Optimized Degradation of Bisphenol A by UV/H₂O₂ coupled to Microwaves in a Novel Reactional Setup

Pedro Ivo Isá Barrenha* and Eduardo Bessa Azevedo

São Carlos Institute of Chemistry, University of São Paulo
C.P.780, São Carlos/SP, CEP 13560-970, Brazil

*Corresponding author:
Phone: + 55 16 98215-4282
E-mail: pbarrenha@gmail.com
ABSTRACT

In this paper, the UV/H\textsubscript{2}O\textsubscript{2}/MW (microwave) process was compared with the UV/H\textsubscript{2}O\textsubscript{2} one, using bisphenol A (BPA) as a model-pollutant. The proposed experimental setup was operated in batch recycle mode and allows for the direct comparison among different processes: UV only, H\textsubscript{2}O\textsubscript{2} only, MW only, UV/H\textsubscript{2}O\textsubscript{2}, UV/MW, H\textsubscript{2}O\textsubscript{2}/MW, and UV/H\textsubscript{2}O\textsubscript{2}/MW, as well as temperature control to minimize thermal effects. The degradation of BPA at near-environmental concentration (100 \mu g L\textsuperscript{-1}) was optimized by an experimental design approach (Response Surface Methodology) and its residual concentration was measured by HPLC. Approximately 95% of the initial BPA amount could be removed in 30 min at the optimal conditions (\(C_{H_2O_2} = 20\) mg L\textsuperscript{-1}, flow rate = 700 mL min\textsuperscript{-1}, and MW power = 245 W). The experiments designed for comparing the UV/H\textsubscript{2}O\textsubscript{2} and the UV/H\textsubscript{2}O\textsubscript{2}/MW processes showed that the use of MW doubled the initial pseudo-first-order degradation rate (from 0.046 to 0.10 min\textsuperscript{-1}) and significantly increased the maximum oxidation capacity of the system (from 86 to 100\%). Although the reasons behind those results are still unclear, it seems that the existence of non-thermal effects of the MW irradiation should be considered.

KEYWORDS: Bisphenol A; AOP; Microwaves; Experimental Design; UV/H\textsubscript{2}O\textsubscript{2}
DECLARATIONS

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

All data generated or analyzed during this study are included in this published article.

Competing interests

The authors declare that they have no competing interests.

Funding

The funding for this project was possible by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES – Finance code 001) and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq – Process 159001/2015-3).

Authors’ contributions

PIIB performed all experiments, data treatment and interpretation. EBA, as responsible for the project, monitored the whole process and provided all the technical and personal support. Both authors had major contribution for the composition of this manuscript and both authors read and approved its final version.

Acknowledgements

The authors thank the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES – Finance code 001) and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq – Process 159001/2015-3), and Prof. Maria Olímpia de Oliveira Rezende for financial and analytical support, respectively.
1. INTRODUCTION

The production of plastics has been increasing exponentially since the 1960’s, reaching more than 8000 metric tons in 2015. Most of those end up as waste, polluting superficial waters and soil (GEYER et al., 2017). Furthermore, many compounds used in the production of plastics, such as resins and phenols, are hazardous to the biota as a whole. One of those compounds is Bisphenol A (BPA).

BPA (4,4’-isopropylidenediphenol; Nº CAS 80-05-7) is largely used in the production of polycarbonate (KRISHNAN et al., 1993). Due to its moderate solubility (0.15 mg mL$^{-1}$) and log $D_{\text{pH}=7.4}$ (4.04), it can be found in surface waters, groundwaters, domestic and industrial sewage, sediments, and organisms (STAPLES et al., 1998; HING-BIU; PEARL, 2000; YAMAMOTO et al., 2001; MOLINA-MOLINA et al., 2019). Its hazardous effects are significant: endocrine disruption, carcinogenic and estrogenic activities, even in human beings (HOWDESHELL et al., 1999; DOUNG et al., 2009; GRINGRICH et al., 2019; BERGER et al., 2018). As it is also highly persistent in the environment, the development of treatment technologies capable of removing BPA from the environment is of utmost importance.

Advanced Oxidation Processes (AOP) are technologies increasingly studied for the removal of many persistent compounds in the environment, mainly in the aqueous medium. They can be defined as processes that generate highly-reactive, non-selective hydroxyl radicals in sufficient amounts for oxidizing the majority of the complex chemicals present in a wastewater (GOGATE; PANDIT, 2004; CHONG et al., 2010; OLLIS et al., 2011; SILANPÄÄ et al., 2018).

Among the various AOP, the UV/H$_2$O$_2$ process can lead to the complete degradation and mineralization (the conversion into CO$_2$ and H$_2$O) of many organic pollutants (LEGRINI et al., 1993; RIBEIRO et al., 2015). Generally, such systems consist of the addition of H$_2$O$_2$ and the use of a UV light source emitting between 200 and 280 nm (AL-KDASH et al., 2004; STASINAKIS, 2008). That combination leads to increased quantum yields, since both H$_2$O$_2$ and the majority of the organic compounds absorb energy within that range (CHU, 2001; YUAN et al., 2009; SHU et al., 2013). The accepted mechanism for the photolysis of hydrogen peroxide is the homolysis of the molecule into hydroxyl radicals, according to Equation 1 (ESPLUGAS et al., 2002).

$$\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot \text{OH} \quad (1)$$

The UV/H$_2$O$_2$ process has a number of advantages: low waste generation and robustness, as H$_2$O$_2$ is miscible in water and has almost no limitation regarding pH. However, H$_2$O$_2$ in excess acts as a $\cdot$OH radicals scavenger, decreasing the removal efficiency. Nevertheless, long treatment times are usually necessary for achieving total mineralization of the organic matter present, increasing the power consumption.
and hindering its applications at larger scales. Therefore, many studies try to combine the UV/H₂O₂ process to other techniques (BOLTON et al., 1998; KURBUS et al., 2003).

