АКАДЕМИЈА НАУКА И УМЈЕТНОСТИ РЕПУБЛИКЕ СРПСКЕ

НАУЧНИ СКУПОВИ
Књига LVII

ОДЈЕЉЕЊЕ ПРИРОДНО-МАТЕМАТИЧКИХ И ТЕХНИЧКИХ НАУКА
Књига 46

САВРЕМЕНИ МАТЕРИЈАЛИ

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SCIENTIFIC WORK

INVESTIGATION OF BENZOPHENONE-3 ELECTROCHEMICAL DEGRADATION ON TITANIUM ELECTRODE

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Abstract: Benzophenone-3 is a well-known molecular UV filter, mainly found in commercial cosmetic preparation for sunscreen and skincare. Due to 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 endocrine disruptor and has a carcinogenic and mutagenic effect on humans and other living organisms. As such, poses a health risk to all living beings and need to be removed from the environment. Electrochemical techniques for wastewater treatment of organic pollutants show advantages over commercial techniques as practicality, safety, and simple application on both, small and large systems. 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.

Key words: benzophenone-3, electrochemical degradation, titanium electrode

1. INTRODUCTION

Benzophenone-type UV filters represent a very diverse group of chemicals that are used across a range of industrial sectors around the world. They are found within different environmental compartments (e.g. surface water, groundwater, wastewater, sediments and biota) at concentrations ranging from ng/L to mg/L. Benzophenone-3 (2-hydroxy4-methoxybenzophenone or oxybenzone) is one of the most commonly used organic UV filters in recent decades. It is mainly used as ultraviolet light filters in sunscreen agents, but it can also be found in other cosmetic products such as lipsticks, skin lotions, facial creams, and fragrances, and in various personal care products, including shampoos, body washes, toilet soaps, hair sprays, and insect repellents, because they can prevent polymer degradation or pigmentation [1, 2].

Benzophenone-3 has two benzene rings joined by a carbonyl group. As with other organic UV filters, benzophenone-3 is a photostable, lipophilic and potentially bioaccumulative compound. The relatively high log-Kow value of benzophenone-3, i.e., 4.0, suggests its slow biodegradation, tendency to adsorb to suspended solids and sediments, and low volatilization potential from water surfaces. Benzophenone-3 has been shown to degrade by about 4% after 28 days in water indicating its persistence in aquatic environment. During summer, the half-life of BP-3 in surface water was estimated at a few weeks, and the persistence appeared to be 7 to 9 times greater in winter under mid-latitude conditions [3]. As a consequence, this compound has frequently been detected in both, environment and biota. Widespread occurrences of this compound have led to its frequent detection in fish and in human urine, serum, and breast milk [4, 5, 6]. Absorbed benzophenone-3 can be hydroxylated to form metabolic byproducts such as benzophenone-1, benzophenone-8, or 2,3,4-trihydroxybenzophenone. Benzophenone-1 is also believed to be one of the major metabolites of benzophenone-3 in fish and humans.

A number of in vitro studies indicate that UV filters such as benzophenone-3 and benzophenone-1, as benzophenone-3 metabolite, have endocrine-disrupting capacities. Benzophenone-3 has been frequently reported for endocrine disruption. Experimental animal and in vitro studies have shown that benzophenone-3 influences reproduction and sex hormone signaling. Benzophenone-1 is reported to possess even greater estrogen receptor binding affinity compared to BP-3 and for these benzophenonones it is suspected to influence on hormone-dependent diseases, and are associated with the birth outcome of humans [7, 8]. In recent studies, it found that dermal application of benzophenone-3, with representative daily internal dose of 50 $mg/kg_{body\ weight}$, has negative impacts on fetal development in pregnant mice, both in terms of growth restriction and sex ratio [9]. Furthermore, a correlation between the urinary benzophenone-3 concentration and the prevalence of osteoarthritis in humans was verified [10].

European Chemicals Agency reported that environmental contamination levels for benzophenone-3 exceed the predicted no-effect concentration of 0.67 $\mu g\ L^{-1}$. According to REACH (Registration, Evaluation, Authorization and Restriction of

Chemicals), endocrine disruptors may be identified as substances of very high concern that need to be restricted in terms of use and spread in cases of confirmed hazard. Denmark initiated an endocrine disruptor assessment for benzophenone-3, which is still ongoing. The German Environment Agency (UBA) is currently working on a strategy for hazard assessment of benzophenone-type UV filters [8].

