Development of catalytic microreactors by plasma processes: application to wastewater treatment
Da Silva, B.T.

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Chapter 5: Numerical simulation of the pyruvic acid degradation by catalytic ozonation in a catalytic microreactor

1. Introduction

Ozone is often used in industry for the disinfection of a great number of micropollutants, as well as in improving the taste, smell and destruction of colors and pathogenic germs [329-330]. The mechanisms of its reaction with different pollutants have been extensively studied over the last 25 years [319,324,331]. Once dissolved in water, ozone decomposes and generally leads to the formation of unstable elements with a lifetime that may extend from a few milliseconds to several days.

However, its decomposition mostly leads to the formation of hydroxyl radicals with a high oxidation potential [332]. The self-decomposition of ozone in water depends on the temperature, its concentration in water, on the alkalinity of the solution to be treated and pH.

Indeed, it has been demonstrated that an increase in the pH accelerates the self-decomposition and that ozone behaves as a precursor agent of hydroxyl radicals [333]. This indirect reaction and non-selective attack may lead to a full mineralization. In contrast, at a lower pH, ozone will behave as a disinfecting agent, by reacting directly on the pollutants in solution. In this case, the reaction is selective and may lead to an accumulation of by-products in the solution to be treated. In order to increase the decomposition of ozone into hydroxyl radicals, ozone has often been coupled with UV light and/or H₂O₂ [334,335].

These types of AOPs are efficient for the elimination of a large number of pollutants which are difficult to be degraded by simple ozonation such as carboxylic acids. However, they require a heavy maintenance and a good
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In order to avoid the formation of scavengers for hydroxyl radicals [336-338], therefore, a possible solution may reside in the use of catalytic ozonation where a supported catalyst such as activated carbon or metallic oxides is introduced in the reaction system.

In spite of an impressive number of papers devoted to catalytic ozonation [339-341], no clear consensus on the mechanisms of degradation of organic pollutants was reached. The reason can be that the mechanisms differ according to (i) the nature of the pollutant, (ii) the nature of the catalyst and (iii) the solution properties such as pH and conductivity.

The objective of this study is to propose a Computational Fluid Dynamics (CFD) model in order to find suitable mechanisms describing the degradation of an ozone refractory compound, pyruvic acid (PA), in the presence of ozone in a catalytic microreactor containing a plasma-deposited cobalt oxide coating. The model will be elaborated on the basis of the previous experimental dataset (Chapter 4) and by taking into account deactivation of the catalyst.

2. Ozone self-decomposition and simple ozonation simulation model

2.1 Description of the simple ozonation simulation model

As shown in the previous chapter, the mixed solution of dissolved ozone and pyruvic acid passes through the catalytic microreactor, via the use of a syringe pump, by pulling backward the mixed solution from the batch reactor into a syringe.

However, before performing a numerical simulation of the catalytic microreactor, kinetics in the bulk have to be determined. For this purpose, the numerical modeling of the self-decomposition of ozone and further reaction with pyruvic acid was assessed by elaborating a 0D model. This model takes into account direct (ozone as the reactant) and indirect (hydroxyl radicals as reactive species) ozonation of pyruvic acid. In addition, assuming that oxalic acid and acetic acid
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are possibly by-products of the oxidation of pyruvic acid, indirect and direct ozonation of the latter were also taken into account.

The model used for ozone self-decomposition derives from [342] whereas kinetics for direct and indirect ozonation of pyruvic acid derives from [87]. The model used in this study is presented in Table 17.

Table n°17: Simplified kinetic model describing the self-decomposition of ozone and reaction with pyruvic acid.

