INVESTIGATION OF BENZOPHENONE-3 ELECTROCHEMICAL DEGRADATION ON TITANIUM ELECTRODE

Danka Aćimović[1], Branislava Savić[1], Tanja Brdarić[1], Dragana Vasić Anićijević[1], Marija Ječmenica Dučić[1], Milica Ćurčić[1], Danijela Maksin[1]

[1]„VINČA" Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, Mike Petrovića Alasa 12–14, 11000 Belgrade, Serbia, dankavla@gmail.com

ABSTRACT

Benzophenone-3 is a well-known molecular UV filter, mainly found in commercial cosmetic preparation for sunscreen and skincare. Due to the increased use of sunscreens, it could be found in surface water and wastewater, which could affect the water quality and human health. Research indicates that benzophenone-3 act as an endocrine disruptor and has a carcinogenic and mutagenic effect on humans and other living organisms. The aim of the presented research is to examine the possibility of using titanium anode plates for electrochemical degradation of benzophenone-3 in 0.05M aqueous sodium chloride solution. Electrolysis was performed in galvanostatic mode at a current density of 25 mA cm^{-2}. During 40 minutes of electrolysis, the degradation efficiency of benzophenone-3 is 98.3 %. Additional studies of process kinetics show that degradation of benzophenone-3 follows first-order kinetics.

INTRODUCTION

In recent decades, there has been a growing concern about the presence of cosmetic agents in aquatic environments [1, 2]. Benzophenone-3 is the most frequently used ultraviolet light filter in sunscreen agents. Due to its endocrine disruption effect, cancerogenic and mutagenic ability, it is necessary to develop methods for detection, tracking, and degradation in the aquatic environment, to make it safe for living beings and the environment [3, 4]. biodegradation and sorption are efficient ways to eliminate benzophenone-3 from water [5, 6]. Electrochemical oxidation processes, including anodic oxidation, due to strong oxidation ability, simple application, and environmental compatibility, can be promising techniques for the removal of toxic organic pollutants. To our knowledge, there are no publications that describe using titanium anode plates for electrochemical degradation of benzophenone-3 in aquatic media. The literature contains studies relating to the degradation of benzophenone-3 on Ti/SnO_2-Sb/Ce-PbO_2 anode and TiO_2 nanotubular array electrodes [7, 8]. This study has investigated the possibility of using titanium anode plates for electrochemical degradation of benzophenone-3 in 0.05 M aqueous sodium chloride solution at a current density of 25 mA cm^{-2}. Kinetic analysis of that electrochemical process was performed by zero-order, first-order, second-order, and pseudo-first-order kinetic models, and the results are reported in this paper. This work is useful to deepen our knowledge of whether electrochemical oxidation on the simple electrode without modification is a suitable treatment for removing sunscreen's organic constituents in wastewater. Additionally, it is possible to predict the time required for complete degradation using a kinetic model.

MATERIALS AND METHODS

For presented experiments following chemicals were used: Benzophenone-3 (Energy Chemical Reagent, Shanghai, China, purity 98%), sodium-chloride, NaCl (Sigma-Aldrich) and deionized water (18 MΩcm,) obtained from a Milli-Q Millipore system. The electrochemical experiment was done using GamryPotentiostat/Galvanostat/ZRA06230 (Gamry Instruments, USA). Electrolysis of 4.381 10^{-5} M solutions of benzophenone-3 in 0.05 M NaCl was carried in an undivided, three-electrode electrolytic cell on current density of 25 mA cm^{-2} at room temperature, with a mixing speed of 200 rpm. Titanium plate (Ti), active surface area of 2.86 cm^2, was used as anode, platinum foil as cathode and standard Ag/AgCl electrode as the reference electrode. The distance between the anode and cathode was 2 cm. The aliquots were taken in different time intervals and absorbance at maximum absorbance peak (at 310 nm) were recorded on UV/VIS spectrophotometer Lambda 35 (Perkin Elmer, SAD).

RESULTS AND DISCUSSION

The electrolytic concentration profile and appropriate UV spectrum during electrochemical oxidation of benzophenone-3 were presented in Figure 1b.

- with increasing of electrolysis time, concentration of benzophenone-3 decreases,
- degradation of benzophenone-3 was fast within the initial 10 minutes,
- determined efficiency is about 61%,
- during further electrolysis treatment, the concentration of benzophenone-3 slowly decreases,
- complete degradation of benzophenone-3 with efficiency above 98.4% were achieved after 40 minutes.

