Eclética Química Journal

Original article

iq.unesp.br/ecletica

| Vol. 46 | n. 2 | 2021 |

Heterogeneous photodegradation of bisphenol A and ecotoxicological evaluation post treatment

Bianca Veloso Goulart[1], Patrícia Maralyne Lopes Lisboa Fagundes[1], Amanda Rosa Peres[1], Alessandra Carolina da Costa[1], Ana Lúcia Fonseca[2], Márcia Matiko Kondo[1], Sandro José de Andrade[1+]

1. Federal University of Itajubá, Institute of Physics and Chemistry, Itajubá, Brazil.
2. Federal University of Itajubá, Institute of Natural Resources, Itajubá, Brazil.

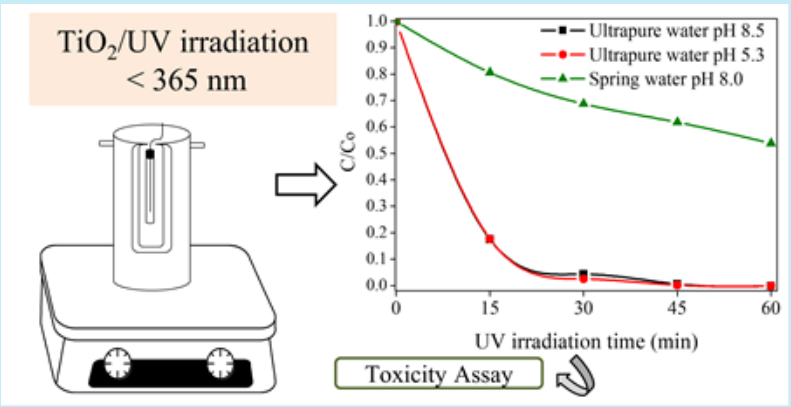
+Corresponding author: Sandro José de Andrade, **Phone:** +55 (35) 3629-1885, **Email address:** sandroandrade@unifei.edu.br

ARTICLE INFO

Article history:
Received: May 12, 2020
Accepted: September 08, 2020
Published: April 01, 2021

Keywords
1. emerging contaminants
2. titanium dioxide
3. ecotoxicological assays
4. *Daphnia similis*
5. *Raphidocelis subcapitata*

ABSTRACT: Bisphenol A (BPA) is an emerging pollutant with endocrine disrupting properties that can be found at trace levels in various aqueous environments. Conventional water and wastewater treatments are not designed to efficiently remove these substances. Therefore, this work investigates the removal of BPA by an Advanced Oxidation Process (AOP), specifically heterogeneous photocatalysis using TiO_2. The influences of the TiO_2 concentration (1.0–10.0 mg L^{-1}), pH (5.3 and 8.5) and effects matrix composition were studied for the removal of BPA at a concentration of 0.8 mg L^{-1}. The results indicated that BPA was completely removed after 45 min of treatment using 7.5 and 10 mg L^{-1} of TiO_2, under constant aeration and artificial UV irradiation, at the different pH values. The use of solar radiation as an UV source was also effective, removing BPA after 60 min of irradiation at pH without adjustment, as well as at pH 8.5. Ecotoxicological evaluation indicated that the post-treatment samples did not present acute effects towards *Daphnia similis*. Evaluation of chronic toxicity with *Raphidocelis subcapitata* showed that there was a reduction in the negative effect of BPA under the growth rate of algae biomass after 60 min of treatment, compared to the initial sample.



ISSN: 1678-4618
DOI: 10.26850/1678-4618eqj.v46.2.2021.p48-56

1. Introduction

The endocrine disruptors (EDs) are a class of substances that can interfere in the natural functioning of the endocrine system, resulting in health problems in animals and humans[1]. Several studies have associated exposure to EDs with disturbance of the human reproduction system, with effects including infertility, endometrioses, breast cancer, prostate cancer and decreased sperm production[2]. Substances such as natural and synthetic hormones, as well as some drugs, are included in this class of substances[2,3]. Endocrine disruptors have been found at trace levels (from μg L^{-1} to ng L^{-1}) in various aqueous environments, including superficial water, groundwater, domestic wastewater, and even potable water[4].

Among the synthetic compounds that are considered EDs, one that is of increasing concern is bisphenol A [BPA, 2,2-bis(4-hydroxyphenyl) propanol]. The worldwide production of BPA in 2015 exceeded 5.4 million tons. The BPA monomer is used in the production of polycarbonate plastics, epoxy resins, stickers, pipes, fire retardants and thermal papers. The main route of human exposure to BPA is by food and potable water consumption[5–9].

Conventional water and wastewater treatments present limitations in terms of the ability to efficiently remove EDs[10]. Therefore, several alternative treatments are being investigated in order to improve their removal. Among these, the advanced oxidation processes (AOPs) have shown high efficiency in the removal of organic contaminants, including BPA, from aqueous systems[9,11,12].

