KINETIC MODEL DESCRIBING THE UV/H₂O₂ PHOTODEGRADATION OF PHENOL FROM WATER

Article Highlights
- A kinetic model for organic pollutant degradation through the UV/H₂O₂ system is developed.
- The model is validated using independent experimental data from literature for phenol abatement.
- A high extent of agreement was found between the calculated and the experimental data.
- The kinetic model allows determining the optimal conditions for an efficient pollutant removal.

Abstract
A kinetic model for phenol transformation through the UV/H₂O₂ system was developed and validated. The model includes the pollutant decomposition by direct photolysis and HO⁻, HO₂⁻ and O₂⁻ oxidation. HO⁻ scavenging effects of CO₃²⁻, HCO₃⁻, SO₄²⁻ and Cl⁻ were also considered, as well as the pH changes as the process proceeds. Additionally, the detrimental action of the organic matter and reaction intermediates in shielding UV and quenching HO⁻ was incorporated. It was observed that the model can accurately predict phenol abatement using different H₂O₂/phenol mass ratios (495, 228 and 125), obtaining an optimal H₂O₂/phenol ratio of 125, leading to a phenol removal higher than 95% after 40 min of treatment, where the main oxidation species was HO⁻. The developed model could be relevant for calculating the optimal level of H₂O₂ efficiently degrading the pollutant of interest, allowing saving in costs and time.

Keywords: H₂O₂ level, kinetic model, matrix background, phenol pollution, UV/H₂O₂.

The rapid economic growth of the last decade has led to an increase in the number of pollutants in the aquatic environment, positioning advanced oxidation processes (AOPs) as alternatives to the conventional techniques water treatment plants are operating with [1-6], which are unable to completely transform inhibitory organics such as phenol.

Phenol is a colorless to pink-colored solid or dense liquid substance with a particular sweet odor. It is highly soluble in water but also in organic solvents. It is a ubiquitous pollutant commonly found as a component of oil refinery wastes. It is also produced in pharmaceuticals and phenol manufacturing plants. Phenol can also be generated from the production of metallurgical coke from coal, and it is used in the manufacture of fertilizers, textiles and paints. Additionally, phenol can be formed from natural sources, such as the decomposition of organic matter [7]. Nevertheless, anthropogenic processes contribute in a larger extension in comparison with natural ones.

Once phenol is in the environment, it can enter aquatic environments due to its solubility in aqueous media, posing a risk for living beings. Furthermore, it can react with other components, such as chlorine,
increasing its hydrophobicity and, subsequently, its tendency to be bioaccumulated through the food chain.

Phenol is a toxic compound. The toxicity of phenol is related to the reactivity of the compound with biomolecules, being responsible for the death of organisms when exposed to high amounts of this substance. It is also involved in reproductive problems, reducing fertility and producing changes in appearance and behavior, since living being hormonal system function can be affected [7]. Furthermore, it exhibits mutagenic and carcinogenic potential [7,8]. As a matter of fact, researchers evidenced mutagenic activity of phenol from hamster fibroblasts [7]. In addition, it induces immunotoxic, hematological and physiological effects [8]. In fact, it is included by the US Environmental Protection Agency in the List of Priority Pollutants [7]. Therefore, it must be removed from water.

In recent decades, different AOPs have been used for destroying organic compounds. Among the AOPs applied for water decontamination, the UV/\(\text{H}_2\text{O}_2\) system implementation has risen drastically in recent years for water treatment purposes [6]. This process involves the photolysis of hydrogen peroxide (\(\text{H}_2\text{O}_2\)) using ultraviolet radiation (UV), resulting in the production of hydroxyl radicals (HO\(^\cdot\)) [9-11]. The HO\(^\cdot\) is very reactive and attack non-selectively a variety of organic and inorganic substances because their oxidation potential (\(E = 2.8 \text{ V}\)) [12] is higher than other oxidizing agents such as ozone (\(E = 2.07 \text{ V}\)) and chlorine (\(E = 1.36 \text{ V}\)), transforming those substances into CO\(_2\), H\(_2\text{O}\) and inorganic salts [10,13].

The efficiency of the UV/\(\text{H}_2\text{O}_2\) system depends on various parameters, such as the oxidant dosage, pollutant concentration and structure, UV-light intensity and predominant wavelength, irradiation time, solution initial pH, temperature and matrix constituents (including natural organic matter and inorganic ions, which may quench HO\(^\cdot\) and/or shield UV radiation penetration into the bulk), among other parameters [3,10].

This homogeneous chemical oxidation process has several advantages in comparison to other water treatment methods, such as no mass transfer limitations occur and no sludge requiring a subsequent treatment and disposal is produced. Additionally, it can be produced at room temperature and pressure [6,10]. Nevertheless, this process has associated high electrical and oxidizing agent costs [10,14,15], and kinetic models seem to be a good option to optimize operating conditions without incurring in high operating costs.

This work is aimed at proposing a kinetic model for the prediction of phenol decontamination by the UV/\(\text{H}_2\text{O}_2\) system including the action of HO\(^\cdot\), O\(_2^\cdot\) and HO\(_2^\cdot\). The HO\(^\cdot\) scavenging effects of carbonate (\(\text{CO}_3^{2-}\)), bicarbonate (\(\text{HCO}_3^-\)), sulfate (\(\text{SO}_4^{2-}\)) and chloride (\(\text{Cl}^-\)) ions were considered on the performance of the system as well as the pH changes in the bulk as the oxidation process proceeds. Additionally, the detrimental action of the organic matter and reaction intermediates in shielding UV and quenching HO\(^\cdot\) was incorporated. The model is based on the extensively accepted chemical and photochemical reactions, and the rate constants involved in the studied AOP. On the other hand, MATLAB software was used to find the numerical solution to the set of ordinary differential equations (ODE) characterizing the current model. In addition, the proposed kinetic model was validated by comparing the experimental data from Alnaizy and Akgerman study [16] and the model predictions obtained at different operating conditions in terms of phenol abatement.

**EXPERIMENTAL**

A kinetic model describing the UV/\(\text{H}_2\text{O}_2\) process was developed taking into account the impact of radical species such as HO\(^\cdot\), HO\(_2^\cdot\), O\(_2^\cdot\), CO\(_3^{2-}\), SO\(_4^{2-}\), H\(_2\text{ClO}_4^-\), Cl\(^-\) and Cl\(_2^\cdot\) on the pollutant conversion. In addition, the role of the dissolved organic matter (DOM), in terms of dissolved organic carbon (DOC), and the degradation by-products in absorbing UV radiation and scavenging radicals were included. In the development of the proposed kinetic model, the contribution of UV radiation in phenol transformation was also taken into account. Furthermore, the model incorporates the change of pH in the solution as the advanced oxidation process proceeds due to the formation of short chain organic acids.

**Mechanistic kinetic model**

The chemical and photochemical reaction scheme, reaction rate constants and values of the parameters involved in the UV/\(\text{H}_2\text{O}_2\) system are compiled in Tables 1 and 2.

As it can be observed from the tables, 22 different chemical species (including radicals, radical ions, inorganic ions and molecules) and 51 reactions (differentiated in photolysis reactions - first-order reactions, equilibrium reactions - acid-base reactions, and second-order reactions, corresponding to the elementary reactions and those ones related to the matrix background) were considered.

