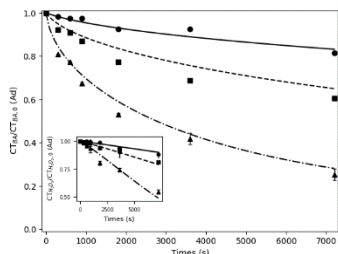


# Numerical and experimental evaluation of the initial concentration and pH effect on the oxidation of benzoic acid by UVC/H<sub>2</sub>O<sub>2</sub> process

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The study aims to evaluate the oxidation of benzoic acid (BA) by the UVC/H<sub>2</sub>O<sub>2</sub> process under various experimental conditions and develop a mathematical model to understand the reaction mechanism. Experimental and numerical data validate the model's accuracy and assess the effects of initial BA concentration and pH on the oxidation efficiency. Additionally, the study seeks to estimate reaction constants and elucidate the reactivity of HO<sup>•</sup>, with BA and BA<sup>-</sup> in their acidic and basic forms, respectively. These insights contribute to optimizing BA remediation strategies in produced water treatment processes.

## Introduction

Naphthenic acids (NAs) are emerging contaminants, raising international concerns about water contamination. Classified as aliphatic and alicyclic carboxylic acids, NAs naturally occur in crude oil and can migrate to produced water (PW) during processing due to temperature, pressure, pH, and salinity variations [1].

Among the NAs, benzoic acid (BA) stands out for its stability against common oxidants such as air, increasing the chemical oxygen demand of effluents and posing environmental concerns [2].

An alternative to remediate BA present in PW is the UVC/H<sub>2</sub>O<sub>2</sub> process. This process generates hydroxyl radicals (HO<sup>•</sup>), capable of efficiently oxidizing most organic pollutants, resulting in carbon dioxide, water, and inorganic ions, or partially mineralizing them into biodegradable by-products with lower toxicity. In this scenario, the study aims to evaluate BA oxidation by the UVC/H<sub>2</sub>O<sub>2</sub> process under different experimental conditions and develop a mathematical model to understand the reaction mechanism.

## Material and Methods

Oxidation of BA by UVC/H<sub>2</sub>O<sub>2</sub> process was conducted in an experimental chamber equipped with a 0.30 L reactor and a UVC lamp positioned at a distance of 0.15 m from the reactor. Degradation experiments were conducted under different combinations of variables: initial BA concentrations of 10.00, 25.00 and 50.00 mg/L, initial H<sub>2</sub>O<sub>2</sub> concentration of 75.00 mg/L, initial pH of 3.00, 5.00 and 7.00, and light intensity (LI) of 8 W, over a total reaction time of 120 minutes. Initially, all assays had their pH adjusted to the specified value and were monitored throughout the experiment without further adjustments.

The mechanism of photochemical oxidation of BA in aqueous solution using the UVC/H<sub>2</sub>O<sub>2</sub> process depends mainly on the photolysis of H<sub>2</sub>O<sub>2</sub>, which generates HO<sup>•</sup>, that reacts with BA. To describe the BA oxidation by the UVC/H<sub>2</sub>O<sub>2</sub> process, a reaction scheme was developed based on the work Crittenden et al., (1999) [3], as shown in Table 1.

**Table 1.** Scheme of oxidation reactions of benzoic acid by UVC/H<sub>2</sub>O<sub>2</sub> process.

| Reactions   | Constants (mol/(Ls))     | Ref.         |
|---|--------------------------|--------------|
| $H_2O_2 + hv \rightarrow 2HO^\bullet$                 | $\Phi_{H_2O_2} = 0.50$   | [3]          |
| $H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O$ | $k_2 = 2.70 \times 10^7$ | [3]          |
| $BA/BA^- + hv \rightarrow Int.^a$                     | $\Phi_{BA/BA^-}$         | <sup>c</sup> |
| $+HO^\bullet \rightarrow Int.$                        | $k_3$                    | <sup>c</sup> |
| $BA^- + HO^\bullet \rightarrow Int.$                  | $k_4$                    | <sup>c</sup> |
| $Int. + HO^\bullet \rightarrow CO_2 + H_2O + MP^b$    | $k_5$                    | <sup>c</sup> |
| $BA \leftrightarrow BA^- + H^+$                       | $pK_{a,BA} = 4.20$       | [4]          |

<sup>a</sup> Intermediaries; <sup>b</sup> Mineralized Products; <sup>c</sup> This Study.