During AOPs, highly reactive radicals, especially the hydroxyl radical (•OH, with E° = 2.8 V), are generated, which can mineralize organic compounds to CO_2, H_2O and inorganic ions[13]. Heterogeneous photocatalysis using TiO_2/ultraviolet (UV) is an example of an AOP. Under ultraviolet irradiation (UV) with energy higher than the bandgap of the TiO_2, electrons from the valence band (VB) are excited to the conduction band (CB), resulting in an electron/hole pair (e^-/h^+) that can interact with adsorbed water or oxygen molecules, generating oxidant radicals[14–16].

Organic contaminants and their degradation products can present potential risks to the environment[17], with intermediate compounds sometimes being less biodegradable or more toxic than the parent compounds. The use of ecotoxicology bioassays represents a useful tool for evaluation of exposure to these substances[18].

The literature shows a great number of studies[8,9,11] using AOP for the removal of BPA from aqueous matrixes; however, there are few works of the ecotoxicological behavior of the samples after AOP. The main objectives of the present work were to evaluate the efficiency of heterogeneous photocatalysis using TiO_2/UV for the removal of BPA (at a concentration of 0.8 mg L^{-1}), as well as to investigate the possible toxic effects of the treated samples towards two trophic levels of aquatic organisms, namely the microalga *Raphidocelis subcapitata* and the microcrustacean *Daphnia similis*.

2. Experimental

2.1 Chemicals

Bisphenol A ($C_{15}H_{16}O_2$, purity ≥ 99.0%) was purchased from Sigma-Aldrich (Brazil). Acetonitrile [high performance liquid chromatography (HPLC) grade] was obtained from Dinamica (Brazil). The TiO_2 (P25) was from Evonik (Brazil). Stock solutions of 1000 mg L^{-1} BPA were prepared in acetonitrile:water (60:40 v/v) and were stored at 8 °C, protected from light. High-purity water was produced using a Milli-Q (Millipore) purification system.

2.2 Photodegradation study

A double-jacketed borosilicate glass reactor, as described by Kondo and Jardim[15], was used for the BPA photodegradation assays. A mercury vapor lamp (125 W, λ_{max} of 365 nm), delivering total accumulated radiation of 55.2 J cm^{-2} after 60 min, was installed in the reactor. The sample solution consisted of a 1.0 L volume containing 0.8 mg L^{-1} BPA. The lamp was turned on 10 min before initiation of the degradation process. Assays were performed without pH adjustment (pH 5.3) and with adjustment to pH 8.5 using 1.0 mol L^{-1} solutions of NaOH or HCl. The TiO_2 was added (1.0–10 mg L^{-1}) and the suspension was

Eclética Química Journal, vol. 46, n. 2, 2021, 48-56
ISSN: 1678-4618
DOI: 10.26850/1678-4618eqj.v46.2.2021.p48-56

irradiated for 1 h at room temperature (23 °C) under constant aeration at a flow rate of 60 mL min^{-1}. Samples were withdrawn at 0, 15, 30, 45 and 60 min, filtered through an ester membrane (0.45 μm pore size) and stored prior to subsequent analysis by HPLC. The natural degradation of BPA was evaluated using a solution containing 0.8 mg L^{-1} BPA, which was kept in the dark for 10 weeks. Control assays were also performed using TiO_2, UV irradiation and aeration separately.

Solar radiation was also used as a source of UV. Suspensions (1 L volume) containing the same initial concentration (0.8 mg L^{-1}) of BPA and 10 mg L^{-1} of TiO_2 were placed in a glass container (30 × 23 cm, 2.8 cm high) and kept under solar irradiation for 1 h (average total radiation of 11.3 J cm^{-2}). These assays were performed in the city of Itajubá, in the state of Minas Gerais, Brazil (latitude 22°24'45'', longitude 45°26'58'', 850 m above sea level), during July 2017.

2.3 Chromatographic analysis

The BPA concentration was monitored by HPLC using an Agilent 1260 Infinity Series chromatograph equipped with a fluorescence detector and a ZORBAX SB-C8 Rapid Resolution HT column (1.8 μm × 3.0 mm × 150 mm). The mobile phase was a mixture of acetonitrile and ultrapure water (60:40 v/v), under isocratic conditions for 10 min, at a flow rate of 0.20 mL min^{-1}. The column temperature was 45 °C. The sample volume was 10 μL and BPA was detected using excitation and emission wavelengths of 275 ($\lambda_{excitation}$) and 300 nm ($\lambda_{emission}$). Validation of the method was carried out according to the guidelines provided by ANVISA (Brazilian National Health Surveillance Agency), considering the following parameters: selectivity, linearity, limit of detection (LOD), limit of quantification (LOQ), precision, accuracy and robustness[19].