In addition, correlation factors (\(\delta_{\text{B}}\)) were included in order to study the generation and consumption of some chemical species as the pH in the bulk is increased or reduced. In this sense, when \(\delta_{\text{B}} = 1\), the
Table 1. Elementary reactions and kinetic equations for species disappearance and formation in the UV/H$_2$O$_2$ system

<table>
<thead>
<tr>
<th>No.</th>
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</tr>
</thead>
</table>
| $R_1$ | H$_2$O$_2$ $\rightarrow$ HO$_2$ + H$^+$ | $k_1 = 3.7 \times 10^{-2}$ s$^{-1}$  
$\Delta H = -4.8 \text{K}$  
$\Delta G = -25.3 \text{K}$  
$\mu = 1.5 \times 10^{-6}$ M$^{-1}$ s$^{-1}$  
$pK_a = 11.6$  
$[17]$ | | $\frac{d[\text{H}_2\text{O}_2]}{dt} = -k_1[\text{H}_2\text{O}_2]$  
$\frac{d[\text{HO}_2]}{dt} = k_1[\text{H}_2\text{O}_2]$  
$\frac{d[H^+]}{dt} = k_1[\text{H}_2\text{O}_2]$ |
| $R_2$ | HO$_2$ + H$^+$ $\rightarrow$ H$_2$O$_2$ | $k_2 = 2.6 \times 10^6$ M$^{-1}$ s$^{-1}$  
$\Delta H = -11.6 \text{K}$  
$\Delta G = -31.2 \text{K}$  
$\mu = 1 \times 10^{-10}$ M$^{-1}$ s$^{-1}$  
$pK_a = 21.2$  
$[21]$ | | $\frac{d[\text{HO}_2]}{dt} = -k_2[\text{HO}_2][\text{H}^+]$  
$\frac{d[H^+]}{dt} = -k_2[\text{HO}_2][\text{H}^+]$  
$\frac{d[H_2O_2]}{dt} = k_2[\text{HO}_2][\text{H}^+]$ |
| $R_3$ | H$_2$O$_2$ $\rightarrow$ 2HO* | $\epsilon_{\text{H}_2\text{O}_2}$(254 nm) = 1800 M$^{-1}$ s$^{-1}$  
$\epsilon_{\text{HO}_2}$(254 nm) = 22800 M$^{-1}$ s$^{-1}$  
$\phi_{\text{H}_2\text{O}_2}$(254 nm) = 0.5 mol Ein$^{-1}$  
$\phi_{\text{HO}_2}$(254 nm) = 0.5 mol Ein$^{-1}$  
pH > 11.6 $\Rightarrow$ $\delta_{R_3} = 0$, $\delta_{R_4} = 1$  
pH < 11.6 $\Rightarrow$ $\delta_{R_3} = 1$, $\delta_{R_4} = 0$  
$[9]$ | | $\frac{d[\text{H}_2\text{O}_2]}{dt} = -\epsilon_{\text{H}_2\text{O}_2}[\epsilon_{\text{H}_2\text{O}_2}][\text{H}_2\text{O}_2]^{\delta_{R_3}} + \epsilon_{\text{HO}_2}[\text{H}_2\text{O}_2]^{\delta_{R_4}}$  
$\frac{d[\text{HO}^*]}{dt} = 2\epsilon_{\text{H}_2\text{O}_2}^{\delta_{R_3}}[\text{H}_2\text{O}_2]^{\delta_{R_4}}$  
$\frac{d[\text{OH}^-]}{dt} = -\epsilon_{\text{H}_2\text{O}_2}^{\delta_{R_3}}[\text{H}_2\text{O}_2]^{\delta_{R_4}}$ |
| $R_4$ | HO$_2$ + H$_2$O $\rightarrow$ 2HO* + OH$^-$ | | | $\frac{d[\text{HO}_2]}{dt} = -\epsilon_{\text{HO}_2}^{\delta_{R_4}}[\epsilon_{\text{HO}_2}][\text{H}_2\text{O}]^{\delta_{R_4}} + \epsilon_{\text{C}}[\text{C}] + \epsilon_{\text{DOC}}[\text{DOC}]$  
$\frac{d[\text{HO}^*]}{dt} = 2\epsilon_{\text{HO}_2}^{\delta_{R_4}}[\text{H}_2\text{O}]^{\delta_{R_4}}$  
$\frac{d[\text{OH}^-]}{dt} = -\epsilon_{\text{HO}_2}^{\delta_{R_4}}[\text{H}_2\text{O}]^{\delta_{R_4}}$ |
| $R_5$ | HO$_2$ $\rightarrow$ O$_2$ + H$^+$ | $k_3 = 1.58 \times 10^5$ s$^{-1}$  
$k_4 = 1.0 \times 10^{10}$ M$^{-1}$ s$^{-1}$  
$pK_a = 4.8$  
$[18]$ | | $\frac{d[\text{HO}_2]}{dt} = -k_3[\text{HO}_2]$  
$\frac{d[\text{O}_2^*]}{dt} = k_3[\text{HO}_2]$  
$\frac{d[H^+]}{dt} = k_3[\text{HO}_2]$ |
| $R_6$ | O$_2^*$ + H$^+$ $\rightarrow$ HO$_2$ | | | $\frac{d[\text{O}_2^*]}{dt} = -k_4[\text{O}_2^*][\text{H}^+]$  
$\frac{d[H^+]}{dt} = -k_4[\text{O}_2^*][\text{H}^+]$  
$\frac{d[\text{HO}_2]}{dt} = k_4[\text{O}_2^*][\text{H}^+]$ |
Table 1. Continued