The simultaneous application of microwaves (MW) and UV light leads to better results in photochemical processes. KLÁN et al. (2001) proposed one of the first reactors combining the UV/H₂O₂ process with the MW. The major advantage of MW is its greater ability to accelerate chemical reactions with improved yields and selectivity (PERREUX; LOUPY, 2001; HORIKOSHI et al., 2008).

Several authors have described photochemical reactors in which electrodeless discharge lamps (EDL) are used for the simultaneous application of UV and MW irradiation in photochemical experiments. Some recent studies show the feasibility of combining an AOP with MW for the removal of several compounds: batch UV/H₂O₂/MW systems for removal of Hg (HAO et al., 2020); analysis of different catalysts for heterogenous photocatalysis for nitrobenzene and dyes removal (JEONG et al., 2018; GAYATHRI et al., 2019); recycling systems with different sources of •OH for diatroziate and carbamazepine removal (MENG et al., 2017; ZUO et al., 2020), among others.

However, to our knowledge, all of the studies so far depended on the use of an EDL as the source of UV irradiation, what makes it impossible to assess the role of MW in the UV(EDL)/H₂O₂/MW process (FERRARI et al., 2009; CHEN et al, 2011; REMYA and SWAIN, 2019). This paper proposes a novel reactional setup for the UV/H₂O₂/MW process with no EDL as the UV source, allowing for inferring the existence of MW non-thermal effects.
2. MATERIALS AND METHODS

2.1 Reagents

Table 1 shows some information about bisphenol-A. A stock solution of bisphenol A (Sigma-Aldrich) 10 mg L\(^{-1}\) was prepared with ultrapure water, with no pH adjustment. Analytical grade H\(_2\)O\(_2\) (29% in weight – Synth) was used in the degradation studies. Ammonium metavanadate (Vetec) and sulfuric acid (Mallinckrodt) were used in the residual peroxide analysis. Ultrapure water, HPLC-grade acetonitrile (Merck) and acetic acid (Merck) composed the mobile phase for BPA quantification.

| Name          | Information | Chemical Structure |
|---------------|-------------|-------------------|
| C. I. number: | 80057       |                   |
| Molecular formula: | C\(_{15}\)H\(_{16}\)O\(_2\) | |
| Molecular weight: | 228.29 g mol\(^{-1}\) | |
| \(\lambda_{\text{max}}\): | 227 nm | |
| Vapor pressure | \(4 \times 10^{-8}\) mmHg (25°C) | |
| \(\log D_{\text{ph,7.4}}\) | 4.04 | |
| \(pK_{a1}\) | 9.6 | |
| \(pK_{a2}\) | 10.2 | |
| Solubility | 300 mg L\(^{-1}\) (H\(_2\)O, 25°C) | |

2.2 Reactional System

The proposed reactional system is shown in Figure 1. It consists of an irradiation unit with a medium-pressure mercury vapor lamp (250 W, Philips HPL-N, radiant flux of 108 kJ m\(^{-2}\) s\(^{-1}\) at \(\lambda > 254\) nm) and a magnetic stirrer, connected to an adapted domestic microwave oven (1100 W, 2450 MHz) by a pumping system with silicon hoses. A ventilation system was installed in the microwave to avoid overheating. In order to minimize thermal effects from the microwave heating, a cooling system was placed between the microwave oven and the irradiation unit. The system temperature was monitored at the exit of the microwave oven and at the entrance of the irradiation unit. Flow rate was measured and controlled by a rotameter placed just before the microwave oven. Both reactors (one inside the irradiation unit and another one inside the microwave oven cavity) consisted of borosilicate glass recipients with 250 and 350 mL nominal volume, respectively. The system working volume was fixed at 800 mL.
Fig. 1 Schematics of the reactional system used in this work.

2.3 Experimental Procedure and Analytical Methods

In a typical run, the system was filled with 800 mL of 100 µg L\(^{-1}\) aqueous BPA (pH = 6.0). The working volume of the reactor inside the irradiation unit was fixed at 150 mL, so that the distance between the lamp and the surface of the solution was kept constant (20 cm). The reactor inside the microwave oven (Figure 2) was completely filled. Prior to the experiments, the system was purged in order to eliminate any bubbles, guaranteeing a steady flow. \(\text{H}_2\text{O}_2\) concentration, flow rate, and MW power in each experiment were set according to a factorial design. The experiments were started when turning on the lamp and the MW oven (during 30 min), simultaneously. With the help of the cooling system, the temperature was kept at 20 ± 2ºC at the entrance of the irradiation unit. Two digital thermometers were placed at the irradiation unit and at the exit of the MW oven, so that the temperature could be measured. Experiments running only ultrapure water with different combinations of flow rate and MW power were performed in order to measure the respective temperature increase.
To check whether the $\text{H}_2\text{O}_2$ decomposition by MW heating was significant, the residual concentration of hydrogen peroxide was measured using ammonium metavanadate (Vetec) in acidic medium with $\text{H}_2\text{SO}_4$ (Mallinckrodt), in a series of experiments. That method is based on the red-orange peroxovanadium cation formation when $\text{H}_2\text{O}_2$ reacts with the metavanadate ion, which is monitored at 457 nm (NOGUEIRA; OLIVEIRA; PATERLINI, 2005). Absorbances were measured with a Nanocolor® UV/Vis spectrophotometer (Macherey-Nagel) at 457 nm. The experiments were performed at conditions that favored the degradation of hydrogen peroxide: $\text{H}_2\text{O}_2$ 1 mg L$^{-1}$, BPA 100 µg L$^{-1}$, flow rate 300 mL min$^{-1}$, and MW power 525 W. The experiments were reproduced in the absence of MW radiation and at constant temperature of 20ºC, for comparison purposes. All experiments were performed in triplicate.

