MODELING OF A SOLAR REACTOR FOR WATER PURIFICATION, EMPLOYING THE PHOTO-FENTON REACTION

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OUTLINE

- Introduction
- Mass Balances
- Kinetic Model
- Radiation Field
- Model Parameters and Numerical Solution
- Predicted and Experimental Results
- Effects of the Reaction Temperature
- Final Remarks
INTRODUCTION

- The Fenton reaction is a chemical system involving hydrogen peroxide and ferrous salts that generates highly reactive hydroxyl radicals.
- The oxidation ability of the Fenton mixture can be greatly enhanced using UV (or UV/Vis) radiation: the photo-Fenton Reaction.

- In this work, the degradation of formic acid (a model pollutant) in aqueous solution using the Fenton and photo-Fenton systems is presented.
- The reaction was conducted in a flat-plate solar reactor placed inside the loop of a batch recycling system.
INTRODUCTION: PREVIOUS WORK


Temperature Effects on the Photo-Fenton Degradation of Formic Acid, ENPROMER 2005, Río de Janeiro, Brasil; III EPOA, Campinas, Brasil.
Keys: (1) storage tank, (2) stirrer, (3) thermometer, (4) liquid sampling, (5) pump, (6) valve, (7) solar radiation, (8) flat-plate reactor, (9) heat exchanger, and (10) thermostatic bath.
PICTURE OF THE EXPERIMENTAL DEVICE

- Flat-plate solar reactor
- Broadband UV Radiometer CUV3 of Kipp & Zonen

- Well-stirred batch recycling photoreactor
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MASS BALANCES

(F: formic acid; P: Hydrogen Peroxide)

\[
\frac{dC_F}{dt} = \frac{V_R}{V_T} \langle R_F(x, t) \rangle_{V_R} + \left( \frac{V_{Tk}}{V_T} \right) R_F^t(t)
\]

\[
\frac{dC_P}{dt} = \frac{V_R}{V_T} \langle R_P(x, t) \rangle_{V_R} + \left( \frac{V_{Tk}}{V_T} \right) R_P^t(t)
\]

- Photo-Fenton
- Fenton

Initial conditions:
\[
\begin{align*}
t &= 0 & C_F &= C_F^0 \\
t &= 0 & C_P &= C_P^0
\end{align*}
\]

- $V_R/V_T$ for photo-Fenton
- $V_{Tk}/V_T$ for Fenton
- The average value must be retained in order to account for spatial variations of the photo-Fenton reaction rate
- Spatial variations of the Local Volumetric Rate of Photon Absorption (LVRPA)

N $VR/VT$ for photo-Fenton
N $VTk/VT$ for Fenton
N The average value must be retained in order to account for spatial variations of the photo-Fenton reaction rate
N Spatial variations of the Local Volumetric Rate of Photon Absorption (LVRPA)
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# Reaction Scheme (*)

<table>
<thead>
<tr>
<th>Stage</th>
<th>Reaction</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initiation</strong></td>
<td>Fe$^{3+}$ + H$_2$O $\xrightarrow{h\nu}$ Fe$^{2+}$ + HO.$\cdot$ + H$^+$</td>
<td>$\phi$</td>
</tr>
<tr>
<td></td>
<td>Fe$^{3+}$ + H$_2$O$_2$ $\rightarrow$ Fe$^{2+}$ + HO$_2$.• + H$^+$</td>
<td>$k_1$</td>
</tr>
<tr>
<td></td>
<td>Fe$^{2+}$ + H$_2$O$_2$ $\rightarrow$ Fe$^{3+}$ + HO.$\cdot$ + HO$^-$</td>
<td>$k_2$</td>
</tr>
<tr>
<td><strong>Propagation</strong></td>
<td>H$_2$O$_2$ + HO.$\cdot$ $\rightarrow$ HO$_2$.• + H$_2$O</td>
<td>$k_3$</td>
</tr>
<tr>
<td></td>
<td>H$_2$O$_2$ + HO$_2$.• $\rightarrow$ HO.$\cdot$ + H$_2$O + O$_2$</td>
<td>$k_4$</td>
</tr>
<tr>
<td><strong>Termination</strong></td>
<td>2 HO.$\cdot$ $\rightarrow$ H$_2$O$_2$</td>
<td>$k_5$</td>
</tr>
<tr>
<td></td>
<td>2 HO$_2$.• $\rightarrow$ H$_2$O$_2$ + O$_2$</td>
<td>$k_6$</td>
</tr>
<tr>
<td></td>
<td>HO$_2$.• + HO.$\cdot$ $\rightarrow$ H$_2$O + O$_2$</td>
<td>$k_7$</td>
</tr>
<tr>
<td></td>
<td>Fe$^{3+}$ + HO$_2$.• $\rightarrow$ Fe$^{2+}$ + H$^+$ + O$_2$</td>
<td>$k_8$</td>
</tr>
<tr>
<td></td>
<td>Fe$^{2+}$ + HO$_2$.• + H$^+$ $\rightarrow$ Fe$^{3+}$ + H$_2$O$_2$</td>
<td>$k_9$</td>
</tr>
<tr>
<td><strong>Decomposition</strong></td>
<td>HCOOH + HO.$\cdot$ $\rightarrow$ CO$_2$.• + H$_2$O + H$^+$</td>
<td>$k_{10}$</td>
</tr>
<tr>
<td></td>
<td>CO$_2$.• + O$_2$ + H$^+$ $\rightarrow$ CO$_2$ + HO$_2$.•</td>
<td>$k_{11}$</td>
</tr>
</tbody>
</table>