2.4 Acute toxicity test with Daphnia similis

The acute toxicity assay was performed according to Brazilian Association of Technical Standards (NBR 12713/2016)[20]. Samples of natural spring water were spiked with 0.8 mg L^{-1} of BPA, the pH was adjusted to 8.0 and the photocatalytic process was conducted using 10 mg L^{-1} of TiO_2 under artificial UV irradiation. Samples were removed at different oxidation times (0, 15, 30, 45 and 60 min), followed by filtration (10 mL) and introduction of five neonates of *D. similis* (aged between 6 and 24 h). The samples were incubated at 22 °C in a static system with a 12 h light/dark photoperiod. The immobilized organisms were quantified after exposure times of 24 and 48 h. Determinations were made of the initial and final values of conductivity, dissolved oxygen, pH and temperature. All experiments were performed with the samples in quadruplicates.

Determination of the median effective concentration (EC_{50}) was performed using different concentrations of BPA (3.0, 5.0, 8.0, 10.0 and 12.0 mg L^{-1}), with the calculations employing Spear software[21]. The EC_{50} was used in order to establish whether the degradation samples caused any acute effects in the organisms.

2.5 Chronic toxicity test with R. subcapitata

Chronic toxicity bioassays using the microalgae *R. subcapitata* were performed according to NBR 12648/2011[22]. The inocula were incubated in autoclaved LC Oligo culture medium. Algae aged between 5 and 7 days (exponential phase of growth) were inoculated in 125 mL Erlenmeyer flasks containing 100 mL of test solution (94.0 mL of LC Oligo culture medium and 6.0 mL of treated sample), in order to obtain 10^5 cells mL^{-1}. A control sample was prepared using 100.0 mL of LC Oligo medium containing 10^5 cells mL^{-1}. The inoculated samples were maintained for 72 h at 23 ± 2 °C, under 4500 μmol photons m^{-2} s^{-1}, with shaking at 120 rpm. The Erlenmeyer flasks containing the test media were arranged randomly on the table of the orbital shaker (Model MA140, Marconi), with their positions being changed daily. After 72 h, 5.0 mL aliquots of the samples were removed and fixed using 5% lugol in order to quantify the algal biomass. All the experiments were performed using the samples in triplicate.

The final algal growth was analyzed by cell quantification using a Neubauer chamber and an optical microscope. The results were calculated as the

Eclética Química Journal, vol. 46, n. 2, 2021, 48-56
ISSN: 1678-4618
DOI: 10.26850/1678-4618eqj.v46.2.2021.p48-56

final algal biomass and the growth inhibition percentage (%I), according to Eq. 1:

$$\%I = \frac{Mc-Ma}{Mc}\ x\ 100 \quad (1)$$

where M_c is the average for the control cells and M_a is the average for the cells in the test solution.

3. Results and discussion

3.1 Chromatographic conditions and method validation

The quantification results showed a linear regression coefficient of 0.9995. The LOD and LOQ values were 5.0 and 10.0 µg L^{-1}, respectively. The retention time was 5.6 min and the method was selective and robust (± 5.0%). The accuracy was quantified using ultrapure water spiked with 0.3, 0.5 and 0.8 mg L^{-1} of BPA, with average recoveries between 95 and 102%. The precision of the method was determined considering the repeatability and the intermediate precision.

3.2 Stability of BPA in aqueous solution

The weekly evaluation of solutions of BPA at 0.8 mg L^{-1} showed an average recovery between 88 and 101% after 10 weeks. According to Corrales *et al.*[23], the half-life time of BPA in the environment is 38 days. Under natural conditions, BPA can be removed by direct photolysis and biological degradation. In the present work, the natural degradation of BPA was not observed since the stability assays were performed in a closed and controlled environment.

3.3 Control assays

The experiments using TiO_2, UV irradiation and aeration separately did not show any BPA removal after 1 h, indicating that BPA was not adsorbed onto the TiO_2 surface and that aeration was ineffective in transferring BPA from the aqueous solution to the gas phase. In both cases, the BPA decrease was less than 1% of the original concentration. Direct photolysis at pH 8.5 resulted in a 3% decrease of BPA after 1 h of irradiation, while no concentration change was observed using pH without adjustment.

These results are similar to those obtained by Silva *et al.*[24], who used 120 mg L^{-1} TiO_2 (Sigma–Aldrich), without irradiation, and observed no removal of 5.0 mg L^{-1} BPA after 2 h. Repousi *et al.*[25] reported that 260 µg L^{-1} BPA in 20 mg L^{-1} humic acid solution did not undergo direct photolysis after 45 min of irradiation using a 100 W Xe/O_3 lamp.