<table>
<thead>
<tr>
<th>Nº</th>
<th>Reaction</th>
<th>Reaction rate constant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$O_3 + HO^- \rightarrow O_2^- + HO^*$</td>
<td>$k_1 = 70 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$</td>
<td>[326]</td>
</tr>
<tr>
<td>2</td>
<td>$HO^* \rightarrow H^* + O_2^-$</td>
<td>$k_2 = 3.2 \times 10^5 \text{ s}^{-1}$</td>
<td>[71]</td>
</tr>
<tr>
<td>3</td>
<td>$H^+ + O_2^- \rightarrow HO^*$</td>
<td>$k_3 = 2 \times 10^{10} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$</td>
<td>[71]</td>
</tr>
<tr>
<td>4</td>
<td>$O_3 + O_2^- \rightarrow O_3^* + O_2$</td>
<td>$k_4 = 9 \times 10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$</td>
<td>[328]</td>
</tr>
<tr>
<td>5</td>
<td>$O_3^* + H_2O \rightarrow HO^* + OH^- + O_2$</td>
<td>$k_5 = 5.2 \times 10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$</td>
<td>[319]</td>
</tr>
<tr>
<td>6</td>
<td>$PA + \cdot OH \rightarrow AC$</td>
<td>$k_6 = 3.1 \times 10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$</td>
<td>[71]</td>
</tr>
<tr>
<td>7</td>
<td>$PA + \cdot OH \rightarrow AOX$</td>
<td>$k_6 = 3.1 \times 10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$</td>
<td>[71]</td>
</tr>
<tr>
<td>8</td>
<td>$AC + \cdot OH \rightarrow CO_2 + H_2O$</td>
<td>$k_7 = 1.4 \times 10^6 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$</td>
<td>[285]</td>
</tr>
<tr>
<td>9</td>
<td>$AOX + \cdot OH \rightarrow CO_2 + H_2O$</td>
<td>$k_8 = 1.6 \times 10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$</td>
<td>[285]</td>
</tr>
<tr>
<td>10</td>
<td>$PA + O_3 \rightarrow AC$</td>
<td>$k_9 = 1.3 \times 10^{-1} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$</td>
<td>[284]</td>
</tr>
<tr>
<td>11</td>
<td>$PA + O_3 \rightarrow AOX$</td>
<td>$k_9 = 1.3 \times 10^{-1} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$</td>
<td>[284]</td>
</tr>
<tr>
<td>12</td>
<td>$AC + O_3 \rightarrow CO_2 + H_2O$</td>
<td>$k_{10} = 3 \times 10^{-5} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$</td>
<td>[284]</td>
</tr>
<tr>
<td>13</td>
<td>$AOX + O_3 \rightarrow CO_2 + H_2O$</td>
<td>$k_{11} = 0.4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$</td>
<td>[284]</td>
</tr>
</tbody>
</table>

In this model, ozone self-decomposition leads to the formation of two types of radicals: the oxygen super-oxide ($O_2^-$) and the hydroxyl radical 'OH. To the best of our knowledge, the first one is not selective and its reaction mechanism was poorly studied, whereas the hydroxyl radical action mechanism was thoroughly studied and the literature is rich in matters of kinetic constant values [71]. Therefore, the oxygen super-oxide will not be taken as an oxidizing agent in our simulations.
The reaction of ozone on pyruvic acid (PA) was taken here as direct (reactions 10-11) and indirect (reactions 6-7) and by assuming that the degradation of pyruvic acid leads to two kind of intermediate species: oxalic acid (AOX) and acetic acid (AC). In addition, direct or indirect ozonation of the intermediate pollutants is further assumed to lead to full mineralization.

As initial data for the simulation, initial concentrations of PA and O$_3$ (0.3 mol/m$^3$) as well as the pH value (pH = 3) are known.

### 2.2 Simulation results of simple ozonation in batch reactor

A numerical simulation with the previous established model (Table 17) was carried out.

![Graph of Simulations results of the evolution of the concentrations of PA, AOX and AC in the batch reactor as a function of time (pH= 3, [PA]$_0$= 0.3 mol/m$^3$, [O$_3$] = 0.3 mol/m$^3$).](image)

As shown in Figure 55, after one hour of simple ozonation, the concentration of pyruvic acid reaches a value of 0.195 mol/m$^3$ corresponding to 35% of
Chapter 5: Numerical simulation of the pyruvic acid degradation by catalytic ozonation in a catalytic microreactor degradation of PA. This value has to be compared with the experimental one obtained in similar conditions.