In order to optimize the system, an experimental design methodology, namely the response surface methodology (RSM), was used. First, a preliminary $2^3$ full factorial design was performed, with duplicates of each experiment. The studied factors were: initial $\text{H}_2\text{O}_2$ concentration, flow rate, and MW power (the respective levels are shown in Table 2), and the response variable was BPA degradation (BEZERRA et al., 2008).

| Factors          | Levels               |
|------------------|----------------------|
| $C_{\text{H}_2\text{O}_2}$: Concentration of $\text{H}_2\text{O}_2$ (mg L$^{-1}$) | Low (−1)  | High (+1) |
| Flow:            |                      |
| Flow rate (mL min$^{-1}$) | 300          | 600        |
| MW:              |                      |
| Microwave power (W) | 245          | 525        |

The experiments were randomly performed to minimize systematic errors. The experimental error was determined by the joint variance (Equation 2), in which $s$ is the experimental error, $v_i$ and $s_i^2$ are the degree of freedom and the variance of each duplicate, respectively.
\[ s = \sqrt{\frac{\nu_1 s_1^2 + \nu_2 s_2^2 + \cdots + \nu_n s_n^2}{\nu_1 + \nu_2 + \cdots + \nu_n}} \]  

Second, based on the obtained results, a series of experiments were performed along the path of steepest ascent, i.e., aiming at increasing degradation, until the optimal region was reached (Table 4). Finally, the optimal degradation condition was obtained with additional experiments that followed an experimental design with more than two levels (BEZERRA et al., 2008). The Statistica® 11.0 software was used for the necessary calculations.

Due to the low initial concentration of BPA, extraction and concentration were necessary. The selected methodology was the vortex-assisted liquid-liquid microextraction (VALLME) (YIANTZI et al., 2010). Ten milliliters of sample, collected immediately after degradation, were placed into a 15-mL Falcon tube. Afterwards, 0.1 mL of n-octanol was added and mixed with a vortex mixer (Vortex NA 3600, Norte Científica) for 2 min at 2800 rpm and centrifuged (Hettich Rotina 380, Andreas Hettich GmbH & Co.) at 3000 rpm for 5 min. The organic phase was recovered with a micro-syringe and placed into a 150-µL insert for analysis. The same procedure was performed with stock solutions with concentrations of 5, 10, 20, 50, 75 and 100 µg L\(^{-1}\) in order to obtain a calibration curve to quantify the concentration of BPA (\(R^2 = 0.996\)).

The BPA concentration was measured by liquid chromatography with UV-detection (LC-UV), using a Shimadzu LC 20 AD HPLC. The selected column was a reverse-phase Agilent Zorbax SB-C\(_8\). The mobile phase was composed of H\(_2\)O + 1% acetic acid (Panreac) and acetonitrile (Panreac) at 50:50 ratio (in volume), flow rate 1.0 mL min\(^{-1}\). The acquisition time was 8 min, injection volume 20 µL, and detection wavelength 230 nm (ARAUJO; SANTOS; TEIXEIRA, 2017).

In order to assess the effects of the MW irradiation on the system, kinetic tests were performed with and without the use of the MW oven. Nine runs were performed, meaning 0, 5, 10, 15, 20, 25, 30, 40, 50, and 60 min of reaction. The reactional conditions were defined by the optimized ones obtained with the experimental design.

The removal kinetics of BPA was estimated based on the model proposed by Chan and Chu (CHAN; CHU, 2004) in which \(C\) is the concentration of BPA at time \(t\) (h), \(C_0\) is the initial concentration of BPA, \(\rho\) (h) and \(\sigma\) (dimensionless) are two characteristic constants related to the reaction kinetics and the oxidation capacity, respectively (Equation 3).

\[ \frac{C}{C_0} = 1 - \frac{t}{\rho + \sigma t} \]  

The slope of the decay curve at any time can be mathematically determined by taking its derivative in time (Equation 4).
\[
\frac{d(C/C_0)}{dt} = -\frac{\rho}{(\rho + \sigma t)^2}
\]  

(4)

When \( t \) tends to zero, the slope tends to \(-1/\rho \) (h\(^{-1}\)) and its physical meaning is the initial (pseudo-first-order) removal rate of BPA. The removal rate here has no concentration units because \( C/C_0 \) is dimensionless.

On the other hand, when \( t \) is long enough, tending to infinity, \( 1/\sigma \) is the theoretical maximum removal fraction, which is equivalent to the maximum oxidation capacity (MOC) of the system (Equation 5).

\[
\frac{1}{\sigma} = 1 - \frac{C_{t=\infty}}{C_0}
\]  

(5)

The characteristic constants (\( \rho \) and \( \sigma \)) were estimated with the aid of the Solver package (Excel\textsuperscript{®} software), using the Generalized Reduced Gradient (GRG) nonlinear solving and least squares methods.
3 RESULTS AND DISCUSSION

3.1 Temperature Increase and \( \text{H}_2\text{O}_2 \) Decomposition by Microwave Heating

From the exit of the cooling system to the entrance of the MW oven, the temperature was maintained at 20 ± 2°C. Some experiments evaluating the temperature increase at the exit of the MW oven, depending on flow rate and MW power, are described in Table 3. As expected, the lowest flow rate combined with the highest MW power generated the greatest temperature increase: 15 ± 2°C.

Table 3. Temperature at the exit of the MW oven, depending on flow rate and MW power, after 30 min.

| Flow Rate (mL min\(^{-1}\)) | MW Power (W) | Temperature (°C) |
|------------------------------|--------------|------------------|
| 600                          | 245          | 24 ± 2           |
| 600                          | 525          | 32 ± 2           |
| 300                          | 245          | 28 ± 2           |
| 300                          | 525          | 35 ± 2           |

Nonetheless, the observed temperature increases seemed not to significantly interfere with the concentration of hydrogen peroxide at the end of the reaction period (30 min): 601 ± 8 \( \mu \)g L\(^{-1}\) and 616 ± 5 \( \mu \)g L\(^{-1}\) with and without MW irradiation, respectively. Those results show the temperature increase due to the MW radiation did not significantly decompose hydrogen peroxide.