3.4 Bisphenol A photodegradation study

3.4.1 Influence of TiO_2 concentration on BPA degradation

Considering the range of TiO_2 concentrations tested (from 1.0 to 10.0 mg L^{-1}), the best efficiencies were obtained using 7.5 and 10.0 mg L^{-1}, with removal of > 99% BPA after 45 min of irradiation, at both pH values employed (Fig. 1). When 5.0 mg L^{-1} of the catalyst was used, BPA removal exceeded 98% after 1 h of reaction. Use of TiO_2 at a concentration of 2.5 mg L^{-1} resulted in BPA removals of up to 80 and 88% after 1 h of irradiation at pH 5.3 and 8.5, respectively. At a TiO_2 concentration of 1.0 mg L^{-1}, 40% BPA removal was obtained at both pH values.

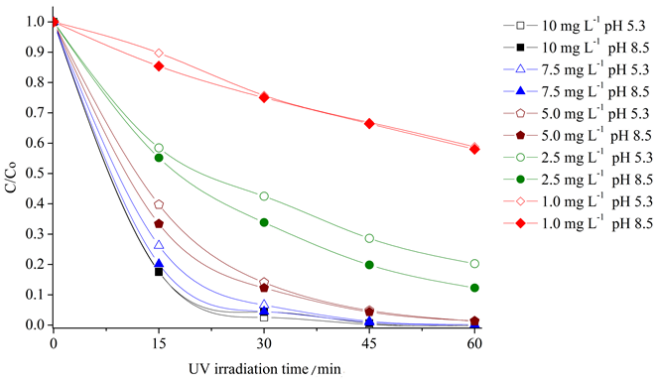


Figure 1. Comparison of the removal of 0.8 mg L^{-1} BPA from ultrapure water using artificial UV, TiO_2 and aeration.

As can be seen in Fig. 1, there were no significant differences between the BPA removals achieved at the different pH values. The effect of pH on the BPA

Eclética Química Journal, vol. 46, n. 2, 2021, 48-56
ISSN: 1678-4618
DOI: 10.26850/1678-4618eqj.v46.2.2021.p48-56

removal efficiency was due to the ionization of the molecule at basic pH, along with different surface charges of the catalyst[26]. TiO_2 semiconductor particles present a zero point of charge (ZPC) pH of 6.0, so the particles are negatively charged at pH lower than 6.0[27]. Since the photocatalytic process occurs at the interface, lower efficiency can be expected at pH 8.5, due to electrostatic repulsion and, consequently, reduced adsorption of BPA molecules onto the TiO_2 surface[28]. Nevertheless, more hydroxyl radicals are generated at alkaline pH, due to the higher concentration of hydroxyl ions in the solution, which probably overcame the decreased BPA adsorption, resulting in efficient removal of the compound[27].

Use of a higher TiO_2 concentration increased the surface area and the quantity of active sites available, resulting in increased BPA removal efficiency[26,27].

Tsai *et al.*[28] reported that removal of BPA at 10.0 mg L^{-1} reached > 99% after 1 h of irradiation using TiO_2/UV, with an initial catalyst concentration of 0.5 g L^{-1}. Abo *et al.*[11] studied the removal of 25.0 mg L^{-1} BPA at pH 5.8, using different semiconductors. Removal of up to 98% BPA was observed after 1 h of irradiation, using 0.1% (w/w) of TiO_2 and 0.5 mmol L^{-1} of sodium hypochlorite.

3.4.2 Solar radiation

No removal of BPA was observed after 1 h of direct photolysis under solar irradiation. The accumulated UV radiation doses were 10.6 and 12.3 J cm^{-2} for the assays using solutions without pH adjustment and at pH 8.5, respectively. However, combining the optimized TiO_2 concentration of 10 mg L^{-1} and solar radiation resulted in complete depletion of the initial BPA concentration after 1 h, at both pH values (5.3 and 8.5). The accumulated UV radiation doses were 11.4 and 9.45 J cm^{-2} for pH 5.3 and 8.5, respectively.

3.4.3 Influence of the matrix on BPA degradation

Evaluation of BPA removal using spring water, instead of ultrapure water, was necessary for the subsequent ecotoxicological investigations. Under these conditions, BPA removal reached 46% after 1 h of reaction at unadjusted pH 8.0, under artificial UV irradiation (Fig. 2). The lower BPA removal efficiency, compared to the value obtained using ultrapure water (> 99% removal in 45 min of irradiation) could be attributed to the presence of ions (85.4 µS cm^{-1}) and organic compounds in the spring water, which were not present in the ultrapure water. Teixeira and Jardim[26] reported that anions, such as Cl^-, SO_4^{2-} and PO_4^{3-} could reduce the photomineralization ratio in a range from 20 to 70%, due to adsorption of the anions onto the oxidant sites of the catalyst. Furthermore, the presence of species, such as HCO_3^- and CO_3^{2-}, could hinder the photocatalytic process, since these anions could react with the hydroxyl radicals, hence competing with the target compound[29].