In the previous chapter, it was shown that a final value of 30% of degradation was found experimentally after one hour of ozonation with an initial PA concentration of 0.3 mol/m$^3$ and at pH = 3. By comparing the overall shapes of the evolution of PA concentration between the simulation results and the one obtained by the previous HPLC measurements, it can be concluded that the model previously established fits the experimental results.

The model was then used to determine the respective roles of direct and indirect ozonation according to the value of pH. Indirect ozonation is normally due to the reaction of hydroxyl radicals on PA (reaction n°6 in Table 17). However, the production of hydroxyl radicals is severely limited by the first step (reaction n°1 in Table 17) as the reaction rate constant ($70 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) is the lowest in ozone self-decomposition.

Figure 56 was obtained by reporting the following reaction rates for indirect and direct ozonation performed after one hour:

$$v_{\text{indirect}} = k_1[OH^-][O_3]$$

$$v_{\text{direct}} = k_{10}[O_3][PA]$$
Figure n°56: Contribution of the reaction rate between indirect and direct ozonation as a function of pH (domain located between 3 and 9).

The simulation results shown in Figure 56 indicate that the contribution of ozone (direct ozonation) is more important than the contribution of hydroxyl radicals (indirect ozonation) for an acidic pH ranging between 3 and 7 for an initial concentration of PA of 0.3 mol/m$^3$.

At a pH = 3, it can be seen that the ratio of the two reaction rates is very low ($1.8 \times 10^{-5}$) indicating a poor contribution of hydroxyl radicals (indirect ozonation). The latter is increased when pH increases from 7 to 9, the ratio becoming greater than 1 at a pH = 8 until a value of 18 is reached at a pH = 9.

Therefore, the reaction rates ratio increasing along with pH indicates that ozone decomposes more rapidly in a basic solution than in an acidic one. Moreover, by increasing the pH, the probability of encounter between O$_3$ and OH$^{-}$ in the reaction system increases, leading to a greater production of hydroxyl radicals. Thus, the latter will not contribute in degrading PA and its intermediates at a low pH.
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These results are in agreement with previous studies indicating that ozonation self-decomposition is slower in acidic solutions [287] and confirm that indirect ozonation can be neglected in our simulations.

Based on the assumption that hydroxyl radicals poorly contribute in the ozonation of pyruvic acid as stated in the literature [286], the following reaction rate can be considered:

\[ PA + O_3 \xrightarrow{k_{O_3,PA}} \text{Products} \]

With the reaction rate: \( r = k_{O_3,PA} \times [PA] \times [O_3] \)

Figure n°57: First-order kinetic of the simple ozonation of pyruvic acid in batch reactor (pH= 3, \([PA]_0= 0.3 \text{ mol/m}^3\), \([O_3] = 0.3 \text{ mol/m}^3\)).

As shown in Figure 57, the pyruvic acid decay was fitted with a linear regression curve. Indeed, ozone being produced in a continuous mode, an analysis of the decay can be assimilated to a first-order kinetic assuming the following reaction:

\[ r_{app} = k_{app} \times [PA] \]
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With: \( k_{app} = kO_3PA \times [O_3] \) in s\(^{-1}\)

The differential equation can be written as:

\[ r_{app} = -\frac{d[PA]}{dt} = k_{app} \times [PA] \]

And by rearranging the previous equation:

\[ -\frac{d[PA]}{[PA]} = k_{app} \times t \]

Finally, integration of the latter leads to the following equation:

\[ \ln \frac{[PA]}{[PA]_0} = -k_{app} \times t \]

Therefore, the variation of the PA concentration as a function of time inside the batch reactor can be written as follows:

\[ C_{PA}(t) = C_{PA}^0e^{-k_{app}t} \]

With: \( k_{app} = 1 \times 10^{-4} \text{s}^{-1} \). A value of \( 1 \times 10^{-4} \text{s}^{-1} \) at a pH 3 with a good correlation (R\(^2 = 0.98\)) was found for the apparent first-order rate constant. The global reaction rate corresponding to a second-order reaction can be therefore calculated and a value of \( 3.3 \times 10^{-1} \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \) is obtained. This value is in good agreement (same order of magnitude) with the ones reported in the literature in the same range of concentration for pyruvic acid and pH (\( kO_3AP = 1.3 \times 10^{-1} \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \) and \( 9.8 \times 10^{-1} \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \) respectively at pH = 1 and 7 [284]).