<table>
<thead>
<tr>
<th>No.</th>
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<th>Kinetic equations</th>
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<tbody>
<tr>
<td>$R_7$</td>
<td>$\text{H}_2\text{O}_2 + \text{HO}^- \rightarrow \text{O}_2^- + \text{H}^+ + \text{H}_2\text{O}$</td>
<td>$k_5 = 2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td>19</td>
<td>$\frac{d[\text{H}_2\text{O}_2]}{dt} = -k_5[\text{H}_2\text{O}<em>2][\text{HO}^-]\delta</em>{b5}$</td>
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<td>$\frac{d[\text{HO}^-]}{dt} = -k_5[\text{H}_2\text{O}<em>2][\text{HO}^-]\delta</em>{b5}$</td>
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<td>$\frac{d[\text{O}_2^-]}{dt} = k_5[\text{H}_2\text{O}<em>2][\text{HO}^-]\delta</em>{b5}$</td>
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<td>$\frac{d[\text{H}^+]}{dt} = k_5[\text{H}_2\text{O}<em>2][\text{HO}^-]\delta</em>{b5}$</td>
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<tr>
<td>$R_8$</td>
<td>$\text{H}_2\text{O}_2 + \text{HO}^- \rightarrow \text{HO}_2^+ + \text{H}_2\text{O}$</td>
<td>$k_6 = 7.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td>20</td>
<td>$\frac{d[\text{H}_2\text{O}_2]}{dt} = -k_6[\text{H}_2\text{O}<em>2][\text{HO}^-]\delta</em>{b6}$</td>
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<td>$\frac{d[\text{HO}^-]}{dt} = -k_6[\text{H}_2\text{O}<em>2][\text{HO}^-]\delta</em>{b6}$</td>
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<td>$\frac{d[\text{HO}_2^+]}{dt} = k_6[\text{H}_2\text{O}<em>2][\text{HO}^-]\delta</em>{b6}$</td>
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<tr>
<td>$R_9$</td>
<td>$\text{HO}^+ + \text{HO}_2^- \rightarrow \text{H}_2\text{O}_2$</td>
<td>$k_7 = 5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td>19</td>
<td>$\frac{d[\text{HO}^+]}{dt} = -k_7[\text{HO}^+][\text{HO}_2^-]$</td>
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<td>$\frac{d[\text{H}_2\text{O}_2]}{dt} = k_7[\text{HO}^+][\text{HO}_2^-]$</td>
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<td>$R_{10}$</td>
<td>$\text{HO}^+ + \text{HO}_2^- \rightarrow \text{H}_2\text{O}_2$</td>
<td>$k_8 = 6.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td>21</td>
<td>$\frac{d[\text{HO}^+]}{dt} = -k_8[\text{HO}^+][\text{HO}_2^-]$</td>
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<td>$\frac{d[\text{H}_2\text{O}_2]}{dt} = k_8[\text{HO}^+][\text{HO}_2^-]$</td>
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<td>$R_{11}$</td>
<td>$\text{HO}^+ + \text{O}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$</td>
<td>$k_9 = 7.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td>9</td>
<td>$\frac{d[\text{HO}^+]}{dt} = -k_9[\text{HO}^+][\text{O}_2^-]$</td>
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<td>$\frac{d[\text{O}_2^-]}{dt} = k_9[\text{HO}^+][\text{O}_2^-]$</td>
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<td>$\frac{d[\text{HO}^+]}{dt} = -k_9[\text{HO}^+][\text{O}_2^-]$</td>
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<td>$\frac{d[\text{O}_2^-]}{dt} = k_9[\text{HO}^+][\text{O}_2^-]$</td>
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<td>$R_{12}$</td>
<td>$\text{HO}^+ + \text{O}_2^- \rightarrow \text{HO}_2^+ + \text{OH}^-$</td>
<td>$k_{10} = 8.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td>18</td>
<td>$\frac{d[\text{HO}<em>2^+]}{dt} = -k</em>{10}[\text{HO}_2^+][\text{O}_2^-]$</td>
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<td></td>
<td>$\frac{d[\text{OH}^-]}{dt} = k_{10}[\text{HO}_2^+][\text{O}_2^-]$</td>
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<td></td>
<td>$\frac{d[\text{H}_2\text{O}<em>2]}{dt} = k</em>{10}[\text{HO}_2^+][\text{O}_2^-]$</td>
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</tbody>
</table>
Table 1. Continued

<table>
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</table>
| R14 | $\text{H}_2\text{O}_2 + \text{HO}^+ \rightarrow \text{HO}^+ + \text{H}_2\text{O} + \text{O}_2$ | $k_{14} = 3 \text{ M}^{-1} \text{s}^{-1}$ | [22] | \[
\begin{align*}
\frac{d[\text{H}_2\text{O}_2]}{dt} &= -k_{14}[\text{H}_2\text{O}_2][\text{HO}^+] \\
\frac{d[\text{HO}^+]}{dt} &= -k_{14}[\text{H}_2\text{O}_2][\text{HO}^+] \\
\frac{d[\text{HO}^+]}{dt} &= k_{14}[\text{H}_2\text{O}_2][\text{H}_2\text{O}]
\end{align*}
\] |
| R15 | $\text{H}_2\text{O}_2 + \text{O}_2^- \rightarrow \text{HO}^+ + \text{O}_2 + \text{OH}^-$ | $k_{15} = 0.13 \text{ M}^{-1} \text{s}^{-1}$ | [22] | \[
\begin{align*}
\frac{d[\text{H}_2\text{O}_2]}{dt} &= -k_{15}[\text{H}_2\text{O}_2][\text{O}_2^-] \\
\frac{d[\text{O}_2^-]}{dt} &= -k_{15}[\text{H}_2\text{O}_2][\text{O}_2^-] \\
\frac{d[\text{HO}^+]}{dt} &= k_{15}[\text{H}_2\text{O}_2][\text{O}_2^-] \\
\frac{d[\text{O}_2^-]}{dt} &= k_{15}[\text{H}_2\text{O}_2][\text{O}_2^-]
\end{align*}
\] |
| R16 | $\text{HO}^+_2 + \text{O}_2^- \rightarrow \text{HO}^+_2 + \text{O}_2$ | $k_{16} = 9.7 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$ | [18] | \[
\begin{align*}
\frac{d[\text{HO}^+_2]}{dt} &= -k_{16}[\text{HO}^+_2][\text{O}_2^-] \\
\frac{d[\text{O}_2^-]}{dt} &= -k_{16}[\text{HO}^+_2][\text{O}_2^-] \\
\frac{d[\text{HO}^+_2]}{dt} &= k_{16}[\text{HO}^+_2][\text{O}_2^-] \\
\frac{d[\text{O}_2^-]}{dt} &= k_{16}[\text{HO}^+_2][\text{O}_2^-]
\end{align*}
\] |
| R17 | $\text{C} \rightarrow \text{DOC} + \cdot$ | $\varepsilon_{\text{C}}, \varphi_{\text{C}}$ | - | \[
\begin{align*}
\frac{d[\text{C}]}{dt} &= -\phi_{\text{C}} I_{\text{a}} \\
\frac{d[\text{DOC}]}{dt} &= \varphi_{\text{C}} I_{\text{a}} \left[1 - \exp[-2.3(\varepsilon_{\text{C}} \cdot 0.2 + \varepsilon_{\text{DOC}} (0.2 + \varepsilon_{\text{C}}))]\right]
\end{align*}
\] |
| R18 | $\text{C} + \text{HO}^+ \rightarrow \text{DOC} + \cdot$ | $k_{\text{C, HO}^+} = k_{14}$ | - | \[
\begin{align*}
\frac{d[\text{C}]}{dt} &= -k_{14}[\text{C}][\text{HO}^+] \\
\frac{d[\text{HO}^+]}{dt} &= -k_{14}[\text{C}][\text{HO}^+] \\
\frac{d[\text{DOC}]}{dt} &= k_{14}[\text{C}][\text{HO}^+]
\end{align*}
\] |
| R19 | $\text{C} + \text{HO}^+_2 \rightarrow \text{DOC} + \cdot$ | $k_{\text{C, HO}^+_2} = k_{16}$ | - | \[
\begin{align*}
\frac{d[\text{C}]}{dt} &= -k_{16}[\text{C}][\text{HO}^+_2] \\
\frac{d[\text{HO}^+_2]}{dt} &= -k_{16}[\text{C}][\text{HO}^+_2] \\
\frac{d[\text{DOC}]}{dt} &= k_{16}[\text{C}][\text{HO}^+_2]
\end{align*}
\] |
| R20 | $\text{C} + \text{O}_2^- \rightarrow \text{DOC} + \cdot$ | $k_{\text{C, O}_2^-} = k_{18}$ | - | \[
\begin{align*}
\frac{d[\text{C}]}{dt} &= -k_{18}[\text{C}][\text{O}_2^-] \\
\frac{d[\text{O}_2^-]}{dt} &= -k_{18}[\text{C}][\text{O}_2^-] \\
\frac{d[\text{DOC}]}{dt} &= k_{18}[\text{C}][\text{O}_2^-]
\end{align*}
\] |
### Table 2. Effect of the matrix background in the UV/H$_2$O$_2$ system