3.2 Experimental Design

Table 4 shows the results obtained after performing the preliminary 2\(^3\) full factorial design. The experimental error, calculated by Equation 1, was low enough for continuing with the experiments: 1.8%. It is noteworthy that replicas 5 and 13 presented BPA degradations over 90%. That shows a tendency of increasing degradation with higher \( \text{H}_2\text{O}_2 \) concentration and flow rate.
Table 4. BPA degradation (%) achieved in the preliminary $2^3$ full factorial design.

| Experiment # | $C_{H_2O_2}$ | Flow Rate | MW | Degradation (%) |
|--------------|--------------|-----------|----|-----------------|
| 1            | 1            | -1        | 1  | 41.7            |
| 2            | 1            | 1         | -1 | 38.2            |
| 3            | 1            | -1        | -1 | 54.4            |
| 4            | 1            | -1        | 1  | 67.3            |
| 5            | 1            | 1         | -1 | 90.1            |
| 6            | 1            | 1         | 1  | 81.0            |
| 7            | 1            | -1        | 1  | 55.2            |
| 8            | 1            | -1        | -1 | 76.4            |
| 9            | 1            | 1         | -1 | 45.0            |
| 10           | 1           | -1        | 1  | 41.3            |
| 11           | 1           | -1        | -1 | 58.6            |
| 12           | 1           | 1         | 1  | 66.5            |
| 13           | 1           | 1         | -1 | 90.6            |
| 14           | 1           | 1         | 1  | 80.5            |
| 15           | 1           | -1        | 1  | 58.3            |
| 16           | 1           | -1        | -1 | 77.1            |

The Pareto chart shown in Figure 3 allows one to assess the statistical significance of each factor and of their respective interactions (bars that cross the red line, 95% confidence interval). All factors and interactions were significant within the studied ranges. The $C_{H_2O_2}$ factor was the most significant one, as hydrogen peroxide is the source of hydroxyl radicals, responsible for BPA degradation. Its positive effect (positive number next to the respective bar) means that degradation increased when the $C_{H_2O_2}$ factor was varied from the low to the high level. The flow rate factor also had a positive effect probably because increased flow rates allow for greater volumes of solution to be irradiated during the reaction time.

On the other hand, MW power presented a negative effect within the studied range. As showed before, the variation of temperature seems to not influence the production of hydroxyl radicals. However, one cannot state whether the presence of MW radiation does or does not influence BPA degradation kinetics and/or the generation of the degradation products. Moreover, that negative effect does not necessarily mean that the MW radiation was detrimental to the system, when compared to another system without it.
The next step was performing experiments along the path of steepest ascent. The results are summarized in Table 5. Due to the impossibility of freely changing the MW power, it was set at 245 W (low level). Within 60 minutes, removal values of BPA close to 95% were achieved with experiment 20, whereas experiments 21 and 22 both achieved 95.9% of removal. Those figures were too high to proceed with the optimization procedure. Therefore, the following experiments were performed during 30 min (half of the time).

### Table 5. Factors (and levels) evaluated in the path of steepest ascent and the respective degradations.

| Experiment # | $C_{\text{H}_2\text{O}_2}$ (mg L$^{-1}$) | Flow Rate (mL min$^{-1}$) | Degradation (%) |
|--------------|---------------------------------|---------------------------|-----------------|
| 17           | 3                               | 450                       | 69.1            |
| 18           | 5                               | 529                       | 80.2            |
| 19           | 7                               | 608                       | 86.5            |
| 20           | 9                               | 687                       | 94.1            |
| 21           | 11                              | 766                       | 95.9            |
| 22           | 13                              | 845                       | 95.9            |

From the results of the experiments along the path of steepest ascent, a new $2^3$ full factorial design was performed, central point in triplicate (Table 6). Experiment 24 was the one with the greatest BPA degradation, achieving 91.2% of removal with higher concentration of H$_2$O$_2$ and lower flow rate. According to the Pareto chart (Figure 4), the variation of $C_{\text{H}_2\text{O}_2}$ had a positive effect on the reaction system and was statistically significant within the studied range; on the other hand, the increment of flow.
rate values tends to reduce the removal of BPA, although it was not statistically significant, again within the studied range.

Table 6. BPA degradations achieved in the $2^2$ full factorial design

| Factors               | Levels          |          |          |
|-----------------------|-----------------|----------|----------|
| $C_{H_2O_2}$: Concentration of $H_2O_2$ (mg L$^{-1}$) | Low (−1)       | Central (0) | High (+1) |
| Flow: Flow rate (mL min$^{-1}$)  | 8.0              | 11.0     | 14.0     |
| 700                   | 760             | 820      |

| Experiment # | $C_{H_2O_2}$ | Flow | Degradation (%) |
|--------------|--------------|------|-----------------|
| 23           | +1           | +1   | 89.6            |
| 24           | +1           | −1   | 91.2            |
| 25           | −1           | +1   | 79.3            |
| 26           | −1           | −1   | 84.0            |
| 27           | 0            | 0    | 84.8            |
| 28           | 0            | 0    | 85.1            |
| 29           | 0            | 0    | 86.3            |

Fig. 4 Pareto chart for BPA degradation: $2^2$ full factorial design.

The response surface for the latter experiments (Figure 5) showed that the optimal condition was not achieved yet. Therefore, a new series of experiments were performed, varying only $C_{H_2O_2}$ and setting MW power and flow rate factors at 245 W and 700 mL min$^{-1}$, respectively. The results are shown in Table 6. With $C_{H_2O_2}$ at 20 mg L$^{-1}$, BPA removal reached a plateau and slightly decreased with greater concentrations. Perhaps an excess of $H_2O_2$ was acting as a hydroxyl radical scavenger, reducing the efficiency of the reaction (WATTS; ROSENFIELD; LINDEN, 2007; KATSOYIANNIS; CANONICA; von GUNTHER, 2011).
Fig. 5 Response surface for the $2^2$ full factorial design.