Based in the oxidation reactions outlined in Table 1, the variations in the concentrations of H<sub>2</sub>O<sub>2</sub>, CT<sub>BA</sub>, BA/BA<sup>-</sup> and HO<sup>•</sup> can be described in differential equations:

$$\frac{d[CT_{H_2O_2}]}{dt} = -\Phi_{H_2O_2} E_{H_2O_2, \lambda} - k_2 [CT_{H_2O_2}] [HO^\bullet] \quad (1)$$

$$\frac{d[CT_{BA}]}{dt} = -\Phi_{BA} E_{BA, \lambda} - \Phi_{BA^-} E_{BA^-, \lambda} - (k_3 [BA] + k_4 [BA^-]) [HO^\bullet] \quad (2)$$

$$\frac{d[BA]}{dt} = \left( \frac{[H^+]}{[H^+] + K_{a,BA}} \right) \frac{dCT_{BA}}{dt} \quad (3)$$

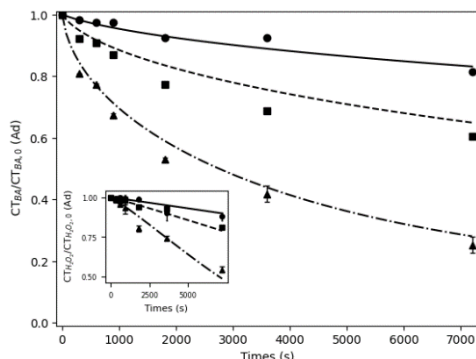
$$\frac{d[BA^-]}{dt} = \left( \frac{K_{a,BA}}{[H^+] + K_{a,BA}} \right) \frac{dCT_{BA}}{dt} \quad (4)$$

$$[HO^\bullet] = \frac{\Phi_{H_2O_2} E_{H_2O_2, \lambda}}{k_2 [CT_{H_2O_2}] + k_3 [BA] + k_4 [BA^-] - k_5 ([CT_{BA}]_0 + [CT_{BA}])} \quad (5)$$

where  $\phi_{H_2O_2}$ ,  $\phi_{BA/BA^-}$ ,  $E_{H_2O_2,\lambda}$  e  $E_{BA/BA^-,\lambda}$  are, respectively, the quantum yield of  $H_2O_2$  and  $BA/BA^-$ , and the volumetric rate photons absorbed by  $H_2O_2$  and  $BA/BA^-$  (Einstein/(m<sup>3</sup> s)), respectively.

## Results and Discussion

Figures 1 and 2 present the experimental results alongside the data predicted by the mathematical model proposed for different initial concentrations of BA and pH in the oxidation by the UVC/ $H_2O_2$  process.



**Figure 1.** Experimental and numerical results of the effect of the initial BA concentration in oxidation by the UVC/ $H_2O_2$  process. Experimental conditions:  $CT_{BA}$  = (•) 50.00, (■) 25.00 and (▲) 10 mg/L, pH = 3, LI = 8 W, and  $C_{H_2O_2}$  = 75 mg/L.

The kinetics model accurately predicts the experimental data and the effects of initial BA concentration and pH. Additionally, the sub-plot of Figure 1 reveals an inversely proportional relationship between the initial concentration of BA and  $H_2O_2$  consumption during the reaction, observed both experimentally and numerically. At

## Conclusions

The research showcased the effectiveness of the UVC/ $H_2O_2$  process in oxidizing BA in PW. The findings offer valuable insights into reaction kinetics and the effects of experimental conditions. This knowledge is crucial for developing effective strategies for contaminated water treatment.

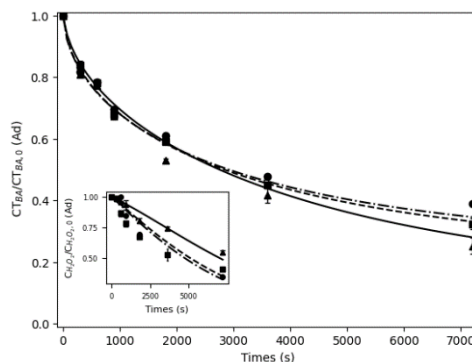
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higher BA concentrations, Reactions 3 and 4 predominate over Reaction 2, leading to faster decomposition of  $HO^*$  and immediate BA attack. Conversely, at lower BA concentrations,  $HO^*$  are more likely to accumulate, resulting in greater  $H_2O_2$  consumption, in addition to attacking BA,  $H_2O_2$  and intermediates.



**Figure 2.** Experimental and numerical results of the effect of the initial pH in oxidation by the UVC/ $H_2O_2$  process. Experimental conditions: pH = (•) 7.00, (■) 5.00 and (▲) 3 mg/L,  $CT_{BA}$  = 10 mg/L, LI = 8 W, and  $C_{H_2O_2}$  = 75 mg/L.

The unknown constants were estimated as follows:  $\phi_{BA/BA^-}$  =  $2.75 \times 10^{-4}$ ,  $k_3$  =  $8.97 \times 10^{11}$ ,  $k_4$  =  $4.91 \times 10^{11}$  and  $k_5$  =  $2.18 \times 10^{13}$  L/(mol s). Comparing the reaction constants of the  $HO^*$  with BA and  $BA^-$  in their acidic and basic forms, respectively, it is observed that the kinetic reaction constant of  $HO^*$  with BA,  $k_3$ , is nearly twice that of  $HO^*$  with  $BA^-$ ,  $k_4$ . This indicates that the acidic species of BA is more reactive than the basic species, suggesting that the oxidation of BA is more effective at low pH levels.