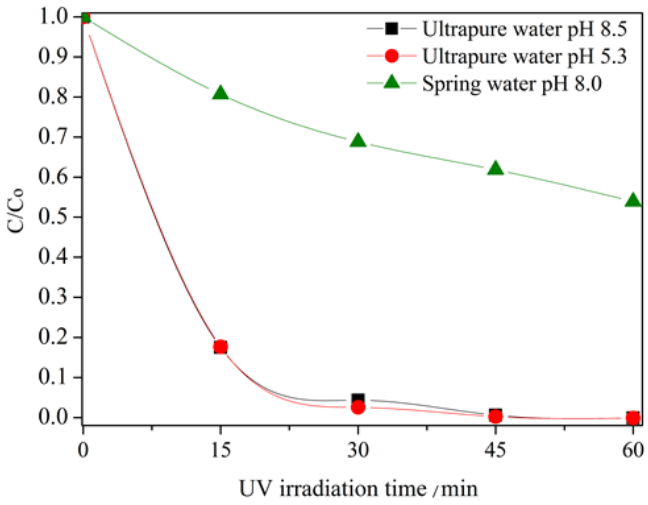


Figure 2. Comparison of the efficiencies of BPA removal from ultrapure water and natural spring water using the heterogeneous photocatalyst system (TiO_2/O_2/artificial UV). [TiO_2] = 10.0 mg L^{-1}.

The chromatograms acquired during the BPA removal study using spring water showed signals at retention times different to that for BPA, which was indicative of the generation of BPA degradation intermediates.

3.5 Toxicity assays

The results of the toxicity assays indicated that the samples obtained during BPA removal using the photocatalytic degradation process did not present acute effects towards *D. similis*. This absence of any

Eclética Química Journal, vol. 46, n. 2, 2021, 48-56
ISSN: 1678-4618
DOI: 10.26850/1678-4618eqj.v46.2.2021.p48-56

acute effects towards the microcrustacean could be explained by the fact that all the solutions used contained BPA at concentrations lower than the EC_{50} value of 8.97 mg L^{-1} (Fig. 3). The results of this bioassay also showed that there was no toxicity associated with any possible intermediates generated.

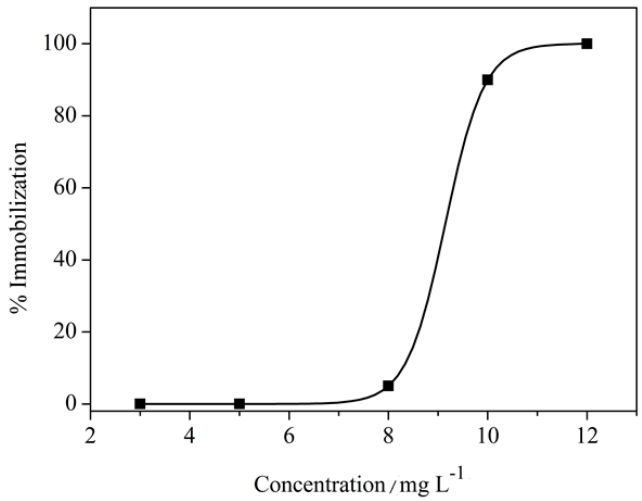


Figure 3. Dose-response curve after 48 h exposure of *D. similis* to BPA.

In a similar study with *Daphnia magna*, Erjavec *et al.*[30] investigated the acute effects of BPA degradation by heterogeneous photodegradation using TiO_2 supported on glass fiber filters. The immobilization rate of the organism exceeded 30% after 24 h of exposure to the original 10 mg L^{-1} solution of BPA. It was also observed that the samples removed during the AOP process presented lower toxicity compared to the original solution, which was suggested to be due to the decrease of the BPA concentration during the heterogeneous photocatalysis process.

Initial samples containing 0.8 mg L^{-1} BPA caused 25% growth inhibition of *R. subcapitata*, compared to the control. Samples removed after 15 and 30 min of irradiation in the presence of TiO_2 caused 18 and 15% enhancements of algal biomass growth, respectively. However, samples removed after 45 and 60 min of irradiation once again inhibited algal growth, with 10 and 7% decreases, respectively (Fig. 4). Statistical analysis (ANOVA) indicated that there were significant differences among the algal biomasses obtained for the control and the samples collected after different oxidation times (95% confidence, p = 0.0007), even after 72 h of exposure. Statistical analysis showed that in the absence of BPA, the heterogeneous photocatalysis process did not affect the algal biomass, with no significant difference relative to the control (ANOVA, 95% confidence, p = 0.745).