Table 6. BPA degradations accordingly to $C_{H_2O_2}$.

| Experiment # | $C_{H_2O_2}$ (mg L$^{-1}$) | Degradation (%) |
|--------------|---------------------------|-----------------|
| 30           | 14.0                      | 91.2            |
| 31           | 16.0                      | 91.4            |
| 32           | 18.0                      | 93.1            |
| 33           | 20.0                      | 94.8            |
| 34           | 24.0                      | 94.8            |
| 35           | 28.0                      | 94.7            |
| 36           | 23.0                      | 94.6            |

Finally, the optimal degradation conditions were set: $C_{H_2O_2} = 20$ mg L$^{-1}$, flow rate = 700 mL min$^{-1}$, and MW power = 245 W. In 30 min, approximately 95% of the initial BPA was removed.

3.3 The Effect of MW Radiation

The main feature of the proposed setup is the possibility of performing degradations by several means: UV only, H$_2$O$_2$ only, MW only, UV/H$_2$O$_2$, UV/MW, H$_2$O$_2$/MW, and UV/H$_2$O$_2$/MW. Therefore, the BPA degradation by the UV/H$_2$O$_2$/MW and the UV/H$_2$O$_2$ combinations were directly compared. At the optimal conditions, no significant difference was observed between them, both achieving 95% BPA degradation in 30 min. This finding contradicts the preliminary factorial design, which demonstrated that MW radiation did have a significant effect.
Then, it was hypothesized that high H$_2$O$_2$ concentrations could “mask” the effect MW have, resulting in similar results. To check that hypothesis, the reaction conditions were changed to the ones of experiments # 5/13 from the preliminary factorial design (C$_{H_2O_2}$ = 5 mg L$^{-1}$, flow rate = 600 mL min$^{-1}$, and MW = 245 W). The corresponding results are presented in Figure 6.

![Figure 6 BPA removal kinetics with and without MW irradiation: (a) Control experiments and (b) BPA degradation experiments. Symbols: experimental data. Solid lines: adjusted Chan and Chu (2004) model. Modeling parameters: $\rho$ and $\sigma$. Modeling results: $r_0$, MOC, and $R^2$.](image)

The results showed a significant difference between the UV/H$_2$O$_2$ and the UV/H$_2$O$_2$/MW systems: in 60 min, 65 and 95% BPA degradations were achieved, respectively. Moreover, the MW roughly doubled the initial pseudo-first-order degradation rate (from 0.046 to 0.10 min$^{-1}$) and the MOC increased from 86 to 100%.

The reasons behind those results are still unclear. The temperature increase of 4 ± 2°C inside the MW oven does not seem to be solely responsible for doubling the initial degradation rate. As argued by many researchers, MW radiation may favor some reaction mechanisms among others, which may lead to different degradation rates and oxidation capacities. As discussed before, the real effects of MW radiation on any reactional system are still under debate in the scientific community, remaining the existence of non-thermal MW effects an open question (NÜTCHER et al., 2004; DUDLEY et al., 2015; DÍAZ-ORTIZ et al., 2019; TIAN; LIO; ZU, 2020).

### 3.4 Comparison with the literature

Comparing the present study with others already published is a challenge. Different initial BPA and H$_2$O$_2$ concentrations, pH, treatment times, removal rates, irradiation sources, reactors geometries, as well as their operating mode (batch or batch recycle) makes that task almost impossible. Moreover, no papers dealing with the UV/H$_2$O$_2$/MW degradation of BPA were found.
Nevertheless, within the last six years, three papers studied the degradation of BPA by UV/H$_2$O$_2$. Sharma, Mishra, and Kumar compared two processes: UV/H$_2$O$_2$ and UV/S$_2$O$_8^{2-}$ (SHARMA; MISHRA; KUMAR, 2015). Araujo, Santos, and Teixeira assessed the role of process variables through an experimental design approach (batch recycle mode) (ARAUJO; SANTOS; TEIXEIRA, 2017). Liu et al. specifically tested the UV/H$_2$O$_2$/O$_3$ process (LIU et al., 2018). Table 7 summarizes (and somewhat compares) this work with those other three.

As one can see in Table 7, regarding the UV/H$_2$O$_2$ process, the normalized removal rate, $\bar{r}$, obtained by Sharma, Mishra, and Kumar (2015) is one order of magnitude lower than the other two. Moreover, the use of O$_3$ by Liu et al. (2018) did not improve BPA degradation. However, two points must be highlighted.

First, the results reported by Liu et al. (2018) are difficult to be compared with the others due to the pH they used (9.0), which is close to the pKa of BPA (9.6). Certainly, at that pH, the concentration of the conjugated base of BPA is quite significant. Therefore, the reactions involved in the BPA degradation were probably different. Second, as Sharma, Mishra, and Kumar (2015) did not optimize the reaction using a multivariate approach, it is not fair to compare optimized and non-optimized degradations.

