Evaluation of Direct Photolysis of Benzoic Acid by UVC Advanced Process: Numerical and Experimental Analysis

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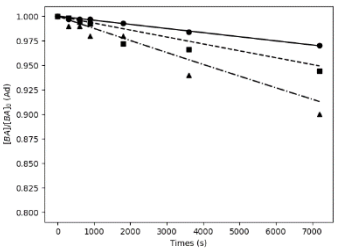

The study investigated the direct photolysis of benzoic acid (BA) by the UVC process. The research showed that the molar extinction coefficient of BA is pH-dependent, indicating a higher absorption capacity of photons at low pH. A model predicting the molar extinction coefficient over a pH range of 0 to 14 was developed. Experimental results are correctly predicted by the kinetic model, proposing a quantum yield of BA of 0.025×10^{-2} mol/Einstein.

Introduction

Benzoic acid (BA) is classified as a naphtenic acid (NA). NAs are refractory carboxylic acids considered one of the main causes of toxicity in produced water (PW) by the oil and gas industry [1]. Several treatment processes are being studied to degrade NAs, including BA, such as the UVC/H_2O_2 process [2]. However, to perform mathematical modeling aiming at a better understanding of the oxidation reaction mechanism of a specific compound, it is necessary to determine certain parameters, such as quantum yield. Quantum yield is defined as the fraction of photons that decompose the compound over the total number of photons absorbed by the compound [3]. In this scenario, the aim of this study is to evaluate the direct photolysis of BA by the UVC process under different experimental conditions and develop a mathematical model to determine the quantum yield of BA.

Material and Methods

A direct photolysis of BA by UVC 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 the following variables: initial concentration of BA at 1.00, 5.00 and 10.00 mg/L; initial pH at 3.00, 5.00 and 7.00; and light intensity (LI) at 4, 6 and 8 W, over a total reaction time of 120 minutes. Initially, all assays were adjusted to the specified pH and monitored throughout the experiment without further adjustments.

The photolysis of BA in a photochemical reaction can be described as

$$BA + h\nu \rightarrow Intermediaries \quad (1)$$

The rate of local photolysis incident on a control volume (mol/(m^3 s)) can be described as

$$r_{BA}^{photon} = \phi_{BA} E_{BA,\lambda} \quad (2)$$

where ϕ_{BA} is the quantum yield of BA (mol/Einstein) and $E_{BA,\lambda}$ is the volumetric rate of photons absorbed by BA (Einstein/(m^3 s)) at λ = 254 nm. According to Lambert-Beers's law, the volumetric rate of photons absorved by BA can be expressed as

$$E_{BA,\lambda} = \frac{E_{0,R}^{\lambda}}{l}[1 - exp(-\ln 10\, L \varepsilon_{BA}[BA])] \quad (3)$$

where $E_{0,R}^{\lambda}$ is the spectral photon flux along the collimated beam (Einstein/(m^2 s)), L is the depth of the collimated beam (m) and ε_{BA} is the molar extinction coefficient of BA at λ = 254 nm (m^2/mol). The constants of the compounds are often measured on bench scales. Therefore, the setups are considered perfectly stirred batch reactors, for which we can express, considering Eqs. (2) and (3), the following ordinary differential equation

$$\frac{d[BA]}{dt} = \frac{\phi_{BA} E_{0,R}^{\lambda}}{l}[1 - exp(-\ln 10\, L \varepsilon_{BA}[BA])] \quad (4)$$

where t is the irradiation time (s). The molar extinction coefficient, ε_{BA}, can be measured by UV-Vis spectrometry, the spectral photon flux along the collimated beam, $E_{0,R}^{\lambda}$, can be determined by in situ actionometry, and the quantum yield of BA, ϕ_{BA}, is an adjustable parameter.

Results and Discussion

In Table 1, the molar extinction coefficients of BA (ε_{BA}) are shown for different pH values. At lower pH (1.00 and 3.00), ε_{BA} is 3 to 4 times higher than at higher pH values. This difference is likely due to the conjugated acid-base pair, BA^+ and BA^-. With a pKa of 4.20, BA^+ predominates at pH values below 4.20, while BA^- predominates at higher pH values. This suggests that BA^+ has a greater light absorption capacity than BA^-.