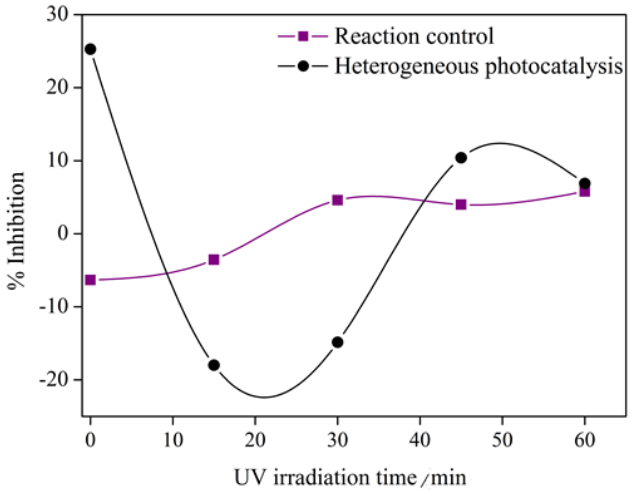


Figure 4. Percentage inhibition of *R. subcapitata* in filtered samples collected after different times of oxidation of 0.8 mg L^{-1} BPA and the reaction control, using natural spring water containing 10.0 g L^{-1} TiO_2 suspension, with irradiation using a 125 W medium-pressure Hg vapor lamp.

Similar results were obtained by Candido *et al.*[31] during evaluation of the chronic toxicity towards *R. subcapitata* of ibuprofen solutions after heterogeneous photocatalysis using TiO_2/O_2/UV. It was observed that the initial samples containing 1.0 mg L^{-1} ibuprofen caused 20% inhibition of algal growth, while samples removed after 5 and 10 min of reaction induced 10% increases of the algal biomass. However, statistical analysis showed no significant differences among the Chl-a values after exposure for 96 h.

The abiotic parameters that could interfere in the ecotoxicological evaluation were monitored at the beginning and the end of each experiment. The data in Tab. 1 show the physicochemical parameters such as conductivity, pH, temperature and dissolved oxygen (DO) concentration during the *D. similis* bioassays. As the initial and the final values of those parameters do not show significant difference, the abiotic interference was not observed.

Eclética Química Journal, vol. 46, n. 2, 2021, 48-56
ISSN: 1678-4618
DOI: 10.26850/1678-4618eqj.v46.2.2021.p48-56

Table 1. Physicochemical variables of spring water samples during the acute ecotoxicity assay with *D. similis*, in the determination of EC_{50} and in the times t_0 and t_{60} of the heterogeneous photocatalytic process in the presence and absence of BPA.

Samples		pH	Conductivity / µS cm^{-1}	DO / mg L^{-1}	Temperature / °C
Spring water	Initial	8.21	75.8	7.53	23.0
	Final	8.86	88.2	7.59	23.6
Reaction control (t_0)	Initial	7.94	67.7	9.05	22.4
	Final	8.64	82.1	7.64	22.9
Reaction control (t_{60})	Initial	7.34	73.3	8.69	22.6
	Final	8.47	85.8	7.65	23.3
Heterogeneous photocatalysis (t_0)	Initial	7.58	73.8	8.51	22.9
	Final	8.53	84.8	7.70	22.9
Heterogeneous photocatalysis (t_{60})	Initial	7.50	73.6	8.56	22.8
	Final	8.44	83.6	7.66	22.9
EC_{50} 3.0 mg L^{-1}	Initial	7.25	73.9	7.72	23.1
	Final	8.31	87.6	7.60	23.3
EC_{50} 8.0 mg L^{-1}	Initial	7.36	71.6	7.76	23.0
	Final	8.33	83.4	7.57	23.3
EC_{50} 12.0 mg L^{-1}	Initial	7.57	72.3	7.77	23.0
	Final	8.22	87.1	7.53	23.2

EC_{50}: effective concentration 50; DO: dissolved oxygen.

The tendency of the obtained results for the chronical assay indicated that the treated samples showed interference to the algal biomass growth of the *R. subcapitata*. However, the extrapolation of obtained results in laboratorial conditions are limited, since in the natural environment synergic effects of different exogenous substances may occur. Therefore, more detailed studies are necessary in order to predict the harmful effects due to the presence of BPA in the environment.

4. Conclusions

The TiO_2/O_2/artificial UV process was effective in degrading BPA present in aqueous solution with total removal (BPA concentration lower than the LOQ) within 45 min of reaction, under the pH conditions tested using 10 mg L^{-1} TiO_2. When solar UV irradiation was used, total removal of BPA was observed after 60 min, under the same conditions employed in the assays with artificial UV.

The BPA EC_{50} value for *D. similis* was 8.97 mg L^{-1}. Acute toxicity assays performed using samples after AOP treatment indicated that there were no negative effects towards the microorganisms after 48 h of exposure. In the chronic assays using the alga *R. subcapitata*, a 25% inhibition of algal biomass growth was observed using the initial BPA solution of 0.8 mg L^{-1}, while samples collected after 15 and 30 min of irradiation in the presence of TiO_2 caused an increase of 18 and 15% in algal biomass growth, respectively.