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>R$_{21}$</td>
<td>DOC + HO$^+$ $\rightarrow$ H$_2$CO$_3$ + H$_2$O</td>
<td>$k_{\text{doc, hpr}} = k_{17} = 2.0 \times 10^3$ M$^{-1}$ s$^{-1}$</td>
<td>[23]</td>
<td>$\frac{d\text{DOC}}{dt} = -k_{17} \left[\text{DOC}\right]\left[\text{HO}^+\right]$</td>
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<td></td>
<td>$\frac{d[\text{HO}^+]}{dt} = -k_{17} \left[\text{DOC}\right]\left[\text{HO}^+\right]$</td>
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<td></td>
<td>$\frac{d[\text{H}_2\text{CO}<em>3]}{dt} = k</em>{17} \left[\text{DOC}\right]\left[\text{HO}^+\right]$</td>
</tr>
<tr>
<td>R$_{22}$</td>
<td>DOC $\rightarrow$ ?</td>
<td>$k_{18} = 3.9 \times 10^4$ M$^{-1}$ s$^{-1}$</td>
<td>[19]</td>
<td>$\frac{d[\text{CO}<em>3^{2-}]}{dt} = -k</em>{18} \left[\text{CO}_3^{2-}\right]\left[\text{HO}^+\right]$</td>
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<td></td>
<td></td>
<td>$\frac{d[\text{OH}^-]}{dt} = -k_{18} \left[\text{CO}_3^{2-}\right]\left[\text{HO}^+\right]$</td>
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<td></td>
<td>$\frac{d[\text{CO}<em>2^{3-}]}{dt} = k</em>{18} \left[\text{CO}_3^{2-}\right]\left[\text{HO}^+\right]$</td>
</tr>
<tr>
<td>R$_{23}$</td>
<td>HCO$_3^-$ + HO$^+$ $\rightarrow$ CO$_3^{2-}$ + H$_2$O</td>
<td>$k_{19} = 8.5 \times 10^4$ M$^{-1}$ s$^{-1}$</td>
<td>[19]</td>
<td>$\frac{d[\text{HCO}<em>3^-]}{dt} = -k</em>{19} \left[\text{HCO}_3^-\right]\left[\text{HO}^+\right]$</td>
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<td></td>
<td>$\frac{d[\text{CO}<em>3^{2-}]}{dt} = k</em>{19} \left[\text{HCO}_3^-\right]\left[\text{HO}^+\right]$</td>
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<td></td>
<td>$\frac{d[\text{H}<em>2\text{O}]}{dt} = k</em>{19} \left[\text{HCO}_3^-\right]\left[\text{HO}^+\right]$</td>
</tr>
<tr>
<td>R$_{24}$</td>
<td>H$_2$O$_2$ + CO$_3^{2-}$ $\rightarrow$ HCO$_3^-$ + HO$_2$</td>
<td>$k_{20} = 4.3 \times 10^5$ M$^{-1}$ s$^{-1}$</td>
<td>[24]</td>
<td>$\frac{d[\text{H}_2\text{O}<em>2]}{dt} = -k</em>{20} \left[\text{H}_2\text{O}_2\right]\left[\text{CO}_3^{2-}\right]$</td>
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<td>$\frac{d[\text{CO}<em>3^{2-}]}{dt} = k</em>{20} \left[\text{H}_2\text{O}_2\right]\left[\text{CO}_3^{2-}\right]$</td>
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<td></td>
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<td></td>
<td>$\frac{d[\text{HCO}<em>3^-]}{dt} = k</em>{20} \left[\text{H}_2\text{O}_2\right]\left[\text{CO}_3^{2-}\right]$</td>
</tr>
<tr>
<td>R$_{25}$</td>
<td>HO$_2$ + CO$_3^{2-}$ $\rightarrow$ CO$_2^{3-}$ + HO$_2$</td>
<td>$k_{21} = 3.0 \times 10^7$ M$^{-1}$ s$^{-1}$</td>
<td>[24]</td>
<td>$\frac{d[\text{HO}<em>2]}{dt} = -k</em>{21} \left[\text{HO}_2\right]\left[\text{CO}_3^{2-}\right]$</td>
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<td></td>
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<td></td>
<td>$\frac{d[\text{CO}<em>2^{3-}]}{dt} = k</em>{21} \left[\text{HO}_2\right]\left[\text{CO}_3^{2-}\right]$</td>
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<tr>
<td></td>
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<td></td>
<td>$\frac{d[\text{HO}<em>2^+]}{dt} = k</em>{21} \left[\text{HO}_2\right]\left[\text{CO}_3^{2-}\right]$</td>
</tr>
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Table 2. Continued