Table 1. Molar extinction coefficient of BA, ε_{BA}, as a function of pH.

pH	1.0	3.0	5.0	7.0	9.0	12.0
ε_{BA}	2565	2479	733	647	671	700

Based on discrete data of pH and ε_{BA} data from Table 1, along with a pKa = 4.20 of BA, it is deduced that in acidic solutions (pH ≈ 1), only the BA^+ form is present, with a molar extinction coefficient denoted as ε_{BA^+}, measured at 2565 L/(molcm). Similarly, in basic solutions (pH ≈ 12), only the form BA^- is present, with a molar extinction coefficient ε_{BA^-}, measured 700 L/(molcm). These findings were utilized to develop a simple model predicting ε_{BA} over a pH range of 0 to 14

$$\varepsilon_{BA} = \varepsilon_{BA^+}\left(\frac{10^{-pH}}{10^{-pH} + K_{a,BA}}\right) + \varepsilon_{BA^-}\left(\frac{K_{a,BA}}{10^{-pH} + K_{a,BA}}\right) \quad (5)$$

Figures 1 and 2 present the experimental results and the data predicted by the mathematical model proposed for different initial concentrations of BA and different initial pH in oxidation by direct photolysis of BA through the UVC process.

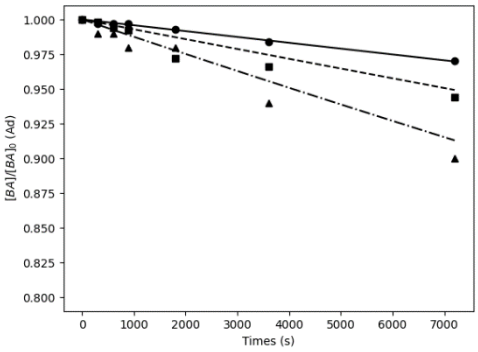

Figure 1. Experimental and numerical results of the effect of the initial BA concentration in oxidation by direct photolysis of BA by UVC process. Experimental conditions: CT_{BA} = (•) 10.00, (■) 5.00 and (▲) 1 mg/L; pH = 3; LI = 8 W.

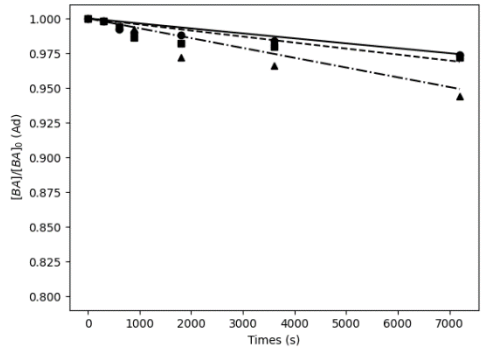

Figure 2. Experimental and numerical results of the effect of the initial pH in oxidation by direct photolysis of BA by UVC process. Experimental conditions: pH = (•) 7.00, (■) 5.00 and (▲) 3.00; C_{BA} = 5 mg/L; LI = 8 W.

The kinetics model, Eq (4), accurately predicts the experimental data and demonstrates the effects of the initial concentration of BA and initial pH. Specifically, lower BA concentrations and pH values result in higher oxidation rates of BA.

To determine the correct ϕ_{BA} of BA, various approaches were conducted, including individual adjustments, adjustments with pH dependence, and a single global fit. Ultimately, it was noticed that there were no significant differences in the results across the different approaches used. An explanation for this pH independence is that different ε_{BA} values were utilized for each pH value from Eq. (5).

The ϕ_{BA} determined was 0.025×10^{-2} mol/Einstein. Comparing with literature data [3], ϕ_{BA} is lower than the quantum yield of benzene (88×10^{-2} mol/Einstein) but it is in the same magnitude as *n*-nitrophenol (0.019×10^{-2} mol/Einstein), considering their similar chemical structures.

Conclusions

The research emphasized the direct photolysis of BA by the UVC process. Through the mathematical model proposed in this study, it was determined that the quantum yield of BA is 0.025×10^{-2} mol/Einstein. The knowledge of the quantum yield is fundamental for the mathematical modeling of the UVC/H_2O_2 process.

Acknowledgments

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