In addition, from Figure 55, it can be seen that the kinetic model chosen here leads to an accumulation of acetic acid in the batch reactor. Here, at a pH = 3 after one hour, the average production of AC reaches a value of \( 5.3 \times 10^{-2} \text{mol/m}^3 \) for an initial concentration of \( 0.3 \text{mol/m}^3 \) of pyruvic acid.

Regarding the concentration of oxalic acid, the model gives a low and almost constant concentration of the oxalic acid in solution as shown in Figure 55. The latter reached a value of \( 9.75 \times 10^{-5} \text{mol/m}^3 \) for an initial concentration of 0.3
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mol/m³ of pyruvic acid. In fact, as shown in Figure 58 (magnification of the concentration of oxalic acid shown in Figure 55), oxalic acid is produced rapidly and then decreases in time.

![Graph](image)

**Figure n°58:** Evolution of the concentration of AOX in the batch reactor as a function of time (pH= 3, [PA]₀= 0.3 mol/m³, [O₃]₀ = 0.3 mol/m³).

Therefore, the role of indirect ozonation being negligible, the previous set of equations can be reduced to the direct ozonation of PA but also accelerates the convergence of our model in Comsol.

3. **Numerical simulation of the catalytic microsystem**

3.1 **Geometry and mesh used for the system**

The numerical simulations were carried out using a 2D geometry where a 100 µm X 1.5 cm rectangle which represents the side view of the microreactor as shown in Figure 59.
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**Figure n°59**: Geometrical implementation of the catalytic microreactor in Comsol Multiphysics.

**Figure n°60**: Magnification of the mesh used for the simulations in Comsol Multiphysics.

As shown in Figure 60, the mesh used for the computer simulation was refined near the surface for precision of calculation purposes.

The model used for the simulations was a simple convection-diffusion that can be found in the Chemical Engineering module of Comsol Multiphysics. The kinetic models used for the computer simulations are described hereafter.
3.2 Kinetic model used for the degradation of PA in the catalytic microreactor

As demonstrated by Alvarez et al. [341], the contribution of indirect ozonation can be neglected in acidic conditions in the same range of concentrations used in the present study and with the same nature of catalyst, i.e. Co$_3$O$_4$. Alvarez showed that the conversion rate of pyruvic acid increased along with pH giving rise to the indirect way of ozonation through hydroxyl radicals.

The previous kinetic model was simplified by considering only direct ozonation of adsorbed PA and its adsorbed intermediates formed during the reaction. A scenario following an Eley-Rideal mechanism has been chosen to describe the O$_3$/CO$_3$O$_4$/PA interaction.

In this scenario, the various pollutants (noted hereafter $X_i$) are adsorbed on the catalyst and react with the dissolved ozone. This can be described by the following equations:
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**Table n°18:** Kinetic model of catalytic ozonation chosen as an Eley-Rideal scenario.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Adjustable parameters</th>
<th>N°</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PA) + (<em>) (\xrightarrow{k_{ads}PA} (PA)^</em>) (\xleftarrow{k_{des}PA})</td>
<td>(K_A = \frac{k_{ads}PA}{k_{des}PA})</td>
<td>1</td>
</tr>
<tr>
<td>(PA)^* + O_3 (\xrightarrow{k_{q1}} (AOX)^*)</td>
<td>(k_{q1})</td>
<td>2</td>
</tr>
<tr>
<td>(AOX)^* + O_3 (\xrightarrow{k_{raox}} (Product)^*)</td>
<td>(k_{raox})</td>
<td>3</td>
</tr>
<tr>
<td>(AOX)^* (\xrightarrow{k_{ads}AOX} (AOX) + (*)) (\xleftarrow{k_{des}AOX})</td>
<td>(k_{ads}AOX) and (k_{des}AOX)</td>
<td>4</td>
</tr>
<tr>
<td>(PA)^* + O_3 (\xrightarrow{k_{q1}} (AC)^*)</td>
<td>(k_{q1})</td>
<td>5</td>
</tr>
<tr>
<td>(AC)^* (\xrightarrow{k_{ads}AC} (AC) + (*)) (\xleftarrow{k_{des}AC})</td>
<td>(k_{ads}AC) and (k_{des}AC)</td>
<td>6</td>
</tr>
</tbody>
</table>