ASSUMPTIONS FOR THE KINETIC MODEL

The following assumptions have been considered:

- the steady state approximation (SSA) may be applied for highly reactive radicals, such as OH\(\cdot\) and HO\(_2\)\(\cdot\),
- radical-radical termination reactions are neglected as compared with the propagation reactions,
- the ferrous ion concentration remains constant during the reaction time,
- the oxygen concentration is always in excess.
When $\sum_{\lambda} e^a(x,t) = 0$, the pollutant reaction rate is not null. A thermal reaction rate can be identified (Fenton reaction). This term may be represented by the expression:

$$R^t_F(t) = -K_1 \frac{1 + K_2 \left( C_P / C_{Fe^{3+}} \right)}{1 + K_3 \left( C_P / C_F \right)} C_{Fe^{3+}} C_P$$
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Schematic representation of the flat-plate solar reactor

At the top, a window made of glass was located

The surface of radiation entrance receives direct solar radiation \((q_D)\) and diffuse solar radiation \((q_S)\)
RADIATION FIELD MODELING

Radiative Transfer Equation:

\[ \mu \frac{\partial I_\lambda (x, \mu, \phi)}{\partial x} + \kappa_\lambda I_\lambda (x, \mu, \phi) = 0 \]

\[ \mu = \cos \theta \]

\[ \mu = \cos \theta \]

- B.C. at \( x = 0 \): (i) reflection and refraction at the interfaces and (ii) radiation absorption inside the glass window
- B.C. at \( x = L \): radiation intensity reaching the reactor bottom is reflected back to the solution in a diffuse manner

Variation of the Radiation Intensity along the ray path

Radiation absorption
Once the radiation intensity $I_\lambda(x,\mu,\phi)$ is obtained, one can compute the LVRPA:

- Radiation may be arriving at one point (P) inside the reaction space from all directions in space.
- An integration over all the arriving rays ($\theta,\phi$) is required:

$$e_\lambda^a(x) = \kappa_\lambda \int_0^{2\pi} d\phi \int_{-1}^{1} I_\lambda(x,\mu,\phi) d\mu$$

Integrating the previous equation, LVRPA is obtained:
FINAL EXPRESSION OF THE LVRPA

\[ e_{\lambda}^{a}(x) = \kappa_{\lambda} \left\{ q_{D,\lambda} \frac{1 - \rho_{a\cdot p}(\mu^*)}{1 - \tau^2_{\lambda}(\mu')} \rho_{p\cdot w}(\mu') \right\} \exp(-\kappa_{\lambda} x / \mu_{r}) + \]

**Direct solar radiation**

\[ 2q_{S,\lambda} n^2_{w} \int_{n^2_{a\cdot \mu_{er}}}^{1} \frac{1 - \rho_{a\cdot p}(\mu^*)}{1 - \tau^2_{\lambda}(\mu')} \rho_{a\cdot p}(\mu') \rho_{p\cdot w}(\mu') \right\} \exp(-\kappa_{\lambda} x / \mu) d\mu + \]

**Diffuse solar radiation**

\[ 2\rho_{B} q_{B,\lambda} \left\{ \int_{0}^{1} \rho_{w\cdot p}(\mu) \exp[-\kappa_{\lambda}(L + x)/\mu] d\mu + \int_{0}^{1} \exp[-\kappa_{\lambda}(L - x)/\mu] d\mu \right\} \]
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SOLAR RADIATION INCIDENT AT THE REACTOR WINDOW

