

Qualitative Analysis of a Mathematical Model for Kinetic Mechanisms of Complete Mineralization of Phenol by Fe_2^+ , Fe_3^+ and H_2O_2

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Abstract

In this work we study the phenol degradation kinetics through the formulation and analysis of a nonlinear system of ordinary differential equations. The results suggest that the dynamics of the model is consistent with the phenomenon of phenol mineralization.

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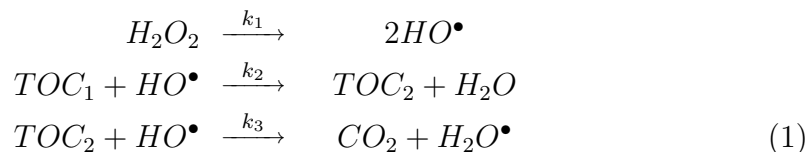
1 Introduction

Natural Organic Matter (NOM) concentration has significantly increased in the past few decades in almost all supply sources employed to produce drinking water all around the world [1]. It has brought several technical and quality problems on the product finally consumed. In the other hand, Catalytic Wet Peroxide Oxidation (CWPO) is an Advanced Oxidation Process (AOP) that has been highlighted thanks to its very low cost and simple operation, depleting very efficiently the concentration of almost any organic contaminant dissolved in water, including NOM [1]. In this sense, to investigate phenol degradation is quite relevant. For this end, it is necessary to study the concentration of toxic intermediates in the degradation mechanisms [7]. However, the dynamics of the formation of these intermediaries is still an open field of research. Notwithstanding the foregoing, the total organic carbon (TOC), instead of phenol and intermediates, is taken as a surrogate parameter of organic matter present in water. TOC is assumed as the sum of the contribution of two types of compounds. The initial phenol concentration is expressed by TOC_1 and the total formation of intermediate is expressed by TOC_2 [7]. Above it has motivated the development of different investigations among which we have [6, 8, 9, 2], where the mineralization of phenol had been modeling.

The following sections present the formulation of the model, qualitative analysis, numerical results and discussion.

2 Mathematical model

Tisa et al. in [7] deduced 21 reactions for complete mineralization of phenol by $Fe^{3+}/Fe^{2+}/H_2O_2$. However, after some assumptions they reduced the mechanism to the following three chemical reactions



where k_1 , k_2 and k_3 are kinetic constants. Let $x_1 = [H_2O_2]$, $x_2 = [HO^\bullet]$, $x_3 = [TOC_1]$, $x_4 = [TOC_2]$, $x_5 = [H_2O^\bullet]$ and $x_6 = [CO_2]$. From the law of

mass action we obtain the following system of differential equations

$$\begin{aligned}
 \frac{dx_1}{dt} &= -k_1x_1 \\
 \frac{dx_2}{dt} &= k_1x_1 - k_2x_2x_3 - k_3x_2x_4 \\
 \frac{dx_3}{dt} &= -k_2x_2x_3 \\
 \frac{dx_4}{dt} &= k_2x_2x_3 - k_3x_2x_4 \\
 \frac{dx_5}{dt} &= k_2x_2x_3 + k_3x_2x_4 \\
 \frac{dx_6}{dt} &= k_3x_2x_4.
 \end{aligned} \tag{2}$$

Since chemical reactions are not reversible, then the initial concentrations satisfy

$$\begin{aligned}
 x_1^0 = [H_2O_2]_0 \neq 0, \quad x_2^0 = [HO^\bullet]_0 = 0, \quad x_3^0 = [TOC_1]_0 \neq 0, \\
 x_4^0 = [TOC_2]_0 = 0, \quad x_5^0 = [H_2O^\bullet]_0 = 0, \quad \text{and} \quad x_6^0 = [CO_2]_0 = 0.
 \end{aligned} \tag{3}$$

The set of chemical interest is given by

$$\Omega = \{x \in \mathcal{R}_+^6 : x_1 + x_2 + x_5 = x_1^0, 2x_3 + x_4 + x_5 = 2x_3^0, x_4 - x_5 + 2x_6 = 0\} \tag{4}$$

The following lemma ensures that the system (2) has chemical sense; that is, every solution that begin there remain there for every $t \geq 0$.