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<tbody>
<tr>
<td>R27</td>
<td>$\cdot + \cdot + \cdot \rightarrow \cdot + \cdot + \cdot$</td>
<td>$k_{22} = 6.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td>[25]</td>
<td>$\frac{d[\cdot]}{dt} = -k_{22}[\cdot][\cdot][\cdot]$</td>
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<td>$\frac{d[\cdot]}{dt} = -k_{22}[\cdot][\cdot][\cdot]$</td>
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<td></td>
<td>$\frac{d[\cdot]}{dt} = k_{22}[\cdot][\cdot][\cdot]$</td>
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<tr>
<td>R28</td>
<td>$\cdot + \cdot + \cdot \rightarrow \cdot + \cdot + \cdot$</td>
<td>$k_{23} = 3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td>[26]</td>
<td>$\frac{d[\cdot]}{dt} = -k_{23}[\cdot][\cdot][\cdot]$</td>
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<td>$\frac{d[\cdot]}{dt} = -k_{23}[\cdot][\cdot][\cdot]$</td>
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<td></td>
<td>$\frac{d[\cdot]}{dt} = k_{23}[\cdot][\cdot][\cdot]$</td>
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<tr>
<td>R29</td>
<td>$\cdot + \cdot + \cdot \rightarrow \cdot + \cdot + \cdot$</td>
<td>$k_{24} = 1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td>[26]</td>
<td>$\frac{d[\cdot]}{dt} = -k_{24}[\cdot][\cdot][\cdot]$</td>
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<td>$\frac{d[\cdot]}{dt} = k_{24}[\cdot][\cdot][\cdot]$</td>
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<tr>
<td>R30</td>
<td>$\cdot + \cdot + \cdot \rightarrow \cdot + \cdot + \cdot$</td>
<td>$k_{25} = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td>[26]</td>
<td>$\frac{d[\cdot]}{dt} = -k_{25}[\cdot][\cdot][\cdot]$</td>
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<td>$\frac{d[\cdot]}{dt} = -k_{25}[\cdot][\cdot][\cdot]$</td>
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<td>$\frac{d[\cdot]}{dt} = k_{25}[\cdot][\cdot][\cdot]$</td>
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<td>R31</td>
<td>$\cdot + \cdot + \cdot \rightarrow \cdot + \cdot + \cdot$</td>
<td>$k_{26} = 3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td>[26]</td>
<td>$\frac{d[\cdot]}{dt} = -k_{26}[\cdot][\cdot][\cdot]$</td>
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<td>$\frac{d[\cdot]}{dt} = -k_{26}[\cdot][\cdot][\cdot]$</td>
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<td>$\frac{d[\cdot]}{dt} = k_{26}[\cdot][\cdot][\cdot]$</td>
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<tr>
<td>R32</td>
<td>$\cdot + \cdot + \cdot \rightarrow \cdot + \cdot + \cdot$</td>
<td>$k_{27} = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td>[26]</td>
<td>$\frac{d[\cdot]}{dt} = -k_{27}[\cdot][\cdot][\cdot]$</td>
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<td>$\frac{d[\cdot]}{dt} = -k_{27}[\cdot][\cdot][\cdot]$</td>
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<td>$\frac{d[\cdot]}{dt} = k_{27}[\cdot][\cdot][\cdot]$</td>
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<tr>
<td>R33</td>
<td>$\cdot + \cdot + \cdot \rightarrow \cdot + \cdot + \cdot$</td>
<td>$k_{28} = 3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td>[26]</td>
<td>$\frac{d[\cdot]}{dt} = -k_{28}[\cdot][\cdot][\cdot]$</td>
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<td>$\frac{d[\cdot]}{dt} = -k_{28}[\cdot][\cdot][\cdot]$</td>
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<td></td>
<td>$\frac{d[\cdot]}{dt} = k_{28}[\cdot][\cdot][\cdot]$</td>
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</table>
| R33  | $\text{H}_2\text{ClO}^\bullet \rightarrow \text{H}_2\text{O} + \text{Cl}^\bullet$ | $k_{28} = 5.0 \times 10^4 \text{ s}^{-1}$ | [26] | $\frac{d[H_2\text{ClO}^\bullet]}{dt} = -k_{28}[H_2\text{ClO}^\bullet]$  
$\frac{d[\text{Cl}^\bullet]}{dt} = k_{28}[H_2\text{ClO}^\bullet]$ |
| R34  | $\text{Cl}^\bullet + \text{Cl} \rightarrow 2\text{Cl}^\bullet$            | $k_{29} = 8.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ | [26] | $\frac{d[\text{Cl}]}{dt} = -k_{29}[\text{Cl}^\bullet][\text{Cl}^\bullet]$  
$\frac{d[\text{Cl}^\bullet]}{dt} = k_{29}[\text{Cl}][\text{Cl}^\bullet]$ |
| R35  | $\text{Cl}_2^\bullet + \text{HO}^\bullet \rightarrow \text{HClO}^\bullet + \text{Cl}^\bullet$ | $k_{30} = 1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ | [27] | $\frac{d[\text{Cl}_2^\bullet]}{dt} = -k_{30}[	ext{Cl}^\bullet][\text{HO}^\bullet]$  
$\frac{d[\text{HClO}^\bullet]}{dt} = -k_{30}[	ext{Cl}^\bullet][\text{HO}^\bullet]$  
$\frac{d[\text{Cl}^\bullet]}{dt} = k_{30}[	ext{Cl}^\bullet][\text{HO}^\bullet]$ |
| R36  | $\text{Cl}_2^\bullet + \text{H}_2\text{O}_2 \rightarrow 2\text{HClO}^\bullet + 2\text{Cl}^\bullet + \text{H}^\bullet$ | $k_{31} = 4.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ | [26] | $\frac{d[\text{Cl}_2^\bullet]}{dt} = -k_{31}[	ext{Cl}^\bullet][\text{H}_2\text{O}_2]$  
$\frac{d[2\text{HClO}^\bullet]}{dt} = -k_{31}[	ext{Cl}^\bullet][\text{H}_2\text{O}_2]$  
$\frac{d[2\text{Cl}^\bullet]}{dt} = 2k_{31}[	ext{Cl}^\bullet][\text{H}_2\text{O}_2]$ |
| R37  | $\text{Cl}^\bullet + \text{H}_2\text{O}_2 \rightarrow \text{HClO}^\bullet + \text{Cl}^\bullet$ | $k_{32} = 1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ | [26] | $\frac{d[\text{Cl}^\bullet]}{dt} = -k_{32}[	ext{Cl}^\bullet][\text{H}_2\text{O}_2]$  
$\frac{d[\text{HClO}^\bullet]}{dt} = -k_{32}[	ext{Cl}^\bullet][\text{H}_2\text{O}_2]$  
$\frac{d[2\text{Cl}^\bullet]}{dt} = 2k_{32}[	ext{Cl}^\bullet][\text{H}_2\text{O}_2]$ |
| R38  | $\text{Cl}_2^\bullet + \text{HO}^\bullet \rightarrow 2\text{Cl}^\bullet + \text{H}^\bullet$            | $k_{33} = 3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ | [26] | $\frac{d[\text{Cl}_2^\bullet]}{dt} = -k_{33}[	ext{Cl}^\bullet][\text{HO}^\bullet]$  
$\frac{d[2\text{Cl}^\bullet]}{dt} = -k_{33}[	ext{Cl}^\bullet][\text{HO}^\bullet]$  
$\frac{d[\text{H}^\bullet]}{dt} = k_{33}[	ext{Cl}^\bullet][\text{HO}^\bullet]$ |
Table 2. Continued

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<td>$R_{38}$</td>
<td>$\text{C}_2^+ + \text{HO}_2^– \rightarrow \text{O}_2^- + 2\text{Cl}^- + \text{H}^+$</td>
<td>$k_{33} = 3.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td>[26]</td>
<td>$\frac{d[H^+]}{dt} = k_{33} [\text{C}_2^+] [\text{HO}_2^–]$</td>
</tr>
</tbody>
</table>
| $R_{39}$ | $\text{C}_2^- + \text{O}_2^– \rightarrow \text{O}_2^- + 2\text{Cl}^- | [26] | $\frac{d[\text{C}_2^-]}{dt} = -k_{34} [\text{C}_2^-] [\text{O}_2^–]$
| | | | | $\frac{d[\text{O}_2^-]}{dt} = -k_{34} [\text{C}_2^-] [\text{O}_2^-]$ |
| | | | | $\frac{d[\text{Cl}^-]}{dt} = 2k_{34} [\text{C}_2^-] [\text{O}_2^-]$ |
| $R_{40}$ | $\text{C} + \text{CO}_3^– \rightarrow \text{DOC} + ?$ | $k_{35}$ | - | $\frac{d[\text{C}]}{dt} = -k_{35} [\text{C}] [\text{CO}_3^–]$ |
| | | | | $\frac{d[\text{DOC}]}{dt} = k_{35} [\text{C}] [\text{CO}_3^–]$ |
| $R_{41}$ | $\text{C} + \text{SO}_4^– \rightarrow \text{DOC} + ?$ | $k_{36}$ | - | $\frac{d[\text{C}]}{dt} = -k_{36} [\text{C}] [\text{SO}_4^–]$ |
| | | | | $\frac{d[\text{DOC}]}{dt} = k_{36} [\text{C}] [\text{SO}_4^–]$ |
| $R_{42}$ | $\text{C} + \text{H}_2\text{ClO}^– \rightarrow \text{DOC} + ?$ | $k_{37}$ | - | $\frac{d[\text{H}_2\text{ClO}^–]}{dt} = -k_{37} [\text{C}] [\text{H}_2\text{ClO}^–]$ |
| | | | | $\frac{d[\text{DOC}]}{dt} = k_{37} [\text{C}] [\text{H}_2\text{ClO}^–]$ |
| $R_{43}$ | $\text{C} + \text{HClO}^– \rightarrow \text{DOC} + ?$ | $k_{38}$ | - | $\frac{d[\text{HClO}^–]}{dt} = -k_{38} [\text{C}] [\text{HClO}^–]$ |
| | | | | $\frac{d[\text{DOC}]}{dt} = k_{38} [\text{C}] [\text{HClO}^–]$ |
| $R_{44}$ | $\text{C} + \text{Cl}^- \rightarrow \text{DOC} + ?$ | $k_{39}$ | - | $\frac{d[\text{Cl}^-]}{dt} = -k_{39} [\text{C}] [\text{Cl}^-]$ |
| | | | | $\frac{d[\text{DOC}]}{dt} = k_{39} [\text{C}] [\text{Cl}^-]$ |
| $R_{45}$ | $\text{C} + \text{Cl}^+_2 \rightarrow \text{DOC} + ?$ | $k_{40}$ | - | $\frac{d[\text{Cl}^+_2]}{dt} = -k_{40} [\text{C}] [\text{Cl}^+_2]$ |
| | | | | $\frac{d[\text{DOC}]}{dt} = k_{40} [\text{C}] [\text{Cl}^+_2]$ |
species considered in the particular reaction $R_i$ were considered; while such as species were obviated if $\delta_{R_i} = 0$. A more detailed explanation about how the pH changes in the solution were addressed has been reported in Rubio-Clemente et al. [29]. Moreover, the ODE set of the chemical species involved in the system can also be consulted in Rubio-Clemente et al. [29].