### Table 7. Comparative table between this work and the literature (last five years).

| Reaction Conditions | UV/H$_2$O$_2$ only | “Improved” UV/H$_2$O$_2$ |
|---------------------|---------------------|--------------------------|
|                     | Sharma et al. (2015)| Araujo et al. (2017)     |
| $C_{BPA}$ (µg L$^{-1}$) | 50,000              | 48,200                   |
| $C_{H_2O_2}$ (mg L$^{-1}$) | 400                 | 260                      |
| $pH^0$            | 6.0 ± 0.5           | 7.0                      |
| Lamp               | 254                 | 254                      |
| Nominal power (W) | 40                  | 36                       |
| Main emission (nm) | 254                 | polychromatic            |
| $V_{total}$ (mL)  | 450                 | 5,000                    |
| $V_{irradiated}$ (mL) | 450               | 3,900                    |
| $Q$ (mL min$^{-1}$) | —                  | 400                      |
| $m_{BPA,removed}$ (µg) | 42,500             | 241,000                  |
| Operating mode     | batch               | batch recycle            |
| $t_{treatment}$ (min) | 360               | 30.0                     |
| $t_{irradiation}$ (min)$^3$ | 360              | 23.4                     |
| Normalized removal rate, $\bar{r}$ (min$^{-1}$)$^4$ | $5.3 \times 10^{-3}$ | $4.3 \times 10^{-2}$ |

$^1$ UV/H$_2$O$_2$/O$_3$; $^2$ UV/H$_2$O$_2$/MW; $^3$ $t_{irradiation} = t_{treatment} \times \frac{V_{irradiated}}{V_{total}}$; $^4$ $\bar{r} = \frac{m_{BPA,removed}}{t_{irradiation} \times C_{BPA} \times V_{total}}$; $^5$ Power emitted below 300 nm, which is the spectral region within which both BPA and H$_2$O$_2$ absorb.
Nevertheless, once more it becomes evident the effect MW had on the system. The amount of BPA removed, $m_{\text{BPA,removed}}$, increased significantly (from 42.2 to 65.5 μg, which is approximately 1.5 times greater), as well as the normalized removal rate (from $9.4 \times 10^{-2}$ to $1.5 \times 10^{-1}$).
4 CONCLUSIONS

• The proposed experimental setup allows for the direct comparison among different processes (UV only, H₂O₂ only, MW only, UV/H₂O₂, UV/MW, H₂O₂/MW, and UV/H₂O₂/MW). Therefore, the true contributions of UV, H₂O₂, and MW to the degradation of any compound/pollutant can be easily assessed.

• The response surface methodology allowed for optimizing the degradation system with a small number of experiments and yet, statistically sound information.

• The effect of microwaves upon BPA degradation was only perceivable at relatively low H₂O₂ concentrations. It was hypothesized that increased H₂O₂ concentrations would allow for the generation of great amounts of hydroxyl radical, “masking” effects of smaller magnitude, as it is the case of that of microwaves in this system.

• The effect microwaves exerted upon the system was two-fold: both the pseudo-first-order degradation rate and the maximum oxidation capacity were significantly enhanced.
REFERENCES

AL-KDASH, A.; IDRIS, A.; SAED, K.; GUAN, C. T. Treatment of textile Wastewater by Advanced Oxidation Processes – A review. Glob. Nest Int. J. 6(3) (2004) 222-230. https://journal.gnest.org/sites/default/files/Journal%20Papers/Al-kdassi-222-230.pdf

ARAUJO, L. G.; SANTOS, F. S.; TEIXEIRA, A. C. S. C. Degradation of bisphenol A by UV and UV/H$_2$O$_2$ processes: Evaluation of process variables through experimental design. Can. J. Chem. Eng. 95(12) (2017) 2278-2285. http://doi.org/10.1002/cjce.22997.

BERGER, K.; ESKENAZI, B.; BALMES, J.; KOGUT, K.; HOLLAND, N.; CALAFAT, A. M.; HARLEY, K. G. Prenatal high molecular weight phthalates and bisphenol A, and childhood respiratory and allergic outcomes. Pediatr. Allerg. Immunol. 30(1) (2018) 36-46. http://doi.org/10.1111/pai.12992.

BEZERRA, A. M.; SANTELLI, R. E.; OLIVEIRA, E. P.; VILLAR, L. S.; ESCALEIRA, L. A. Response surface methodology (RSM) as a tool for optimization in analytical chemistry. Talanta. 76(5) (2008) 965-977. http://doi.org/10.1016/j.talanta.2008.05.019.

BOLTON, J. R.; VALLADARES, J. E.; ZANIN, J. P.; COOPER, W. J.; NICKELSEN, M. G.; KAJDI, D. C.; WAITE, T. D.; KURUCZ, C. N. Figures-of-Merit for Advanced Oxidation Technologies: A Comparison of Homogeneous UV/H$_2$O$_2$, Heterogeneous UV/TiO$_2$ and Electron Beam Processes. J. Adv. Oxid. Technol. 3(2) (1998) 174-181. http://doi.org/10.1515/jaots1998-0211.

CHAN, K. H.; CHU, W. Modeling the reaction kinetics of Fenton’s process on the removal of atrazine. Chemosphere. 51(4) (2004) 305-311. http://doi.org/10.1016/S0045-6535(02)00812-3.

CHEN, H.; BRAMANTI, I.; LONGO, I.; ONOR, M., FERRARI, C. Oxidative decomposition of atrazine in water in the presence of hydrogen peroxide using an innovative microwave photochemical reactor. J. Hazard. Mater. 186(2-3) (2011) 1808-1815. http://doi.org/10.1016/j.jhazmat.2010.12.065.

CHONG, M. N.; JIN, B.; CHOW, C. W. K.; SAINT, C. Recent developments in photocatalytic water treatment technology: A review. Water Res. 44(10) (2010) 2997-3027. http://doi.org/10.1016/j.watres.2010.02.039.

CHU, W. Modeling the quantum yields of herbicide 2,4-D decay in UV/H$_2$O$_2$ process. Chemosphere. 44(5) (2001) 935-941. http://doi.org/10.1016/S0045-6535(00)00556-7.

DIÁZ-ORTIZ, Á.; PIETRO, P.; de la HOZ, A. A critical Overview on the Effect of Microwave Irradiation in Organic Synthesis. Chem. Rec. 19(1) (2019) 85-97. http://doi.org/10.1002/tcr.201800059.

DUDLEY, G. B.; RICHERT, R.; STIEGMAN, A. E. On the existence of and mechanism for microwave-specific reaction rate enhancement. Chem. Sci. 6(4) (2015) 2144-2152. http://doi.org/10.1039/C4SC03372H.