In the present model, the adsorption and desorption rate constants of oxalic acid are adjustable parameters as well as the reaction rate constant between the adsorbed pyruvic acid (kq1), adsorbed oxalic acid (k_{raox}) and ozone. Acetic acid was supposed to be a stable specie which is not further degraded by ozone as shown in Gumuchian’s thesis [317].

In addition, Gumuchian also demonstrated the low adsorption of acetic acid (less than 1 %) on the surface of cobalt oxide powders (500 nm of diameter). Therefore, acetic acid will be assumed to be completely desorbed from the surface of the catalyst by fixing the adsorption rate constant of pyruvic acid, \(k_{ads}AC\), at 1 mol•m^2•s^{-1} and consequently, the desorption rate constant, \(k_{des}AC\) at 10 mol•m^2•s^{-1}.
As demonstrated in the previous chapter, the adsorption/desorption equilibrium constant of PA ($K_a$) and the concentration of active sites ($C_s$) are known and are respectively equal to 2 mg/g and $2 \times 10^{-6}$ mol•m$^{-2}$. However, simulations in Comsol being performed according to a flat geometry, the value for the concentration of active sites was fixed at $2 \times 10^{-3}$ mol•m$^{-2}$ as the geometric surface/developed surface ratio is decreased by a $10^3$ factor as stated by the previous BET measurements (Chapter 4).

As shown in Table n°18, a number of adjustable parameters are left to be determined or varied in the present numerical model in an attempt to follow the deactivation mechanism of the post-treated cobalt oxide layer obtained experimentally.

The adjustable parameters are summarized in Table 19.

### Table n°19: Set of adjustable parameters used for the simulations.

<table>
<thead>
<tr>
<th>Adjustable Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{q1}$</td>
<td>Reaction rate constant of ozone on adsorbed pyruvic acid</td>
</tr>
<tr>
<td>$k_{raox}$</td>
<td>Reaction rate constant of ozone on adsorbed oxalic acid</td>
</tr>
<tr>
<td>$k_{ads;AOX}$</td>
<td>Adsorption rate constant of oxalic acid on the surface of the catalyst</td>
</tr>
<tr>
<td>$k_{des;AOX}$</td>
<td>Desorption rate constant of oxalic acid on the surface of the catalyst</td>
</tr>
</tbody>
</table>

#### 3.2.1 Steady-state model without competition of adsorbed by-products

A first simulation using the stationary mode was carried out by considering the direct ozonation on pyruvic acid with equations 1-2 of Table 18 and by applying the following reaction rate at the surface of the catalyst:

$$ v = \frac{k_{q1}K_{A\;O_3}C_s\;C_{PA}}{1 + K_A C_{PA}} $$

The present model relies on the assumption that ozone reacts very rapidly with the molecules of PA which are adsorbed on the surface of the catalyst and that
there is no competition between adsorbed intermediate species and PA; adsorption of the latter PA being rapid.

Based on the previous assumptions, this first model allows to determine the value of the reaction rate constant \( k_{q1} \), which is the reaction rate constant of the direct ozonation on adsorbed pyruvic acid in a stationary mode.

\[ \text{Figure n°61: Degradation of pyruvic acid versus reaction rate constant of direct ozonation on adsorbed pyruvic acid.} \]

As shown in Figure 61, the degradation of pyruvic acid reaches a plateau at a value of 53%; plateau that reflects the diffusion regime. However, as mentioned in the previous chapter, it was found that the decomposition of pyruvic acid in the presence of the \( \text{Co}_3\text{O}_4 \) catalyst reached a value of 71% ± 3% after one hour of reaction, whereas for the blank microreactor (e.g. without catalyst), a degradation of 31% ± 5% was found.