Considering the reactions, constants and parameters summarized in Tables 1 and 2, the degradation of the pollutant can be estimated as indicated in Eq. (1):

$$-\frac{dC}{dt} = \varphi_{C,i} \cdot C + k_{41} [\text{HO}^+] [\text{C}] + k_{45} [\text{H}^+] [\text{C}] + k_{46} [\text{O}_2^-] [\text{C}] + \sum_{i=35}^{40} k_i [\text{C}] [AR_i]$$
where:
\[ \phi_{\text{UV}, \text{c}} \cdot \sum^{40}_{j=35} k_j [C] \cdot \sum^{40}_{j=35} k_j [AR_j] \]
correspondingly refer to the specific contributions of UV radiation, and the oxidation of HO\(^+\), HO\(_2\)\(^+\), O\(_2\)\(^+\) and the formed anions radicals (AR) (CO\(_3\)\(^-\), SO\(_4\)\(^-\), H\(_2\)ClO\(^-\), HClO\(^-\), Cl\(^-\) and CI\(_2\)\(^-\)) to the overall pollutant degradation.

For examining the role of the terms mentioned above, four parameters \((d, f, g \text{ and } h)\) were included in Eq. (1), resulting in Eq. (2):
\[
\begin{align*}
\frac{dC}{dt} &= \phi_{\text{UV}, \text{c}} + k_{14} [\text{HO}^-][C]d + k_{15} [\text{HO}_2^-][C]f + \\
&+ k_{16} [\text{O}_2^-][C]g + \sum^{40}_{j=35} k_j [C] [AR_j]h
\end{align*}
\]

Consequently, for evaluating the pollutant removal by the exclusive action of UV radiation, \(d = f = g = h = 0\) (i.e., the initial level of oxidant radical species is equal to zero). In turn, HO\(^+\) action was considered when \(d = 1\) and \(f = g = h = 0\). For studying the contribution of HO\(_2\)\(^+\), O\(_2\)\(^+\) and other anion radicals included in Table 2, \(f, g \text{ and } h\) were equaled to 1, respectively.

Since the mathematical model considers the contribution of different anions, such as CO\(_3\)\(^-\), HCO\(_3\)\(^-\), SO\(_4\)\(^-\) and Cl\(^-\), in the pollutant conversion, it might be used for the treatment of water with salt content. This enables the applicability of the developed kinetic model to be expanded depending on the characteristics of the water of interest to be treated.

**Numerical analysis**

In order to obtain the numerical solution of the proposed kinetic model for the degradation of organic pollutants using the UV/H\(_2\)O\(_2\) system, MATLAB software and ODE15S function were used. Additionally, the differential rate equations representing the concentration evolution of the pollutant throughout the reaction time were plotted.

**RESULTS AND DISCUSSION**

Taking into account the reactions compiled in Table 1 and 2, as well as the parameters and the rate constants involved in each chemical and photochemical reaction, a kinetic model was developed. The kinetic model was validated using the experimental values from Alnaizy and Akgerman [16], where phenol was used as the probe compound and the UV/H\(_2\)O\(_2\) process was carried out in a completely mixed batch cylindrical photoreactor made on Pyrex glass. The considered UV-light intensity \((k_b)\) and illuminated path length \((\lambda)\) were 1.516×10\(^6\) Ein L\(^1\) s\(^-1\) (radiation of 254 nm > 90\% and power = 15 W) and 63.5 mm, respectively [16]. The adopted quantum yield and molar extinction coefficient of phenol \((\varphi_{\text{phenol}}\text{ and } \varepsilon_{\text{phenol}}\)) were 0.07 mol Ein\(^-1\) [30] and 51600 M\(^-1\) m\(^-1\) [16], respectively. In turn, the assumed values of the kinetic rate constants of phenol with HO\(^+\) \((k_{14})\), O\(_2\)\(^+\) \((k_{59})\) and CO\(_3\)\(^-\) \((k_{35})\) were respectively 6.6×10\(^3\), 5.8×10\(^3\) and 2.2×10\(^7\) M\(^-1\) s\(^-1\) [31-33]. Additionally, a phenol working solution of 2.23×10\(^{-3}\) M prepared in deionized water was selected and the effect of different H\(_2\)O\(_2\)/phenol ratios (495, 228 and 125), obtained by varying the initial level of H\(_2\)O\(_2\) and keeping the concentration of phenol constant [16], were studied.

**Model hypotheses**

Since the reaction water used in the UV/H\(_2\)O\(_2\) experiments was deionized water [16], the contribution of SO\(_4\)\(^-\), H\(_2\)ClO\(^-\), HClO\(^-\), Cl\(^-\) and CI\(_2\)\(^-\) were not included in the study of phenol conversion. Therefore, among the anions considered in the model, only HCO\(_3\)\(^-\) and CO\(_3\)\(^2-\) were studied. In this sense, to examine the contribution of CO\(_3\)\(^2-\) (due to the reaction between HO\(^+\) and HCO\(_3\)\(^-\)), along with the photolysis and the oxidation of the pollutant through HO\(^+\), \(d = f = h = 1\) and \(f = g = 0\). On the other hand, to analyze the role of HO\(_2\)\(^+\) in the pollutant degradation, as well as HO\(^+\) and CO\(_3\)\(^2-\), \(d = f = h = 1\) and \(g = 0\). In turn, when \(d = f = g = h = 1\), and no inorganic anions different from HCO\(_3\)\(^-\) and CO\(_3\)\(^2-\) are present in the studied water, in addition to the species mentioned above, the kinetic model considers the action of O\(_2\)\(^+\).

