cr}}) > 0 \), then there exists time \( T > 0 \), such that \( S_{\text{ph}}(t) < S^0_{\text{ph}} \) and \( S_{\text{cr}}(t) < S^0_{\text{cr}} \) hold true for all \( t > T \).

**Proof.** The existence of the equilibrium point \( E^* \) means that there exists some \( D^+ \in (0, D^+) \) such that \( \mu(S^*_{\text{ph}}, S^*_{\text{cr}}) = D^* \) is satisfied. Assume that \( S_{\text{ph}}(t) \geq S^0_{\text{ph}} \) and \( S_{\text{cr}}(t) \geq S^0_{\text{cr}} \) hold for each \( t > 0 \). Then we have from (2) that

\[ \frac{dS_{\text{ph}}(t)}{dt} = -k_{ph}\mu(S_{\text{ph}}, S_{\text{cr}})X(t) + D \left( S^0_{\text{ph}} - S_{\text{ph}}(t) \right) < 0 \]

Barbălat's Lemma [11] implies that

\[ 0 = \lim_{t \to \infty} \frac{dS_{\text{ph}}(t)}{dt} = \lim_{t \to \infty} \left( -k_{ph}\mu(S_{\text{ph}}, S_{\text{cr}})X(t) + D \left( S^0_{\text{ph}} - S_{\text{ph}}(t) \right) \right) \]

which leads to \( S_{\text{ph}}(t) \to S^0_{\text{ph}} \) and \( X(t) \to 0 \) as \( t \to \infty \). Similarly, using equation (3), we obtain \( S_{\text{cr}}(t) \to S^0_{\text{cr}} \) and \( X(t) \to 0 \) as \( t \to \infty \). Further we have that \( \mu(S^*_{\text{ph}}, S^*_{\text{cr}}) = D^* < D^+ = \mu(S^0_{\text{ph}}, S^0_{\text{cr}}) \). The continuity of \( \mu(\cdot) \) and the relations \( S_{\text{ph}}(t) \to S^0_{\text{ph}} \) and \( S_{\text{cr}}(t) \to S^0_{\text{cr}} \) as \( t \to \infty \) imply that there exists \( v > 0 \) such that
\[\mu(S_{ph}(t), S_{cr}(t)) - D^* = \mu(S_{ph}(t), S_{cr}(t)) - \mu(S_{ph}^*, S_{cr}^*) \geq \nu\]

for all sufficiently large \(t\). It follows then that \(X(t) = (\mu(S_{ph}(t), S_{cr}(t)) - D^*)X(t) \geq \nu X(t)\) for all sufficiently large \(t\), which contradicts the boundedness of \(X(t)\). Hence, there exists a sufficiently large \(T_1 > 0\) with \(S_{ph}(T_1) \leq S_{ph}^0\). Moreover, if the equality \(S_{ph}(T_1) = S_{ph}^0\) holds true, then we have

\[
\frac{dS_{ph}(t)}{dt} = -k_{ph}\mu(S_{ph}(T_1), S_{cr}(T_1))X(T_1) + D\left(S_{ph}^0 - S_{ph}(T_1)\right) = -k_{ph}\mu(S_{ph}(T_1), S_{cr}(T_1))X(T_1) < 0 .
\]

The last inequality shows that \(S_{ph}(t) < S_{ph}^0\) for each \(t > T_1\). Similarly, one can show that there exists \(T_2 > 0\) such that \(S_{cr}(t) < S_{cr}^0\) for each \(t > T_2\). Taking \(T = \max\{T_1, T_2\}\) proves the theorem.

4. Numerical simulation

Using the numerical values in the last column of Table 1, we obtain the following results, which confirm and fill out the theoretical studies from the previous section. We have

\[D^* = \mu(S_{ph}^0, S_{cr}^0) = 0.1068\]

and further

\[\Delta(D) \geq 0 \quad \text{if} \quad D \geq 0.07947 =: D^- .\]

Therefore,

(i) if \(D \in (D^-, D^+)\) then there exist two positive equilibrium points, \(E_1\) and \(E_2\), of the model. \(D = D^+\) is a bifurcation value, leading to \(X = 0\).

(ii) if \(D = D^-\) then \(\Delta(D^-) = 0\) and the two positive equilibria coalesce, i.e. \(E_1 \equiv E_2\). Hence, for \(D \in (0, D^-)\) the point \(E_0\) is the unique equilibrium of the model.

(iii) if \(D \geq D^+\) then \(E_0\) is the unique equilibrium point of the model as a result of bifurcation for \(D = D^+\).

It follows from (i) - (iii) that the practically useful values of the control variable \(D\) belong to the interval \((D^-, D^+)\). The boundedness of \(D \in (D^-, D^+)\) is not restrictive in practical applications, since the dilution rate \(D\) is proportional to the speed of the pumping mechanism which feeds the bioreactor. Thus there always exist a lower and an upper bound for \(D\) [12].

We shall demonstrate below the dynamic behavior of the model solutions on a particular numerical example.

**Example.** \(D = 0.1 \in (D^-, D^+)\)

In this case there exist two positive (internal) equilibrium points

\[E_1 = (0.05126, 0.1002, 0.002687) \quad \text{and} \quad E_2 = (0.01359, 0.5411, 0.2212),\]

such that \(E_1\) is locally unstable (a saddle), \(E_2\) is a locally asymptotically stable equilibrium point (a node), and \(E_0\) is locally unstable steady state (a saddle).

The left plot in Figure 1 shows the solutions \(X(t), S_{ph}(t), S_{cr}(t)\); there, the dash-lines pass through the corresponding components of the stable equilibrium \(E_2\). The right plot in Figure 1 as well as the two plots in Figure 2 illustrate the trajectories of the model in different phase planes with two different initial points. In these figures, the solid circles denote the corresponding components of the stable.
equilibrium $E_2$, the boxes denote the corresponding components of the unstable steady states $E_0$ and $E_1$.

Figure 1. Time evolution of the model solutions (left); trajectories in the $(X; Scr)$-plane (right).

Figure 2. Trajectories in the $(Sph; Scr)$-plane and in the $(X; Sph)$-plane.

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