ESPLUGAS, S.; GIMÉNEZ, J.; CONTRERAS, S.; PASCUAL, E.; RODRÍGUEZ, M. Comparison of different advanced oxidation processes for phenol degradation. Water Res. 36(4) (2002) 1034-1042. http://doi.org/10.1016/S0043-1354(01)00301-3.

FERRARI, C.; LONGO, I.; TOMBARI, E.; BRAMANTI, E. A novel microwave photochemical reactor for the oxidative decomposition of Acid Orange 7 azo dye by MW/UV/H$_2$O$_2$ process. J. Photochem. Photobiol. A: Chem. 204(2-3) (2009) 115-121. http://doi.org/10.1016/j.jphotochem.2009.03.001.

GAYATHRI, P. V.; YESODHARAN, S.; YESODHARAN, E. P. Microwave/Persulfate assisted ZnO mediated photocatalysis (MW/PS/UV/ZnO) as an efficient advanced oxidation process for the removal of RhB dye pollutant from water. J. Environ. Chem. Eng. 7(103122) (2019) 1-16. https://doi.org/10.1016/j.jece.2019.103122
GEYER, R.; JAMBECK, J. R.; LAW, K. L. Production, use and fate of all plastics ever made. Sci. Adv. 3(7) (2017) 1-5, 2017. http://doi.org/10.1126/sciadv.1700782.

GOGATE, P. R.; PANDIT, A. B. A review of imperative technologies for wastewater treatment I: Oxidation technologies at ambient conditions. Adv. Environ. Res. 8(3-4) (2004) 501-551. http://doi.org/10.1016/S1093-0191(03)00032-7.

GRINGRICH, J.; PU, Y.; EHRHARDT, R.; KARTHIKRAI, R.; KANNAN, K.; VEIGA-LOPEZ, A. Toxicokinetics of bisphenol A, bisphenol S and bisphenol F in a pregnancy sheep model. Chemosphere. 220 (2019) 185-194. http://doi.org/10.1016/j.chemosphere.2018.12.109

HAO, H.; WANG, Z.; GONG, Y.; MA, Z.; QIAN, Z.; LUO, Y.; YUAN, B.; ZHAO, Y. Photocatalytic removal of NO and Hg\(^0\) using microwave induced ultraviolet irradiation \(\text{H}_2\text{O}_2/\text{O}_2\) mixture. J. Hazard. Mater. 383(121135) (2020) 1-9. https://doi.org/10.1016/j.jhazmat.2019.121135

HIGGINS, L.; PEART, T. E. Bisphenol A contamination in Canadian municipal and industrial wastewater and sludge samples. Water Qual. Res. J. 35 (2) (2000) 283-298. http://doi.org/10.2166/wqrj.2000.018

HORIKOSHI, S.; TSUZUKI, J.; KAJITANI, M.; ABE, M.; SERPONE, N. Microwave-enhanced radical reactions at ambient temperature Part 3: Highly selective radical synthesis of 3-cyclohexyl-1-phenyl-1-butanone in a microwave double cylindrical cooled reactor. New J. Chem. 32 (2008) 2257-2262. http://doi.org/10.1039/B810142F.

HOWDESHELL, K. L.; HOTCHKISS, A. K.; THAYER, K. A.; VANDERBERGH, J. G.; von SAAL, F. S. Environmental toxins: Exposure to bisphenol A advances puberty. Nat. 401(6755) (1999) 763-764. http://doi.org/10.1038/44517

JEONG, S.; LEE, H.; PARK, H.; JEON, K.-J.; PARK, Y.-K.; JUNG, S.-C. Rapid photocatalytic degradation of nitrobenzene under the simultaneous illumination of UV and microwave radiation fields with a TiO\(_2\) ball catalyst. Catal. Today. 307(1) (2018) 65-72. https://doi.org/10.1016/j.cattod.2017.02.033

KATSOYIANNIS, I. A.; CANONICA, S.; von GUNTER, U. Efficiency and energy requirements for the transformation of organic micropollutants by ozone, \(\text{O}_3/\text{H}_2\text{O}_2\) and \(\text{UV}/\text{H}_2\text{O}_2\). Water Res. 45(13) (2011) 3811-3822. http://doi.org/10.1016/j.watres.2011.04.038.

KLÁN, P.; HÀJEK, M.; CÍRKVA, V. The electrodeless discharge lamp: a prospective tool for photochemistry Part 3: The microwave photochemistry reactor. J. Photochem. Photobiol. A 128(1-3) (2001) 145-149. https://doi.org/10.1016/S1010-6030(01)00422-1.

KRISHNAN, A. V.; STATHIS, P.; PERMUTH, S. F., TOKES, L.; FILEDMAN, D. Bisphenol-A: An estrogenic substance is released from polycarbonate flasks during autoclaving. Endocrinol. 135 (6) (1993) 2279-2286, 1993. http://doi.org/10.1210/endo.132.6.8504731.

KURBUS, T.; LE MARECHAL, A. M.; VONČINA, D. B. Comparison of \(\text{H}_2\text{O}_2/\text{UV}\), \(\text{H}_2\text{O}_2/\text{O}_3\) and \(\text{H}_2\text{O}_2/\text{Fe}^{3+}\) processes for the decolorisation of vinylsulphone reactive dyes. Dye. Pigment. 58(3) (2003) 245-252. http://doi.org/10.1016/S0143-7208(03)00085-8.

LEGRINI, O., OLIVEROS, E., BRAUN, A. M. Photochemical processes for water treatment. Chem. Rev. 93(2) (1993) 671-698. http://doi.org/10.1021/cr00018a003.

LIU, Z.; WARDENIER, N.; HOSSEINZADEH, S.; VERHEUST, V.; DE BUYCK, P.-J.; CHYS, M.; NIKIFOROV, A.; LEYS, C.; van HULLE, S. Degradation of bisphenol A by combining ozone with UV and \(\text{H}_2\text{O}_2\) in aqueous solutions: mechanism and optimization. Clean Technol. Environ. Policy. 20(9) (2018) 2109-2118. http://doi.org/10.1007/s10098-018-1595-2.