On the other hand, and taking into account the high oxidation potential and kinetic reaction rate constant, HO\(^+\) is generally the radical developing the main action in pollutant conversion [6,14,17,23,34-37]. Therefore, a special attention to the evolution of its concentration with time must be paid. In this vein, the evolution of HO\(^+\) level during the reaction time can be expressed as indicated in Eq. (3):
\[
\frac{d[\text{HO}^+]}{dt} = 2\varphi_{\text{UV}, \text{a}} [\text{H}_2\text{O}_2] [\text{HO}^+] \delta_{R_3} + 2\varphi_{\text{HO}, \text{a}} [\text{H}_2\text{O}_2] \delta_{R_4} - k_5 [\text{H}_2\text{O}_2] [\text{HO}^+] \delta_{R_7} - k_5 [\text{H}_2\text{O}_2] [\text{HO}^+] \delta_{R_8} - k_6 [\text{HO}^+] [\text{H}_2\text{O}_2] - k_7 [\text{HO}^+] [\text{HO}^+] + k_{11} [\text{H}_2\text{O}_2] [\text{HO}^+] + f_{R_12} [\text{H}_2\text{O}_2] [\text{O}_2^-] - k_{14} [C] [\text{HO}^+] - k_{17} [\text{DOC}] [\text{HO}^+] - \ (3)
\]
Nevertheless, since HO* is a highly reactive species, it can be assumed that HO* level change during time is negligible. Therefore, HO* concentration can be expressed as Eq. (4):

\[
\Delta C_{HO^*} = \frac{2 \phi_{H_2O_2/a,H_2O_2} \delta_{R3} + 2 \phi_{H_2O_2/a,H_2O_2} \delta_{R4}}{1/(k_5[H_2O_2] \delta_{R7} + k_6[H_2O_2] \delta_{R8} + k_7[HO_2^+] + k_8[HO_2^+] + k_9[O_2^-] + k_{14}[C] + k_{17}[DOC] + k_{18}[CO_3^{2-}] + k_{19}[HCO_3^-] + k_{20}[Cl^-] + k_{30}[Cl_2^-])}
\]

(4)

Considering that the oxidant is in a high level, due to the high H2O2/phenol ratios studied (i.e., k_5[H_2O_2] \delta_{R7} + k_6[H_2O_2] \delta_{R8} >> \sum k_i[X_i], where:

\[
\sum k_i[X_i] = k_6[H_2O_2] + k_9[O_2^-] + k_{18}[CO_3^{2-}] + k_{19}[HCO_3^-] + k_{23}[HSO_4^-] + k_{26}[Cl^-] + k_{30}[Cl_2^-]
\]

and

\[
2 \phi_{H_2O_2/a,H_2O_2} \delta_{R3} + 2 \phi_{H_2O_2/a,H_2O_2} \delta_{R4} >> \sum (k_{14}[C] + k_{17}[DOC] + k_{18}[CO_3^{2-}] + k_{19}[HCO_3^-] + k_{23}[HSO_4^-] + k_{26}[Cl^-] + k_{30}[Cl_2^-])
\]

Eq. (4) can be simplified to Eq. (5). k_i and [X_i] are the rate constants between HO* and species i, and the concentration of species i, respectively:

\[
\Delta C_{HO^*} = \frac{2 \phi_{H_2O_2/a,H_2O_2} \delta_{R3} + 2 \phi_{H_2O_2/a,H_2O_2} \delta_{R4}}{k_5[H_2O_2] \delta_{R7} + k_6[H_2O_2] \delta_{R8}}
\]

(5)

Additionally, the initial concentration of DOC different from the DOC provided by phenol was assumed to be equal to 0.

In agreement with several authors [9,14,37], the decrease in DOC by means of direct photolysis (R_{22} from Table 2) was obviated.

As the process proceeds, DOC from the photo-oxidation of phenol and the intermediates can impair phenol transformation since it can absorb UV-light and react with reactive oxygen species (ROS), such as HO*.

With regard to the amount of light quenched by DOC, it was assumed a DOC molar extinction coefficient (\epsilon_{DOC(280 nm)} of 35967 M^{-1} m^{-1} [38] since this parameter was not considered in Alnaizy and Akgerman study [16].

Finally, the pH variation during the reaction time was included in the proposed kinetic model; as according to Alnaizy and Akgerman [16] the pH decreases as the oxidation process proceeds. In this vein, those kinetic reactions significantly dependent on the pH of the bulk, such as R_3, R_4, R_7 and R_8, were promoted and discriminated as explained in Rubio-Clemente et al. [29].

Degradation of phenol by direct photolysis and UV/H2O2

Considering the previously mentioned hypotheses and in order to study the effect of UV light in phenol conversion, parameters d, f, g and h from Eq. (2) were equaled to 0. Thus, Eq. (2) is reduced to Eq. (6):

\[
-\frac{dC}{dt} = \phi_{c/a,c} \cdot \epsilon_{c/a,c}
\]

(6)

Additionally, for examining the effect of HO* and CO_3^{2-}, d and h were equaled to 1, and f and g, to 0. Therefore, Eq. (2) is simplified as Eq. (7):

\[
-\frac{dC}{dt} = \phi_{c/a,c} + k_{14}[HO^*][C] + \sum_{i=35}^{40} k_i[C][AR_i]
\]

(7)

In Figure 1, the experimental data and those ones calculated by the proposed kinetic model concerning the transformation of phenol by direct photolysis and the contribution of HO* and CO_3^{2-} for 2.23x10^{-3} M phenol and a H2O2/phenol ratio of 495 for a reaction time of 220 min are illustrated.

From the figure, it can be observed that model predictions are in a good agreement with experimental data both related to phenol direct photolysis alone and indirect oxidation with a correlation factor of 98.25 and 99.34%, respectively.

Additionally, it can be found that phenol initial level was reduced about 40% after 220 min of treatment considering the exclusive effect of UV radiation. This can be explained by the photolytic activity of phenol under the irradiation wavelength used in the studied AOP. However, higher removal of phenol is obtained when H2O2 is added to the system, resulting in more than 90% of removal, primarily due to the action of HO*. Between HO* and CO_3^{2-}, the main role in removing phenol was developed by HO*, due to the rate constant between phenol and CO_3^{2-} is comparatively lower than the rate constant between phenol and HO*; and because the CO_3^{2-} level was found to be in a concentration in the range of 10^{-13} M. This fact
was determinant in obviating the action of \( \text{CO}_3\text{•} \) in transforming phenol for the studied working conditions.

On the other hand, the effect of \( \text{HO}_2\text{•} \) and \( \text{O}_2\text{•} \) was investigated. It was observed that both species were in the system in the range of \( 10^{-7} \) M; a very larger concentration in comparison with \( \text{HO}\text{•} (\sim 10^{-14} \) M). Nevertheless, as the pH of the reaction medium decreases, the amount of \( \text{O}_2\text{•} \) is reduced. Additionally, the reaction rate constant between phenol and this radical is \( 5.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1} \) [32]. Therefore, the contribution of \( \text{O}_2\text{•} \) in phenol degradation can be neglected.

With regard to the action of \( \text{HO}_2\text{•} \) in converting phenol, phenol-\( \text{HO}_2\text{•} \) kinetic reaction rate constant must be known. For this purpose, the kinetic reaction rate constant calculated in Rubio-Clemente et al. [29] was used, which was equal to \( 1.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1} \), consistent with literature data \( (2.7 \pm 1.2) \times 10^3 \text{ M}^{-1} \text{ s}^{-1} \) [39]. Including this value in the ODE set of the proposed kinetic model, the degree of agreement between the experimental and the proposed data was calculated to be 99.57%. In this vein, it was found that the correlation factor of the model slightly increases in 0.23%. Therefore, although the amount of \( \text{HO}_2\text{•} \) is far greater than the amount of \( \text{HO}\text{•} \), in this case its action in the UV/\( \text{H}_2\text{O}_2 \) system for transforming phenol can be obviated; probably due to the low reactivity of this radical with the pollutant. Therefore, the main role in phenol conversion for the considered experimental conditions was developed by \( \text{HO}\text{•} \).