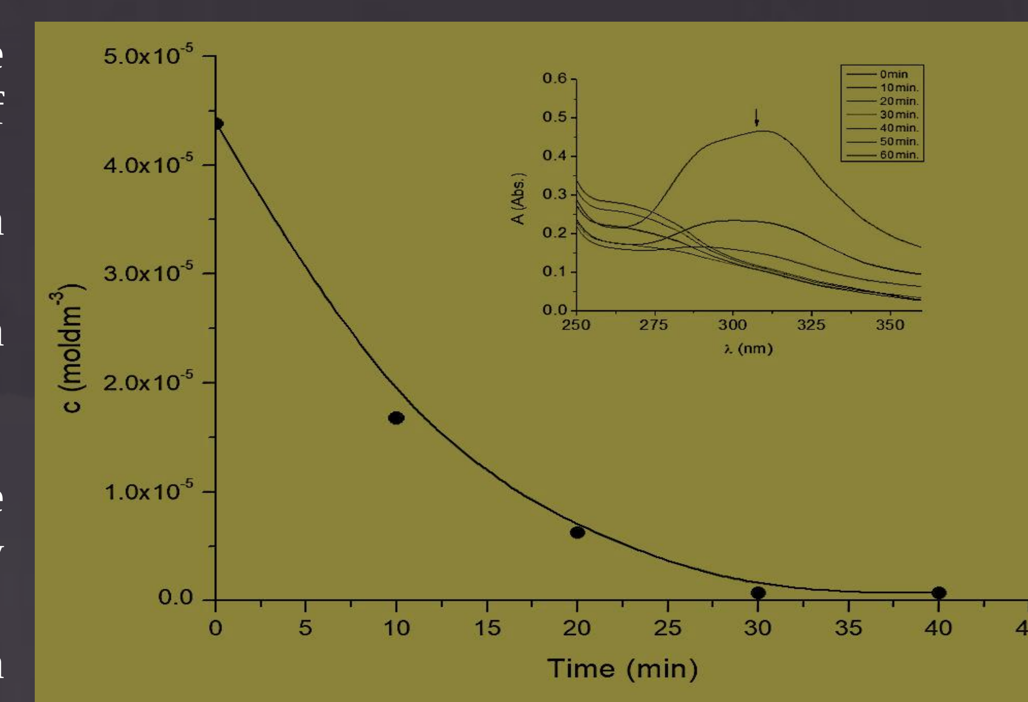

Figure 1. Electrolytic degradation profile of 10 mg·L⁻¹ benzophenone-3 at current density 25 mA cm^{-2}; insert : appropriate UV spectrum

Kinetic analysis

Oxidative electrochemical degradation process of benzophenone-3 by titanium electrode were kinetically modeled using zero order, first order, second order and pseudo first order kinetic models. Coefficients of determination of each of the kinetic models plotted with their linear model equations are presented in Figure 2. The parameters of applied kinetic models, such as rate constants, k and coefficient of determination were calculated from the linear plots. They are presented in Table 1.

Table 1.Benzophenone-3 oxidative degradation parameters of kinetic models

	Rate constants	Coefficient of determination
Zero order mode	-1.380 10^{-6} ($Mmin^{-1}$)	0.684
First order mode	-0.124 (min^{-1})	0.996
Second order mode	38742.86 (M^{-1} min^{-1})	0.936
Pseudo first order mode	0.12 (min^{-1})	0.997