Acknowledgments

The authors would like to acknowledge financial support from the following Brazilian Research agencies: CAPES, CNPq and FAPEMIG.

References

[1] Brieño-Enríquez, M. A., Larriba, E., Del Mazo, J., Endocrine disrupters, microRNAs, and primordial germ cells: a dangerous cocktail, Fertility and Sterility 106 (4) (2016) 871-879. https://doi.org/10.1016/j.fertnstert.2016.07.1100.

[2] Sifakis, S., Androutsopoulos, V. P., Tsatsakisc, A. M., Spandidos, D. A., Human exposure to endocrine disrupting chemicals: effects on the male and female reproductive systems, Environmental Toxicology and Pharmacology 51 (2017) 56-70. https://doi.org/10.1016/j.etap.2017.02.024.

[3] Gavrilescu, M., Demnerová, K., Aamand, J., Agathos, S., Fava, F., Emerging pollutants in the environment: present and future challenges in biomonitoring, ecological risks and bioremediation, New Biotechnology 32 (1) (2015) 147-156. https://doi.org/10.1016/j.nbt.2014.01.001.

[4] Montagner, C. C., Vidal, C., Acayaba, R. D., Contaminantes emergentes em matrizes aquáticas do Brasil: cenário atual e aspectos analíticos, ecotoxicológicos e regulatórios, Química Nova 40 (9) (2017) 1094-1110. https://doi.org/10.21577/0100-4042.20170091.

[5] Michałowicz, J., Bisphenol A – Sources, toxicity and biotransformation, Environmental Toxicology and Pharmacology 37 (2) (2014) 738-758. https://doi.org/10.1016/j.etap.2014.02.003.

[6] CISION. Global BPA Production to Exceed 5.4 Mln Tonnes by 2015, According to In-demand Report by Merchant Research & Consulting. CISION, London, 2014. http://www.prweb.com/releases/2014/04/prweb11761146.htm.

[7] Eladak, S., Grisin, T., Moison, D., Guerquin, M.-J., N'Tumba-Byn, T., Pozzi-Gaudin, S., Benachi, A., Livera, G., Rouiller-Fabre, V., Habert, R., A new chapter in the bisphenol A story: bisphenol S and bisphenol F are not safe alternatives to this compound, Fertility and Sterility 103 (1) (2015) 11-21. https://doi.org/10.1016/j.fertnstert.2014.11.005.

[8] Konieczna, A., Rutkowska, A., Rachoń, D., Health risk of exposure to bisphenol a (BPA), Roczniki Państwowego Zakładu Higieny 66 (1) (2015) 5-11.

[9] Reddy, P. V. L., Kim, K.-H., Kavitha, B., Kumar, V., Raza, N., Kalagara, S., Photocatalytic degradation of bisphenol A in aqueous media: A review, Journal of Environmental Management 213 (2018) 189-205. https://doi.org/10.1016/j.jenvman.2018.02.059.

[10] Jardim, W. F., Montagner, C. C., Pescara, I. C., Umbuzeiro, G. A., Bergamasco, A. M. D. D., Eldridge, M. L., Sodré, F. F., An integrated approach to evaluate emerging contaminants in drinking water, Sep. Purif. Technol. 84 (2012) 3-8. https://doi.org/10.1016/j.seppur.2011.06.020.

[11] Abo, R., Kummer, N.-A., Merkel, B. J., Optimized photodegradation of Bisphenol A in water using ZnO, TiO_2 and SnO_2 photocatalysts under UV radiation as a decontamination procedure, Drink Water Engineering Science 9 (2) (2016) 27-35. https://doi.org/10.5194/dwes-9-27-2016.

[12] Oller, I., Malato, S., Sánchez-Pérez, J. A., Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination – A review, Science of The Total Environment 409 (20) (2011) 4141-4166. https://doi.org/10.1016/j.scitotenv.2010.08.061.

[13] Kondo, M. M., Moraes, R. G. M., Andrade, S. J. de, Silva, M. R. A. da, Processos fenton e foto-fenton no tratamento de águas residuárias dos frutos do cafeeiro, Coffee Science 9 (4) (2014) 506-515. http://www.sbicafe.ufv.br/handle/123456789/8076.

[14] Deng, Y., Zhao, R., Advanced Oxidation Processes (AOPs) in Wastewater Treatment, Current Pollution Reports 1 (3) (2015) 167-176. https://doi.org/10.1007/s40726-015-0015-z.

[15] Kondo, M. M., Jardim, W. F., Photodegradation of chloroform and urea using Ag-loaded titanium dioxide as catalyst, Water Research 25 (7) (1991) 823-827. https://doi.org/10.1016/0043-1354(91)90162-J.