- Sun
- Extraterrestrial Radiation
- Direct radiation
- Diffuse radiation
- Global radiation

θ

Atmosphere
- Ozone
- Oxygen
- Nitrogen
- Carbon Dioxide
- Water Vapor
- Aerosols

Absorption and Scattering
Global radiation on a horizontal surface at ground level for wavelength $\lambda$ (Bird and Riordan, 1986):

$$q_{G,\lambda} = q_{D,\lambda} \cos \theta_Z + q_{S,\lambda} \quad (\theta_Z = \text{zenith angle})$$

Direct radiation on a surface normal to the sun direction:

$$q_{D,\lambda} = H_{0,\lambda} D T_r,\lambda T_a,\lambda T_w,\lambda T_o,\lambda T_u,\lambda$$

Diffuse radiation on a horizontal surface at ground level:

$$q_{S,\lambda} = q_{r,\lambda} + q_{a,\lambda} + q_{g,\lambda}$$

where: Rayleigh scattering ($q_{r,\lambda}$), aerosol scattering ($q_{a,\lambda}$), multiple reflection of radiation between the ground and the air ($q_{g,\lambda}$)
GLOBAL AND DIFFUSE UV SOLAR RADIATION

- Maximum UV solar radiation: $q_{G,max} \approx 45 \text{ W/m}^2$
- At $\theta_Z > 45^\circ$ → Diffuse radiation > Direct radiation

- Measurements and model predictions:
  - horizontal surface
  - clear sky days

- Model predictions:
  - Global (—)
  - Diffuse (−−−)

- Measurements:
  - Global (◇)
  - Diffuse (□)
RATIO OF UV TO TOTAL SOLAR RADIATION (R)

- UV solar radiation: 4 to 5% of the total solar radiation
- R decreases when the zenith angle is increased

Measurements (◊) and predictions (—):
- horizontal surface
- clear sky days

<table>
<thead>
<tr>
<th>$\theta_z(°)$</th>
<th>R%</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>5.2</td>
</tr>
<tr>
<td>20</td>
<td>5.1</td>
</tr>
<tr>
<td>40</td>
<td>4.8</td>
</tr>
<tr>
<td>60</td>
<td>4.2</td>
</tr>
<tr>
<td>80</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Rosario, Argentina
SPECTRAL DATA

- Global ($q_G$), direct ($q_D$) and diffuse ($q_S$) solar radiation (Bird and Riordan, 1986) for:
  - cloudless sky conditions
  - solar zenith angle = 10°

- Molar absorptivity of the iron complex: $\alpha_{Fe(OH)^{2+}}$
- Absorption coefficient of the glass plate: $\kappa_P$
NUMERICAL SOLUTION: COMPUTATIONAL STEPS

Evaluation of the direct and diffuse solar radiation incident at the reactor glass window

Computation of the LVRPA as a function of position

Evaluation of the formic acid and hydrogen peroxide reaction rates

Calculation of the formic acid and hydrogen peroxide concentrations as a function of time

System of two nonlinear, first order, ordinary differential equations
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PREDICTIONS OF THE LVRPA

As expected, the radiation field along the x-coordinate is highly non-uniform: 
$e^a(x = 0.5 \text{ L}) \approx 0.2 \ e^a(x = 0)$

- Three different zenith angles: $10^\circ$, $30^\circ$, $60^\circ$
- Constant absorbing species concentration: $C_{Fe(OH)^{2+}} = 1 \text{ mM}$
PREDICTIONS OF THE LVRPA

\( e^a \) as a function of the x-coordinate for:

- three different ferric ion concentrations: \( C_{Fe(OH)^{2+}} = 0.5, 1, 2 \text{ mM} \)
- a constant solar zenith angle: \( \theta_z = 10^\circ \)

→ When the optical density is increased the shape of the LVRPA curve becomes steeper
PREDICTED AND EXPERIMENTAL RESULTS (T = 25 °C)

- Model predictions and experimental data as a function of time
- Formic acid relative concentration:
  - Fenton (---)
  - photo-Fenton (-----)
- H$_2$O$_2$ relative concentration:
  - Fenton (---)
  - photo-Fenton (-----)

$C_p/C_F = 3.3$
$	heta_z = 12.8°$
A similar representation is shown for a higher $C_p/C_F$.