The degradation due to catalysis reaches a value of 40% ± 8% and it can be concluded that the catalytic ozonation reaction studied in the microreactor is not limited by diffusion with the previous assumptions, (i.e. no competition between adsorbed intermediate species and PA during the first run).

Therefore, a value of 0.3 mol\(^{-1}\)L\(\cdot\)s\(^{-1}\) was found for \( k_{q1} \) corresponding to a degradation of 40% of the initial pyruvic acid concentration.
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3.2.2 Steady-state model with competition of adsorbed by-products

Once the reaction rate constant of ozone on adsorbed pyruvic acid determined, a second model was elaborated by including adsorbed by-products resulting from the oxidation of PA.

Knowing the values of $K_A$, the concentration of active sites and $K_{q1}$, the reaction rate constant between adsorbed pyruvic acid and ozone, the other adjustable parameters were varied in order to retrieve the deactivation kinetic of the cobalt oxide catalyst found experimentally.

As a first assumption, the value for the equilibrium constant of AOX was fixed as equal to the PA one, i.e. $K_A = 2$, leaving $k_{raox}$ as the only adjustable parameter as indicated in Table 19.

**Table n°19:** Parameters used for the catalytic ozonation simulation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value 1</th>
<th>Parameter</th>
<th>Value 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{ads , PA}$</td>
<td>1</td>
<td>$k_{ads , AOX}$</td>
<td>1</td>
</tr>
<tr>
<td>$k_{des , PA}$</td>
<td>$k_{ads , PA} / K_a$</td>
<td>$k_{des , AOX}$</td>
<td>$k_{ads , AOX} / K_a$</td>
</tr>
<tr>
<td>$K_a$</td>
<td>2</td>
<td>$k_{ads , AC}$</td>
<td>0.1</td>
</tr>
<tr>
<td>$k_{q1}$</td>
<td>0.3</td>
<td>$k_{des , AC}$</td>
<td>10</td>
</tr>
<tr>
<td>$k_{raox}$</td>
<td>Adjustable parameter</td>
<td>$C_s$</td>
<td>0.002</td>
</tr>
</tbody>
</table>

**Figure n°62:** Evolution of the degradation of pyruvic acid as a function of the reaction rate constant between ozone and adsorbed oxalic acid.
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As shown in Figure 62, initially, when there is no reaction between ozone and adsorbed oxalic acid, a value of 31.5% of degradation is reached. The steady-state model reflecting long reaction times, the latter value indicates the non-deactivation of the catalyst. However, a value of 14% of degradation was found experimentally after three hours of catalytic ozonation with the plasma post-treated cobalt oxide catalyst. Here, it can be seen that an increase of the reaction rate constant do not lead to a significant change in the degradation of pyruvic acid (4.4% of variation).

Therefore, the equilibrium constant chosen previously for AOX is not accurate, meaning that this chemical specie does not adsorb with the same rate as AP on the surface of the catalyst, thus, in opposition with the initial assumption. Consequently, a simulation with the assumption that AOX is irreversibly adsorbed on the catalyst surface (kdes AOX = 0) was performed.

The values of the different kinetic rate constants taken in this new simulation are summarized in Table 20 hereafter:

Table n°20: Parameters used for the numerical simulation of the degradation of PA in the catalytic microreactor.

<table>
<thead>
<tr>
<th>kads PA</th>
<th>1</th>
<th>kads AOX</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>kdes PA</td>
<td>0.5</td>
<td>kdes AOX</td>
<td>0</td>
</tr>
<tr>
<td>Ka</td>
<td>2</td>
<td>kads AC</td>
<td>0.1</td>
</tr>
<tr>
<td>kq1</td>
<td>0.3</td>
<td>kdes AC</td>
<td>10</td>
</tr>
<tr>
<td>kraox</td>
<td>Adjustable parameter</td>
<td>Cs</td>
<td>0.002</td>
</tr>
</tbody>
</table>
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![Graph showing the evolution of degradation as a function of the reaction rate constant between ozone and adsorbed oxalic acid.](image)

**Figure n°63:** Evolution of the degradation of pyruvic acid as a function of the reaction rate constant between ozone and adsorbed oxalic acid.