MENG, L.; YANG, S.; SUN, C.; HE, H.; XIAN, Q.; LI, S.; WANG, G.; ZHANG, L.; JIANG, D. A novel method for photo-oxidative degradation of diatrizoate in water via electromagnetic induction electrodless lamp. J. Hazard. Mater. 337(1) (2017) 34-46. http://doi.org/10.1016/j.jhazmat.2017.05.005.
MOLINA-MOLINA, J. M.; JIMÉNEZ-DÍAZ, I; FERNANDÉZ, M. F.; RODRIGUEZ-CARRILLO, A.; PEINALDO, F. M.; MUSTIELES, V.; BAROUKI, R.; PICCOLI, C.; OLEA, N.; FREIRE, C. Determination of bisphenol A and bisphenol S concentration and assessment of estrogen- and anti-androgen-like activities in thermal paper receipts from Brazil, France and Spain. Environ. Res. 170 (2019) 406-415. http://doi.org/10.1016/j.envires.2018.12.046

NOGUEIRA, R. F. P.; OLIVEIRA, M. O.; PATERLINI, W. C. Simple and fast spectrophotometric determination of H$_2$O$_2$ in photo-Fenton reactions using metavanadate. Talanta. 66(1) (2005) 86-91. http://doi.org/10.1016/j.talanta.2004.10.001.

NÜTCHER, M.; ONDRUSCHKA, B.; BONRATH, W.; GUM, A. Microwave assisted synthesis – a critical technology overview. Green Chem. 6(3) (2004) 128-141. http://doi.org/10.1039/B310502D.

PERREUX, L.; LOUPY, A. A tentative rationalization of microwave effects in organic synthesis according to the reaction medium, and mechanistic considerations. Tetrahedron. 57(45) (2001) 9199-9223. http://doi.org/10.1016/S0040-4020(01)00905-X.

REMYA, N.; SWAIN, A. Soft drink industry wastewater treatment in microwave photocatalytic system – Exploration of removal efficiency and degradation mechanism. Sep. Purif. Technol. 210 (2019) 600-607. https://doi.org/10.1016/j.seppur.2018.08.051

RIBEIRO, A. R.; NUNES, O. C.; PEREIRA, M. F. R.; SILVA, A. M. T. An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU. Environ. Int. 75 (2015) 33-51. http://doi.org/10.1016/j.envint.2014.10.027.

SHARMA, J.; MISHRA, I. M.; KUMAR, V. Degradation and mineralization of Bisphenol A (BPA) in aqueous solution using advanced oxidation processes: UV/H$_2$O$_2$ and UV/S$_2$O$_8^2$ oxidation systems. J. Environ. Manag. 156 (2015) 266-275. http://doi.org/10.1016/j.jenvman.2015.03.048.

SHU, Z.; BOLTON, J. R.; BELOSEVIC, M.; EL DIN, M. G. Photodegradation of emerging micropollutants using the medium-pressure UV/H$_2$O$_2$ Advanced Oxidation Process. Water Res. 47(8) (2013) 2881-2889. http://doi.org/10.1016/j.watres.2013.02.045.

SILANPÄÄ, M.; NCIBI, M. C.; MATILAINEN, A. Advanced oxidation processes for the removal of natural organic matter from drinking water sources: A comprehensive review. J. Environ. Man. 208 (2018) 56-76. http://doi.org/10.1016/j.jenvman.2017.12.009.

STAPLES, C. A.; DOME, P. B.; KLECKA, G. M.; OBLOCK, S. T.; HARRIS, L. R. A review of the environmental fate, effects, and exposure of bisphenol A. Chemosphere. 36 (10) (1998) 2149-2173. http://doi.org/10.1016/S0045-6535(97)10133-3.

STASINAKIS, A. S. Use of selected Advanced Oxidation Processes (AOPs) for wastewater treatment – A mini review. Glob. Nest J. 10(3) (2008) 376-385. https://journal.gnest.org/sites/default/files/Journal%20Papers/376-385_598_Stasinakis_10-3.pdf

TIAN, W.; LI, Z. WU, L. Experimental demonstration of a microwave non-thermal effect in DMSO-NaCl aqueous solution. Chem. Phys. 528(1) (2020) 1-5. http://doi.org/10.1016/j.chemphys.2019.110523.

WATTS, M. J.; ROSENFELDT, E. J.; LINDEN, K. G. Comparative OH radical oxidation using UV-CI2 and UV-H$_2$O$_2$ processes. J. Water Supply: Res. Technol. Aqua. 56(8) (2007) 469-477. http://doi.org/10.2166/aqua2007.028.

YAMAMOTO, T.; YASUHARA, A.; SHIRAISHI, H.; NAKASUGI, O. Bisphenol A in hazardous waste landfill leachates. Chemosphere. 42(2) (2001) 415-418. http://doi.org/10.1016/S0045-6535(00)00079-5

YIANTZI, E.; PSILLAKIS, E.; TYROVOLA, K.; KALOGERAKIS, N. Vortex-assisted liquid-liquid microextraction of octylphenol, nonylphenol and bisphenol-A. Talanta. 80(5) (2010) 2057-2062. http://doi.org/10.1016/j.talanta.2009.11.005.
YUAN, F.; HU, C.; HU, X.; QU, J.; YANG, M. Degradation of selected pharmaceuticals in aqueous solution with UV and UV/H₂O₂. Water Res. 43(6) (2009) 1766-1774. http://doi.org/10.1016/j.watres.2009.01.008.

ZUO, S.; LI, D.; XU, H.; XIA, D. An integrated microwave-ultraviolet catalysis process of four peroxides for wastewater treatment: Free radical generation rate and mechanism. Chem. Eng. J. 122434 (2020) https://doi.org/10.1016/j.cej.2019.122434