During phenol oxidation, different reaction intermediates are formed; among them 1,2-benzenediol, 1,3-benzenediol and 1,4-benzenediol, corresponding to catechol, resorcinol and hydroquinone, respectively, were reported [16]. Additionally, \( \text{p}-\text{benzoquinone} \) was found among phenol degradation by-products [16]. Once these intermediates are generated, the oxidation action of the oxidant species is continued, especially that of \( \text{HO}\text{•} \), as explained above. Consequently, organic acids, like maleic, formic and oxalic acid, among others, are yielded, resulting in a decrease of the pH in the bulk, as indicated previously.

### Influence of initial concentration of \( \text{H}_2\text{O}_2 \)

Keeping constant the initial level of phenol \( (2.23 \times 10^{-3} \text{ M}) \), the effect of \( \text{H}_2\text{O}_2 \) initial concentration, considering \( \text{H}_2\text{O}_2/\text{phenol} \) mass ratios of 125, 228 and 495, is represented in Figure 2, where the experimental data and the predictions from the proposed kinetic model are compared. It can be observed that the optimal \( \text{H}_2\text{O}_2/\text{phenol} \) ratio causing a transformation of phenol higher than 95% after 40 min of treatment is 125, which corresponds to Alnaizy and Akgerman findings [16]. A further increase of \( \text{H}_2\text{O}_2/\text{phenol} \) ratio from 125 to 228 results in a reduction of phenol degradation, which is magnified when \( \text{H}_2\text{O}_2/\text{phenol} \) ratio is equal to 495.

It is important to note that in the UV/\( \text{H}_2\text{O}_2 \) system, when \( \text{H}_2\text{O}_2 \) is irradiated with a wavelength of 254 nm, \( \text{HO}\text{•} \) is produced according to \( \text{R}_3 \) from Table 1, which exhibits a high oxidation potential [12] and attacks the pollutant, leading to a higher phenol removal in a shorter reaction time. Therefore, it could be thought than an increase in \( \text{H}_2\text{O}_2 \) level would lead to a rise in phenol conversion. However, two opposing conditions are present: on one hand, the amount of \( \text{HO}\text{•} \) increases, which can lead to a higher conversion, while on the other hand, the concentration of \( \text{HO}_2\text{•} \) decreases, which can lead to a lower conversion.
A rise in the initial level of H$_2$O$_2$ results in a higher production of HO$^\bullet$, which is available to attack the organic pollutant. Nevertheless, when H$_2$O$_2$ is in excess, it acts scavenging HO$^\bullet$, as indicated in reaction $R_7$ from Table 1. Furthermore, even though a high H$_2$O$_2$ concentration can generate a great number of HO$_2^\bullet$, they have a lower oxidation potential in comparison with HO$^\bullet$. Moreover, HO$_2^\bullet$ can react with HO$^\bullet$ ($R_{11}$ from Table 1). In addition, when HO$^\bullet$ is in excess, it can suffer recombination ($R_{10}$ from Table 1), reducing the number of HO$^\bullet$ available in the bulk. Hence, the overall efficiency of the applied AOP in removing phenol, and eventually leading to its mineralization is decreased.

The detrimental effect of an excess of H$_2$O$_2$ is supported by Figure 3, representing the time-evolution profiles of the HO$^\bullet$ level for the H$_2$O$_2$/phenol ratios studied. From the figure, it can be observed that the ratio providing the lowest and the highest concentration of HO$^\bullet$ throughout the reaction time is 495 and 125, respectively. These results are coincident with those findings illustrated in Figure 2, where the H$_2$O$_2$/phenol ratio providing the lowest and the highest phenol conversion extent was, correspondingly, 495 and 125.

Consequently, and in order to save in operating costs, H$_2$O$_2$ optimal level achieving an efficient pollutant removal must be found. Nonetheless, this can
be an arduous and expensive task. In this sense, the proposed kinetic model allows calculating the optimal concentration of the oxidizing agent to be used when implementing the UV/H$_2$O$_2$ system for an efficient phenol removal without incurring high costs related to the use of an unnecessary amount of oxidant.

**CONCLUSION**

A kinetic model for pollutant degradation by the UV/H$_2$O$_2$ process was developed. The model predictions were checked with experimental results from Alnaizy and Akgerman work [16] for phenol direct photolysis alone and in combination with indirect oxidation at different H$_2$O$_2$/phenol ratios. It was found that the proposed kinetic model fits well with the experimental data, which is a probe of the accuracy of the model.

Additionally, the model provides an understanding of the impact of the initial level of H$_2$O$_2$ being able to optimize this parameter. In fact, it was observed that the optimal H$_2$O$_2$ concentration enabling a removal of the pollutant higher than 95% after 40 min of treatment corresponded to a H$_2$O$_2$/phenol ratio of 125. The action of HO$_2$ in transforming phenol was also studied due to the high concentration of these species formed during the process compared to HO (\(\sim 10^{-7} \text{ M} \gg \sim 10^{-14} \text{ M}\)). It was found that, although the degree of agreement of the correlation factor was increased from 99.34 to 99.57%, the radical developing the main action in phenol abatement under the operating conditions was HO$^\cdot$.

The developed kinetic model could be of relevance in the optimization of the operating conditions when implementing the UV/H$_2$O$_2$ process, allowing saving in costs and time.

**Nomenclature**

- **AOP** advanced oxidation process
- **AR** anion radicals
- **C** target compound
- **E** oxidation potential (V)
- **\(\varepsilon_X\)** molar extinction coefficient of a species X (M$^{-1}$m$^{-1}$)
- **DOC** dissolved organic carbon
- **DOM** dissolved organic matter
- **\(\delta_{\text{ir}}\)** correction factor
- **\(f_x\)** fraction of the UV radiation absorbed by a species
- **\(I_{a,x}\)** intensity of the UV radiation absorbed by a species (Ein L$^{-1}$ s$^{-1}$)
- **\(I_0\)** incident UV radiation intensity (Ein L$^{-1}$ s$^{-1}$)
- **\(k_i\)** second order (M$^{-1}$ s$^{-1}$) or first order (s$^{-1}$) reaction rate constant
- **l** optical path length of the photoreactor (mm)
- **ODE** ordinary differential equations
- **\(\phi_x\)** quantum yield of the photolysis of a species (mol Ein$^{-1}$)
- **ROS** reactive oxygen species
- **t** irradiation time (min)
- **UV** ultraviolet
- **[X]** concentration of a species X

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KINETIČKI MODEL UV/H₂O₂ FOTODEGRADACIJE FENOLA IZ VODE

Razvijen je i proveren kinetički model za konverziju fenola u UV/H₂O₂ sistemu. Model uključuje razgradnju zagađujućih materija direktnom fotolizom i oksidacijom sa HO•, HO₂• i O₂•, hvatanje HO• pomoću, CO₃²⁻, HCO₃⁻, SO₄²⁻ i Cl⁻, kao i promenu pH za vreme procesa. Takođe, razmotreno je štetno delovanje organskih materija i intermedijera reakcije u UV zaštiti i smanjenju HO• fluorescencije. Uočeno je da model može precizno predvideti smanjenje fenola korишćenjem različitih masnih odnos sa H₂O₂/fenol (495, 228 i 125). Model definiše optimalni odnos H₂O₂/fenola od 125 sa uklanjanjem fenola više od 95% nakon 40 min tretmana, ukoliko HO• je glavna oksidaciona vrsta. Razvijeni model može biti relevantan za izračunavanje optimalnog nivoa H₂O₂ za efikasnu degradaciju zagađivača od interesa, čime se znatno štedi na vremenu i troškovima.

Ključne reči: nivo H₂O₂, kinetički model, zagađenje fenolom, UV/H₂O₂.