Lemma 2.1. *The set Ω defined in (4) is positively invariant for solutions of the system (2).*

Proof. Adding the first, second and fifth equations of (7) we have

$$\frac{dx_1}{dt} + \frac{dx_2}{dt} + \frac{dx_5}{dt} = 0. \tag{5}$$

The solution of (5) subject to the initial conditions (3) is

$$x_1(t) + x_2(t) + x_5(t) = x_1^0.$$

Following a similar process we verify the other restrictions of set Ω . On the other hand, the vector field defined by the right side of (2) points inward in $\partial\Omega$. Therefore, the solutions that start there remain there for all $t \geq 0$. \square

From the restriction conditions defined in Ω we obtain

$$\begin{aligned}x_1 &= -x_5 - x_2 + x_1^0 \\x_3 &= -\left(\frac{x_4 + x_5}{2}\right) + x_3^0 \\x_6 &= \frac{x_5 - x_4}{2}.\end{aligned}\tag{6}$$

Substituting (6) into (2) we obtain the following system of differential equations

$$\begin{aligned}\frac{dx_2}{dt} &= \left(\frac{k_2}{2} - k_3\right)x_2x_4 + \frac{k_2}{2}x_2x_5 - (k_1 + k_2x_3^0)x_2 - k_1x_5 + k_1x_1^0 \\ \frac{dx_4}{dt} &= -\left(\frac{k_2}{2} + k_3\right)x_2x_4 - \frac{k_2}{2}x_2x_5 + k_2x_3^0x_2 \\ \frac{dx_5}{dt} &= \left(k_3 - \frac{k_2}{2}\right)x_2x_4 - \frac{k_2}{2}x_2x_5 + k_2x_3^0x_2\end{aligned}\tag{7}$$

3 Solutions of equilibrium

In this section we will determine the equilibrium solutions of (7), which are given by the solutions of

$$\begin{aligned}\left(\frac{k_2}{2} - k_3\right)x_2x_4 + \frac{k_2}{2}x_2x_5 - (k_1 + k_2x_3^0)x_2 - k_1x_5 + k_1x_1^0 &= 0 \\ -\left(\frac{k_2}{2} + k_3\right)x_2x_4 - \frac{k_2}{2}x_2x_5 + k_2x_3^0x_2 &= 0 \\ \left(k_3 - \frac{k_2}{2}\right)x_2x_4 - \frac{k_2}{2}x_2x_5 + k_2x_3^0x_2 &= 0.\end{aligned}\tag{8}$$

Adding the second and third equation of (8) we obtain

$$2k_2x_2\left(x_3^0 - \frac{x_4}{2} - \frac{x_5}{2}\right) = 0.\tag{9}$$

Replacing $x_2 = 0$ in (8) we have that $x_5 = x_1^0$, x_2 and x_3 can take any real value. On the other hand, if $x_2 \neq 0$ then from (9) we have

$$x_4 = 2x_3(0) - x_5.\tag{10}$$

Substituting (10) in the second equation of (8) we have

$$-\frac{k_2}{2}x_2(2x_3^0 - x_5) - k_3x_2(2x_3^0 - x_5) - \frac{k_2}{2}x_2x_5 + k_2x_3^0x_2 = 0.\tag{11}$$

The solution of (11) is $x_5 = 2x_3^0$, in consequence from (11) and the first equation of (8) we obtain $x_4 = 0$ and $x_2 = x_1^0 - 2x_3^0$. The following lemma summarizes the above result

Lemma 3.1. *Always exist a non-isolated equilibrium E_1 of the system (7). If $x_1^0 > 2x_3^0$, in addition of E_1 there exist a isolated equilibrium given by*

$$E_0 = (x_1^0 - 2x_3^0, 0, 2x_3^0). \tag{12}$$

The following corollary is obtained by replacing the values of x_2^0 , x_4^0 and x_5^0 in (6)