Due to benzophenone-3 potential endocrine disruption effect and toxicity, it is necessary to develop methods for detection, tracking and degradation in aquatic environment, to make it safe for living beings and the environment. In the past few years, conventional technologies, such as coagulation, flocculation, adsorption, ozonization are adapted for the removal of benzophenone-3 from drinking water and surface water . Because of benzophenone-3 high photostability, direct photodegradation with UV radiation is slow process. Also, biodegradation and sorption are efficient ways to eliminate benzophenone-3 from water [11, 12]. However, these processes can be impractical, unsafe and complex for the application on large systems. Therefore, it is crucial to develop a new approach for benzophenone-3 removal in aquatic media.

Advanced Oxidation Processes (AOPs), as a group of depollution methods that use hydroxyl radicals - the strongest known oxidant for the oxidation of organic pollutants, stands out. Significant attention has been paid to developing of these effective techniques for removing organic pollutants.

Electrochemical oxidation processes, including anodic oxidation, due to strong oxidation ability, simple application and environmental compatibility, can be promising techniques for removal of toxic organic pollutant, e. g. organic dyes, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, phenolic compounds, including organophosphates. Nature of anode materials have significant and decisive influence to efficiency of these processes. Also, the choice of the appropriate supporting electrolyte – chloride, sulfate, phosphate etc., plays important role in electrochemical oxidation. During anodic oxidation, electrochemically generated species like activated chlorine species, persulfates, perphosphates, percarbonates, and hydrogen peroxide that are electrochemically generated from compounds present in the bulk solution such as chloride, sulfate, carbonate, phosphate and oxygen can significantly improve these degradation processes. The final result represents a compromise between the acceleration of kinetics and the gained by-products.

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 [13, 14].

In this study, we have investigated the possibility of using titanium anode plates for electrochemical degradation of benzophenone-3 in 0.05 M aqueous sodium chloride solution at current density of 25 $mAcm^{-2}$. The sodium chloride solution was chosen as the supporting electrolyte to obtain a realistic picture of the contaminated water sample in which the chlorides are present. 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 to remove organic constituents of sunscreen in wastewater. Additionally, it is possible to predict the time required for complete degradation using a kinetic model.

2. 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 Gamry Potentiostat/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).

3. RESULTS AND DISCUSSION

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

In contrast to a previous study that used Fe electrode for degradation BPA, the increase of the concentration of benzophenone after 5 minutes of electrolysis is not observed [15]. However, the continuous decrease in BPA concentration during electrolysis is indisputable evidence that chemical reactions such as the formation of complexes a neutral form of BP-3 with some components of electrolyte did not occur in the system.