![Graph showing a magnification of the evolution of degradation as a function of the reaction rate constant between ozone and adsorbed oxalic acid.](image)

**Figure n°64:** Magnification of the evolution of the degradation of pyruvic acid as a function of the reaction rate constant between ozone and adsorbed oxalic acid.

According to Figure 63, when the rate constant of direct ozonation between pyruvic acid and ozone is rapid, a maximum steady state value of 26 % is reached. The aim of this simulation being the determination of the minimum value of $k_{raox}$, it can be seen in Figure 64, that for a value of $k_{raox}$ equal to $1 \cdot 10^{-2}$ mol$^{-1} \cdot$L$\cdot$s$^{-1}$, the steady-state degradation reaches a value of 15 %. Therefore, the value
Chapter 5: Numerical simulation of the pyruvic acid degradation by catalytic ozonation in a catalytic microreactor of the reaction rate constant between oxalic acid and ozone was fixed equal to $1 \times 10^{-2}$ mol$^{-1}$·L$^{-1}$·s$^{-1}$, the final percentage of degradation obtained experimentally after 3 runs being 14 %.

3.2.3 Simulation in the time-dependent model

After determining the previous adjustable parameters, a numerical simulation was performed in a time-dependent model and compared to the experimental results. The parameters chosen for the different constants are summarized in Table 21.

Table n°21: Parameters used for the numerical simulation of the degradation of PA in the catalytic microreactor.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{ads \text{ PA}}$</td>
<td>1</td>
</tr>
<tr>
<td>$k_{ads \text{ AOX}}$</td>
<td>1</td>
</tr>
<tr>
<td>$k_{des \text{ PA}}$</td>
<td>0.5</td>
</tr>
<tr>
<td>$k_{des \text{ AOX}}$</td>
<td>0</td>
</tr>
<tr>
<td>$K_a$</td>
<td>2</td>
</tr>
<tr>
<td>$k_{q1}$</td>
<td>0.3</td>
</tr>
<tr>
<td>$k_{des \text{ AC}}$</td>
<td>10</td>
</tr>
<tr>
<td>$k_{raox}$</td>
<td>0.01</td>
</tr>
<tr>
<td>$C_s$</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Figure n°65: Evolution of the average degradation of pyruvic acid as a function of time at the outlet of the catalytic microreactor.
Chapter 5: Numerical simulation of the pyruvic acid degradation by catalytic ozonation in a catalytic microreactor

The simulation result of the PA decay displayed in Figure 65 show that a degradation of 25 % is reached after a few seconds whereas the deactivation of the catalyst occurs rapidly reaching a plateau at a value of 11.9 % of degradation after 800 seconds.

In the first steady-state model (shown in section 3.2.1), a value of 0.3 mol\(^{-1}\)L\(\cdot\)s\(^{-1}\) was fixed for \(k_{q1}\) in order to obtain a degradation value of 40 % of the initial PA concentration. The latter value should be reached as no competition of the adsorbed by-products occurs at the beginning of the catalytic ozonation. However, only a value of 25 % of degradation is reached in the time-dependent model.

The values of the degradation of pyruvic acid should be 40, 30 and 14 % respectively after 1, 2 and 3 hours of reaction corresponding to the runs performed in the microreactor. The simulation results show that to the expected steady-state value of 15 % is reached after only 400 seconds of reaction. Normally, the PA degradation should tend to a value of 15 % after 3 hours of reaction.

Furthermore, results from the numerical simulation indicate that a stationary state is reached rapidly which is not the case experimentally.

These differences may probably be explained by convergence issues between the stationary models and the time-dependent one. Another explanation may reside in the fact that the deactivation occurs so rapidly that the value of 40 % of degradation of the initial PA expected in the absence of deactivation of the catalyst will probably never be observed in the time-dependent model.