Corollary 3.2. *Always exist a non-isolated equilibrium \bar{E}_1 of the system (2). If $x_1^0 > 2x_3^0$, in addition of \bar{E}_1 there exist a isolated equilibrium given by*

$$\bar{E}_0 = (0, x_1^0 - 2x_3^0, 0, 0, 2x_3^0, x_3^0). \tag{13}$$

4 Stability of the equilibrium solution

Since E_1 is a non-isolated equilibrium, in this section we only discuss the local stability of the isolated equilibrium E_0 . To this end, note that the Jacobian of (8) evaluated in E_0 is given by

$$J(E_0) = \begin{pmatrix} -k_1 & \left(\frac{k_2}{2} - k_3\right)(x_1^0 - 2x_3^0) & \frac{k_2}{2}(x_1^0 - 2x_3^0) - k_1 \\ 0 & -\left(\frac{k_2}{2} + k_3\right)(x_1^0 - 2x_3^0) & -\frac{k_2}{2}(x_1^0 - 2x_3^0) \\ 0 & \left(k_3 - \frac{k_2}{2}\right)(x_1^0 - 2x_3^0) & -\frac{k_2}{2}(x_1^0 - 2x_3^0) \end{pmatrix}. \tag{14}$$

The eigenvalues of (14) are given by $\lambda_1 = -k_1$ and the roots of

$$\lambda^2 + (k_2 + k_3)x_2^0 a_1 \lambda + k_2 k_3 (x_2^0)^2 = 0. \tag{15}$$

The solutions of (15) are given by

$$\begin{aligned} \lambda^\pm &= \frac{-(k_2 + k_3)x_2^0 \pm |(k_2 - k_3)x_2^0|}{2} \\ &= \frac{[-(k_2 + k_3) \pm |k_2 - k_3|]x_2^0}{2}. \end{aligned} \tag{16}$$

We verify from (16) that $\lambda^+ < 0$ and $\lambda^- < 0$. The following lemma summarizes the above result

Lemma 4.1. *The isolated equilibrium E_0 is locally asymptotically stable in Ω .*

5 Numerical simulations

In this section, we present numerical simulations of the chemical concentrations in the phenol mineralization process defined in (1). The velocity constants

$k_1 = 0.0012$, $k_2 = 6.35 \times 10^{-10}$ and $k_3 = 9.6 \times 10^{-7}$, and the initial concentrations $(x_1^0, x_2^0, x_3^0, x_4^0, x_5^0, x_6^0) = (28, 0, 4.4, 0, 0, 0)$ that we used to perform the numerical simulations were obtained from [7].

Figure 1 illustrate the dynamical behavior of the concentrations above mentioned. The time of the simulations is $t = 5000 \text{ seg} \approx 83.3 \text{ min}$. From the graphs we observe that the peroxide ($[H_2O_2]$) is consumed in approximately 83.3 minutes, at same time the hydroxyl radical ($[HO^\bullet]$) reaches the stabilization concentration of 28 mol. While the initial concentration of phenol expressed by $[TOC_1]$ is consumed in approximately 8.3 minutes, time at which the maximum total formation of intermediates expressed $[TOC_2]$ is reached, after this time the concentration of $[TOC_2]$ begins to be consumed slowly. At reaction time both water (H_2O) and carbon dioxide ($[CO_2]$) increase on a very small scale.