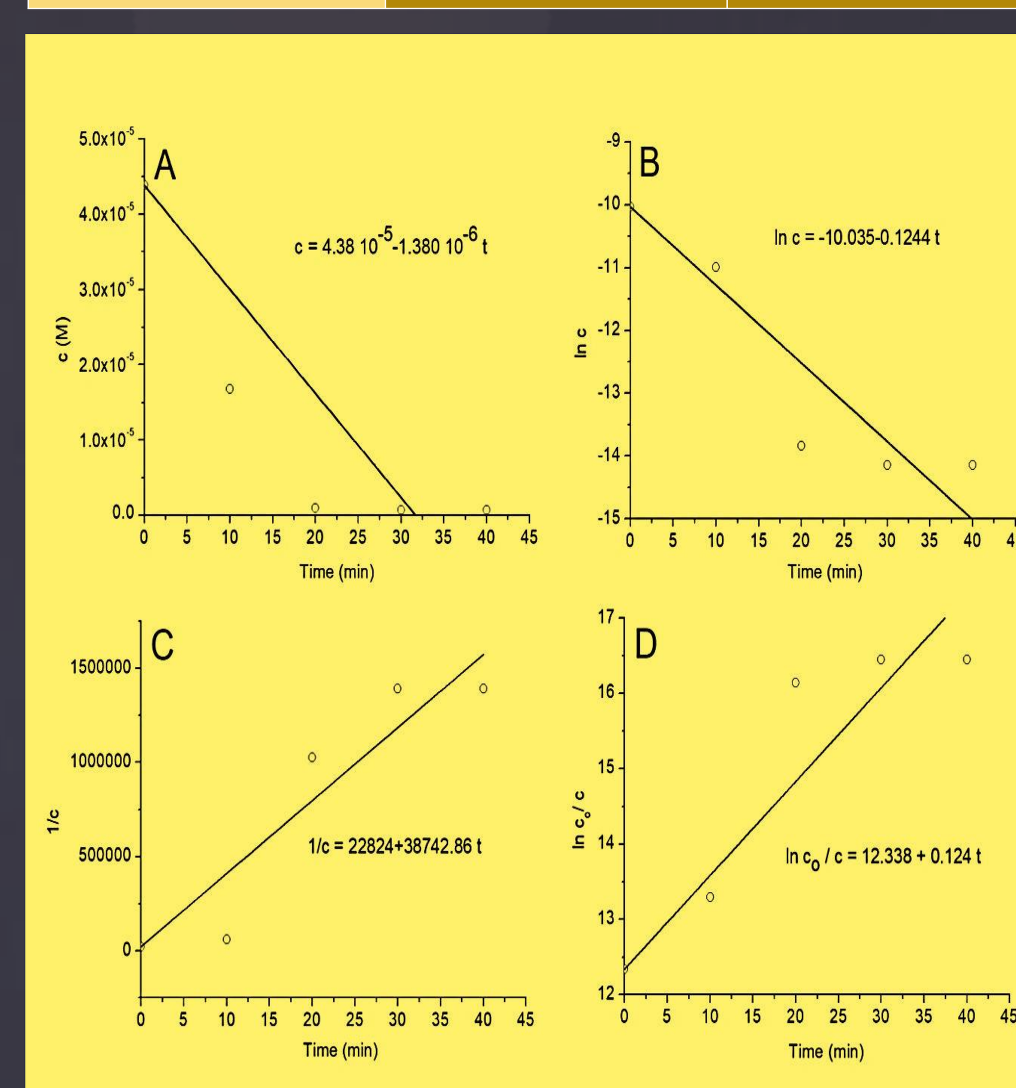

Figure 2. Linear plot of (A) zero order, (B) first order, (C) second order and (D) pseudo first order kinetic model

The coefficient of determination for the pseudo first and first order model was relatively satisfactory and close to 1. This confirms that the degradation of benzophenone-3 by electrolysis follows first-order kinetics. Similarly, several authors have reported that the removal of organic pollutants follows first-order kinetic [9, 10]. The constructed benzophenone-3 degradation kinetics model can be applied to evaluate the degradation level of benzophenone-3 and predict its concentration during the electrolysis time. If the kinetics parameters of k for the benzophenone-3 are obtained based on the method mentioned above, their equations presented on Figure 2 can be used to calculate the c values under different electrolysis time.

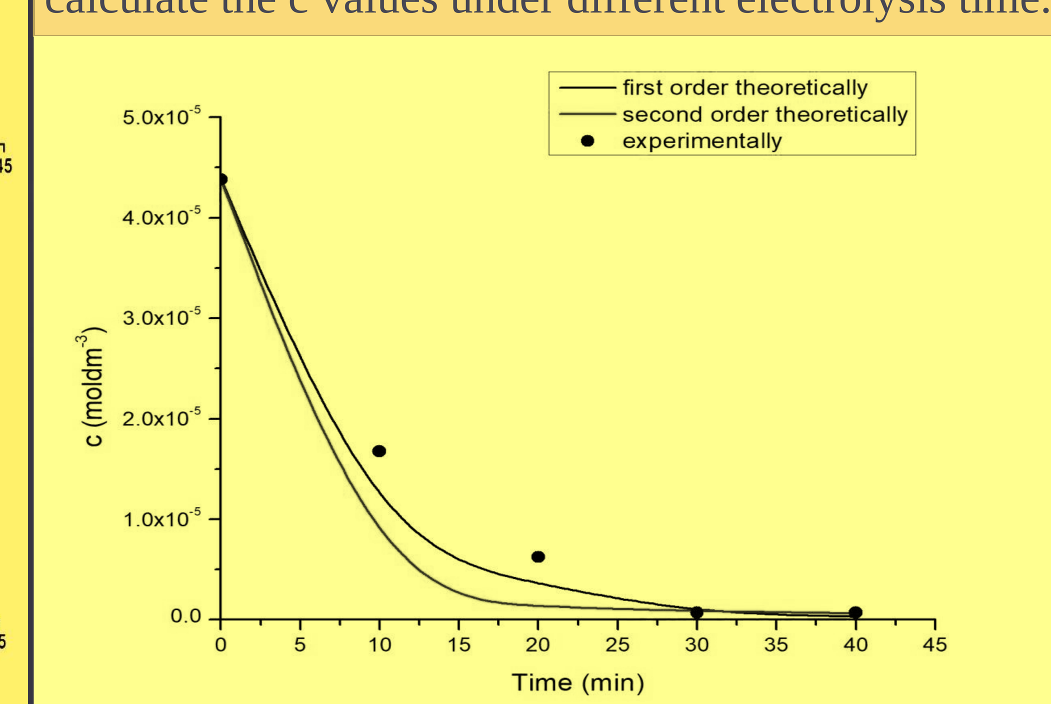

Figure 3.The theoretically calculated electrolytic degradation profile (line) and experimental data (scatter) of benzophenone-3 degraded in 0.05 M NaCl aqueous electrolytes