Nevertheless, the desorption rate constant for oxalic acid onto the surface of the catalyst was varied in a new simulation in order to assess the initial assumption based on the irreversible bonding of oxalic acid on the surface of the catalyst.
Figure n°66: Evolution of the average degradation of pyruvic acid at the outlet of the catalytic microreactor as a function of time and desorption rate constant of oxalic acid on the catalyst.

From Figure 66, it can be seen that when the desorption rate constant of oxalic acid onto the surface of the catalyst increases with a value ranging from 0 to $1 \times 10^{-1}$ m$^2\cdot$s$^{-1}$, the steady-state value of PA degradation percentage increases from 11.9 to 18.2% and this steady-state value is reached more rapidly. In other words, this indicates that when the desorption rate constant increases, oxalic acid is less retained on the surface of the catalyst; thus leading to more available active sites. Therefore, the variation of the desorption rate constant do not enable to get closer to the experimental results.

4. Conclusion

A numerical simulation of the catalytic ozonation of pyruvic acid was performed in a microreactor using the Comsol Multiphysics software. A first stationary model was used to evaluate the role of direct or indirect ozonation of pyruvic acid in the batch reactor. Results showed that direct ozonation mainly contributes to
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the degradation of pyruvic acid. The set of equations was reduced to direct ozonation in second stationary model assuming an Eley-Rideal scenario.

With this second model, the reaction rate of the adsorbed pyruvic acid and ozone was determined and implemented in a time dependent model. The time-dependent model was developed to retrieve the experimental results showing the deactivation of the plasma post-treated cobalt oxide layer in catalytic ozonation of pyruvic acid.

Results showed that the model partially fitted the results obtained in the catalytic microreactor as the value of 15% of degradation was found after 800 seconds instead of the 3 hours expected from the experimental results.

A first explanation would consist in reviewing the initial assumption that catalytic ozonation undergoes an Eley-Rideal mechanism. Recently, De Souza et al [343] proposed an interesting numerical model in order to estimate the key parameters of chemical reactions independently of the catalytic mechanism used. By lack of time, de Souza’s numerical model was not used in our system but seems to be quite promising to investigate for future works.

Moreover, the difference between the simulation results and the experimental ones could be due to the lack of information concerning the different adsorption and desorption reactions rate constants. In order to perform a deeper study, additional information on these reaction rate constants should be obtained, for example, by the use of the temperature jump method [344].

Furthermore, the approach proposed in this study demonstrates that kinetics of catalyzed reactions can be determined in microreactors instead of using conventional batch reactors. For instance, microreactors allow to control of the flow of the reactants which is not the case in conventional batch reactors. Although the use of microreactors strongly limits the diffusion phenomenon as shown in the present chapter, diffusion can still occur for a catalyzed reaction in a given microreactor geometry.

This can be overcome by achieving a downscaling of the microreactor. Nevertheless, the downscaling of a microreactor is limited due to the
technological implementation of such devices. Actually, as an example, a minimal value of 50 µm for the height of a Cyclic Olefin Copolymer based microreactor can be reached.

Finally, it would be interesting to confront the numerical method proposed in this study with an online analytical technique that could allow the monitoring of the chemical reactions occurring in the microreactor. Coherent Anti-Stokes Raman Scattering (CARS) spectroscopy appears to be one of the most promising techniques that could describe the different reaction pathways occurring at the surface of the catalyst, by direct observation of the time dependent evolution of the spatial concentration profiles of both reactants and products in a microreactor. Relying on their inherent vibrational signature using Raman-based microscopy, former studies have demonstrated that this technique could lead to label-free, chemically specific, quantitative determination of local concentrations of reactants and products, with 3D submicron spatial resolution (400 nm in x and y directions, 1.5 µm in z direction) [259,345-347]. Therefore, this quantitative in-situ method opens new avenues for monitoring reactions in microfluidic environments in order to develop a numerical predictive tool. This predictive tool would allow determining the synergistic effect between a given catalyst and the pollutant in catalytic ozonation and more generally, the reactants in catalyzed reactions.