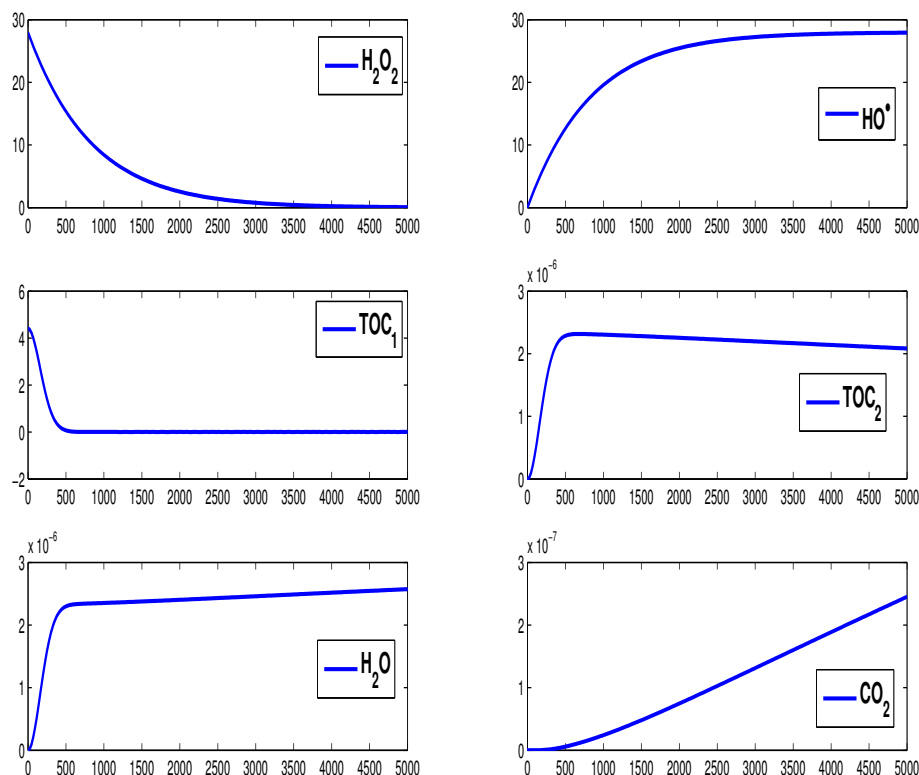


Figure 1: Graph of concentrations $[H_2O_2]$, $[HO^\bullet]$, $[TOC_1]$, $[TOC_2]$, $[H_2O]$ and $[CO_2]$ with respect to time. The time of the simulations is $t = 5000 \text{ seg} \approx 83.3 \text{ min}$.

Figure 2 shown graphs of $[TOC_2]$, $[H_2O]$ and $[CO_2]$ with respect to time. The time of the simulations is $t = 200000 \text{ seg} \approx 55.6 \text{ h}$. This is the time of stabilization of the concentrations mentioned above, in which $[TOC_2]$ is totally consumed, H_2O and $[CO_2]$ reach their maximum concentrations $4.6 \times 10^{-6} \text{ mol}$ and $2.4 \times 10^{-6} \text{ mol}$, respectively.

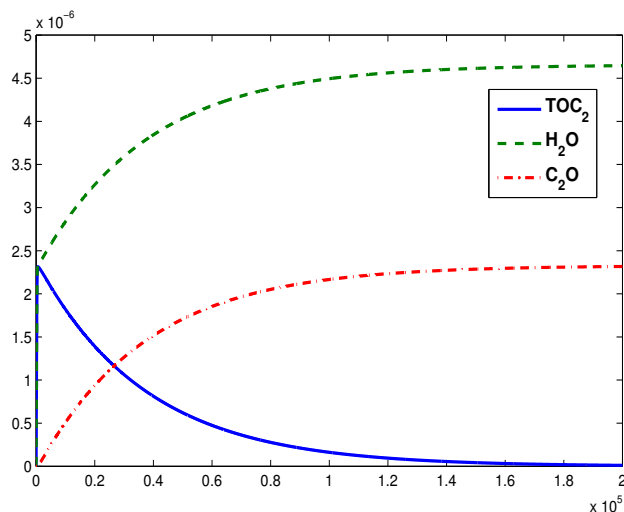


Figure 2: Graph of concentrations $[TOC_2]$, $[H_2O]$ and $[CO_2]$ with respect to time. The time of the simulations is $t = 200000 \text{ seg} \approx 55.6 \text{ h}$.

6 Discussion

In this paper we perform a qualitative analysis similar to the one developed in [3, 4, 5] to analyze a mathematical model for mineralization kinetic of phenol by Fe_2^+ , Fe_3^+ and H_2O_2 assuming a first order kinetics. Our main objective was to determine if the initial value problem defined by (2) and (3) is adjusted to the dynamics of the kinetic reactions defined in (1). In addition, to verify through mathematical modeling if these reactions have a good performance in degradation of the phenol and formation of $[HO^\bullet]$. In fact, as we can see in Figure 1, a complete degradation of the phenol occurs in about 8 minutes, this opens the possibility that in CWPO a complete degradation of NOM can be carried out. Numerical simulations show Figures 1 and 2, we observe that 99.9999% of $[H_2O_2]$ consumed is transformed into $[HO^\bullet]$, $[TOC_1]$ is consumed completely and 0.000001% of the $[H_2O_2]$ remaining is transformed into H_2O and $[CO_2]$.

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