[16] Nogueira, R. F. P., Jardim, W. F., A Fotocatálise Heterogênea e sua aplicação ambiental, Química Nova 21 (1) (1998) 69-72. https://doi.org/10.1590/S0100-40421998000100011.

[17] Van Doorslaer, X., Haylamicheal, I. D., Dewulf, J., Van Langenhove, H., Janssen, C. R., Demeestere, K., Heterogeneous photocatalysis of moxifloxacin in water: Chemical transformation and ecotoxicity, Chemosphere 119 (Suppl.) (2015) S75-S80. https://doi.org/10.1016/j.chemosphere.2014.03.048.

[18] Ribeiro, A. R., Nunes, O. C., Pereira, M. F. P., 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, Environment International 75 (2015) 33-51. https://doi.org/10.1016/j.envint.2014.10.027.

[19] Ribani, M., Bottoli, C. B. G., Collins, C. H., Jardim, I. C. S. F., Melo, L. F. C., Validação em métodos

cromatográficos e eletroforéticos, Química Nova 27 (5) (2004) 771-780. https://doi.org/10.1590/S0100-40422004000500017.

[20] Associação Brasileira de Normas Técnicas (ABNT). NBR 12713/2016) - Aquatic ecotoxicology. Acute toxicity – test with Daphnia spp (Cladocera. Crustacea).

[21] Hamilton, M. A., Russo, R. C., Thurston, R. V., Trimmed Spearman-Karber method for estimating median lethal concentrations in toxicity bioassays, Environmental Science & Technology 11 (7) (1977) 714-719. https://doi.org/10.1021/es60130a004.

[22] Associação Brasileira de Normas Técnicas (ABNT). NBR 12648/2011 - Aquatic ecotoxicology. Chronic toxicity - test with green algae (Chlorophyceae).

[23] Corrales, J., Kristofco, L. A., Steele, W. B., Yates, B.S., Breed, C.S., Williams, E. S., Brooks, B. W., Global Assessment of Bisphenol A in the Environment: Review and Analysis of Its Occurrence and Bioaccumulation, Dose-Response 13 (2015) 1-29. https://doi.org/10.1177/1559325815598308.

[24] Silva, J. C. C. da, Teodoro, J. A. R., Afonso, R. J. de C. F., Aquino, S. F., Augusti, R., Photodegradation of bisphenol A in aqueous medium: Monitoring and identification of by-products by liquid chromatography coupled to high-resolution mass spectrometry, Rapid Communications in Mass Spectrometry 28 (9) (2014) 987-994. https://doi.org/10.1002/rcm.6863.

[25] Repousi, V., Petala, A., Frontistis, Z., Antonopoulou, M., Konstantinou, I., Kondarides, D. I., Mantzavinos, D., Photocatalytic degradation of bisphenol A over Rh/TiO_2 suspensions in different water matrices, Catalysis Today 284 (2017) 59-66. https://doi.org/10.1016/j.cattod.2016.10.021.

[26] Teixeira, C. P. A. B., Jardim, W. F., Advanced Oxidation Process - Theoretical Concepts. Thematic Notebook, 3. Unicamp, Campinas, 2004.

[27] Kaneco, S., Rahman, M. A., Suzuki, T., Katsumata, H., Ohta, K., Optimization of solar photocatalytic degradation conditions of bisphenol A in water using titanium dioxide, Journal of Photochemistry and Photobiology A: Chemistry 163 (3) (2004) 419-424. https://doi.org/10.1016/j.jphotochem.2004.01.012.

[28] Tsai, W.-T., Lee, M.-K., Su, T.-Y., Chang, Y.-M., Photodegradation of bisphenol-A in a batch TiO_2 suspension reactor, Journal of Hazardous Materials 168 (1) (2009) 269-275. https://doi.org/10.1016/j.jhazmat.2009.02.034.

[29] Legrini, O., Oliveros, E., Braun, M., Photochemical processes for water treatment, Chemical Reviews 93 (2) (1993) 671-698. https://doi.org/10.1021/cr00018a003.

[30] Erjavec, B., Hudoklin, P., Perc, K., Tišlera, T., Dolenc, M. S., Pintar, A., Glass fiber-supported TiO_2 photocatalyst: Efficient mineralization and removal of toxicity/estrogenicity of bisphenol A and its analogs, Applied Catalysis B: Environmental 183 (2016) 149-158. https://doi.org/10.1016/j.apcatb.2015.10.033.

[31] Candido, J. P., Andrade, S. J., Fonseca, A. L., Silva, F. S., Silva, M. R. A., Kondo, M. M., Ibuprofen removal by heterogeneous photocatalysis and ecotoxicological evaluation of the treated solutions, Environmental Science and Pollution Research 23 (19) (2016) 19911-19920. https://doi.org/10.1007/s11356-016-6947-z.