Conversion for the photo-Fenton reaction is always higher than that obtained with the Fenton reaction.

Model and experimental results show good agreement.

The maximum error is 9%.
## COMPARISON BETWEEN FENTON AND PHOTO-FENTON CONVERSIONS (25 °C)

<table>
<thead>
<tr>
<th></th>
<th>Fenton $\varepsilon$(%)</th>
<th>Photo-Fenton $\varepsilon$(%)</th>
<th>Enhanc.(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pollutant conversion (%)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_p/C_F$</td>
<td>Exp. Data</td>
<td>Predictions</td>
<td>Exp. Data</td>
</tr>
<tr>
<td>3.3</td>
<td>29.3</td>
<td>31.1</td>
<td>80.7</td>
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<td></td>
<td></td>
<td>6.1</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>5.4</td>
<td>37.6</td>
<td>39.7</td>
<td>80.6</td>
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<tr>
<td></td>
<td></td>
<td>5.6</td>
<td></td>
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<td></td>
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<td></td>
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<tr>
<td>8.4</td>
<td>43.2</td>
<td>45.7</td>
<td>79.3</td>
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<td></td>
<td></td>
<td>5.8</td>
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</table>

- A conversion of 81% has been achieved for the lowest $C_p/C_F$
- The photo-Fenton system produces a conversion up to 175% greater than that obtained with the Fenton reaction ($C_p/C_F=3.3$)
<table>
<thead>
<tr>
<th>C&lt;sub&gt;p&lt;/sub&gt;/C&lt;sub&gt;F&lt;/sub&gt;</th>
<th>Pollutant conversion (%)</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fenton  ε(%)</td>
<td>photo-Fenton ε(%)</td>
</tr>
<tr>
<td>Exp. Data</td>
<td>3.3    29.3</td>
<td>-</td>
</tr>
<tr>
<td>Predictions</td>
<td>3.3    31.1</td>
<td>6.1</td>
</tr>
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<td>Exp. Data</td>
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</tr>
<tr>
<td>Predictions</td>
<td>8.4    45.7</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Notice that the photo-Fenton conversion decreases when the C<sub>p</sub>/C<sub>F</sub> initial molar ratio is increased.
EFFECTS OF THE H2O2 ON FORMIC ACID CONVERSION (T = 25 °C)

The change in the H2O2 concentration (Cp) may have two opposite effects:

- At low Cp, ferrous ion (Fe²⁺) generation may be too low and so will be the OH⁻ generation.
- At high Cp, H2O2 acts as a radical trapping agent, thus competing with the pollutant degradation path and rendering lower degradation rates:

  \[
  \text{H}_2\text{O}_2 + \text{HO}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O}
  \]

- Thus, an optimal molar ratio Cp/Cf should be expected.
PARAMETRIC STUDY: EFFECTS OF THE H₂O₂ ON FORMIC ACID CONVERSION

 XF (t = 1 h) vs. CP/CF:

- Fenton and ph-Fenton

- θZ = 10°, 40°, 70°

† At high values of θZ, increasing the CP/CF ratio increases the conversion

† At low values of θZ (high radiation), an optimal molar ratio CP/CF is observed
COMPARISON BETWEEN FENTON AND PHOTO-FENTON CONVERSIONS (t = 20 min)

- Model predictions of formic acid conversion:
  - Fenton (—)
  - photo-Fenton (—)

- Experimental data:
  - Fenton (▼)
  - photo-Fenton (■)

- Increasing the reaction temperature decreases the enhancement of the pollutant conversion.
UV solar radiation improves the effectiveness of the Fenton process.

For the lowest temperature 25°C, the pollutant conversion is significantly increased.

Intermediate behavior for 40°C.

For the highest temperature 55°C, this effect is less important.
FINAL REMARKS

- Increased reaction temperature can enhance the reaction rate of the Fenton and photo-Fenton processes.

- However, at higher temperatures: (i) this conversion enhancement is less important and (ii) the efficiency of hydrogen peroxide declines: decomposition of $\text{H}_2\text{O}_2$ into oxygen and water (Malik and Saha, 2003).

- It is possible to take advantage of the natural temperature of a wastewater at the end of the process (in the textile industry: Rodríguez et al., 2002).

- Possibility of a combined photochemically and thermally enhanced Fenton process, using solar energy (UV/Vis + IR photons: Sagawe et al., 2001).
THANKS

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