Figure 3 shows the plots of electrolytic degradation profile from the theoretical model (see equations on Figure 2) for the degradation of the benzophenone-3 in 0.05 M NaCl solutions. The data of concentration at degradation time from experimental findings are also presented, which match well with the theoretically curve for the first order reaction.

Acknowledgement

The authors would like to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia for the financial support to the research through institutional funding (Contract number 451-03-9/2021-14/200017).

CONCLUSION

In summary, our proof-of-concept study has established a electrochemical technique for the degradation of benzophenone-3 in NaCl aqueous electrolytes using titanium plate electrodes, which could also be further generalized in other media. The rate equations of the chemical and electrochemical processes in benzophenone-3 degradation follow first-order kinetics. The construction of the benzophenone-3 degradation kinetics model in this work would provide better insight in prediction of benzophenone-3 degradation time and facilitate the optimization of process for practical applications.

REFERENCES

[1] C. P. Da Silva, E. S. Emídio, and M. R. R. De Marchi, “UV filters in water samples: Experimental design on the SPE optimization followed by GC-MS/MS analysis,” *J. Braz. Chem. Soc.*, Vol. 24- 9 (2013) 1433–1441.

[2] S. Kim and K. Choi, “Occurrences, toxicities, and ecological risks of benzophenone-3, a common component of organic sunscreen products: A mini-review,” *Environment International*, Vol. 70 (2014) 143–157.

[3] N. Blüthgen, S. Zucchi, and K. Fent, “Effects of the UV filter benzophenone-3 (oxybenzone) at low concentrations in zebrafish (Danio rerio),” *Toxicol. Appl. Pharmacol.*, Vol. 263-2 (2012) 184–194.

[4] C. A. Downs, E. Kramarsky-Winter, R. Segal, J. Fauth, S. Knutson, O. Bronstein, R. F. Ciner, R. Jeger, Y. Lichtenfeld, C. M. Woodley, P. Pennington, K. Cadenas, A. Kushmaro, Y. Loya,“Toxicopathological Effects of the Sunscreen UV Filter, Oxybenzone (Benzophenone-3), on Coral Planulae and Cultured Primary Cells and Its Environmental Contamination in Hawaii and the U.S. Virgin Islands,” *Arch. Environ. Contam. Toxicol.*, Vol. 70-2 (2016)265–288.

[5] D. Y. Chen, X. F. Guo, H. Wang, and H. S. Zhang, “The natural degradation of benzophenone at low concentration in aquatic environments,” *Water Sci. Technol.*, Vol. 72- 4 (2015) 503–509.

[6] S. A. Snyder *et al.*, “Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals,” *Desalination*, Vol. 202- 1–3 (2007) 156–181.

[7] C. Zhou, Y. Wang, J. Chen, and J. Niu, “Electrochemical degradation of sunscreen agent benzophenone-3 and its metabolite by Ti/SnO2-Sb/Ce-PbO2 anode: Kinetics, mechanism, toxicity and energy consumption,” *Sci. Total Environ.*, Vol. 688 (2019) 75–82.

[8] J. L. Esbenshade, J. C. Cardoso, and M. V. B. Zanoni, “Removal of sunscreen compounds from swimming pool water using self-organized TiO2 nanotubular array electrodes,” *J. Photochem. Photobiol. A Chem.*, Vol. 214 - 2–3 (2010) 257–263.

[9] R. Rathinam, M. Govindaraj, K. Vijayakumar, and S. Pattabhi, “Decolourization of Rhodamine B from aqueous solution by electrochemical oxidation using graphite electrodes,” *Desalin. Water Treat.*, Vol. 57- no. 36 (2016) 16995-17001.

[10] A. Kaur, R. Kaur, and H. Kaur, “Electrochemical degradation of rhodamine B dye,” *Moroccan J. Chem.*, Vol. 4- no. 1 (2016) 1–4.

VINČA INSTITUTE OF NUCLEAR SCIENCES
University of Belgrade
NATIONAL INSTITUTE OF THE REPUBLIC OF SERBIA