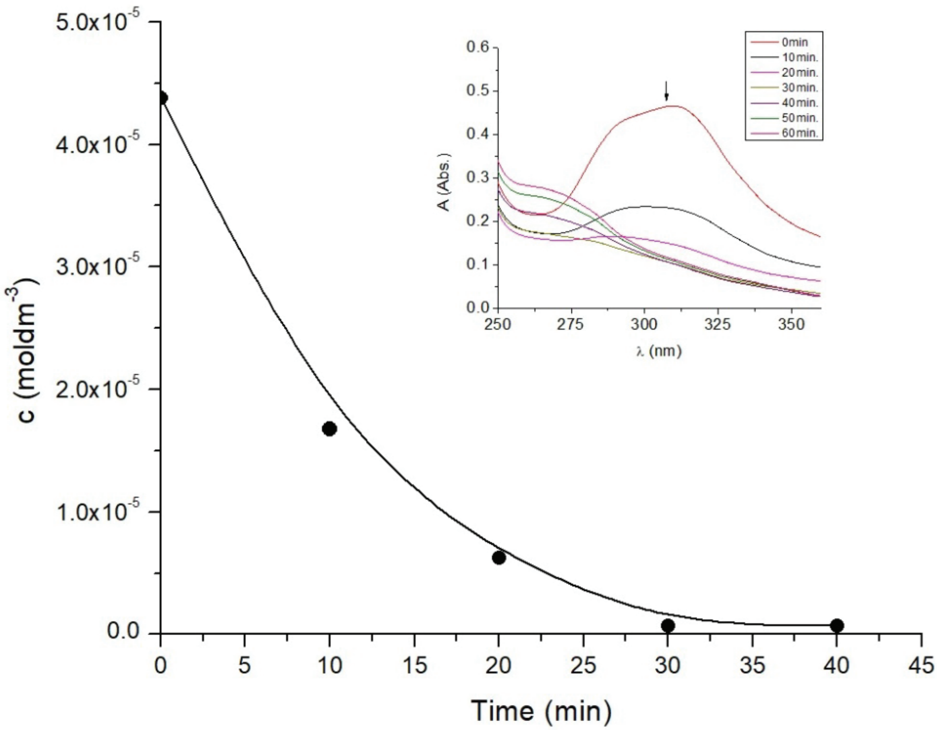

Figure 1. *Electrolytic degradation profile of 10 mg L^{-1} benzophenone-3 at current density 25 mA cm^{-2}; insert : appropriate UV spectrum*

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.

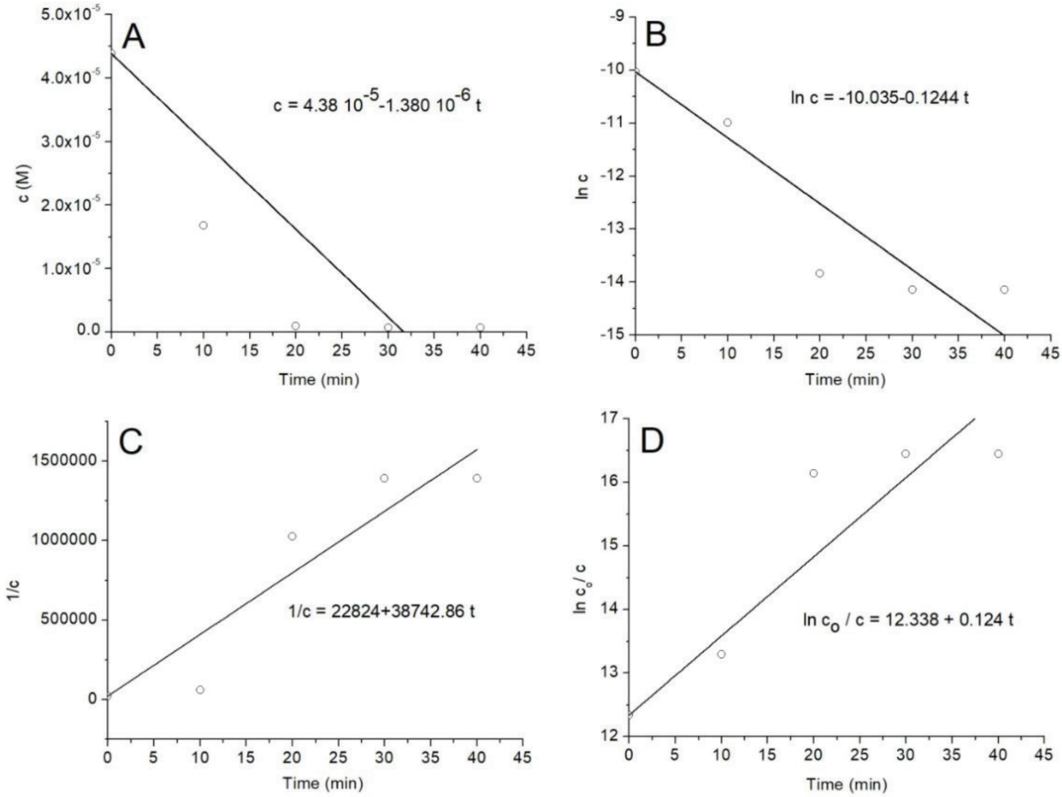

Figure 2. *Linear plot of (A) zero order, (B) first order, (C) second order and (D) pseudo first order kinetic model*

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

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 [16, 17].

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.

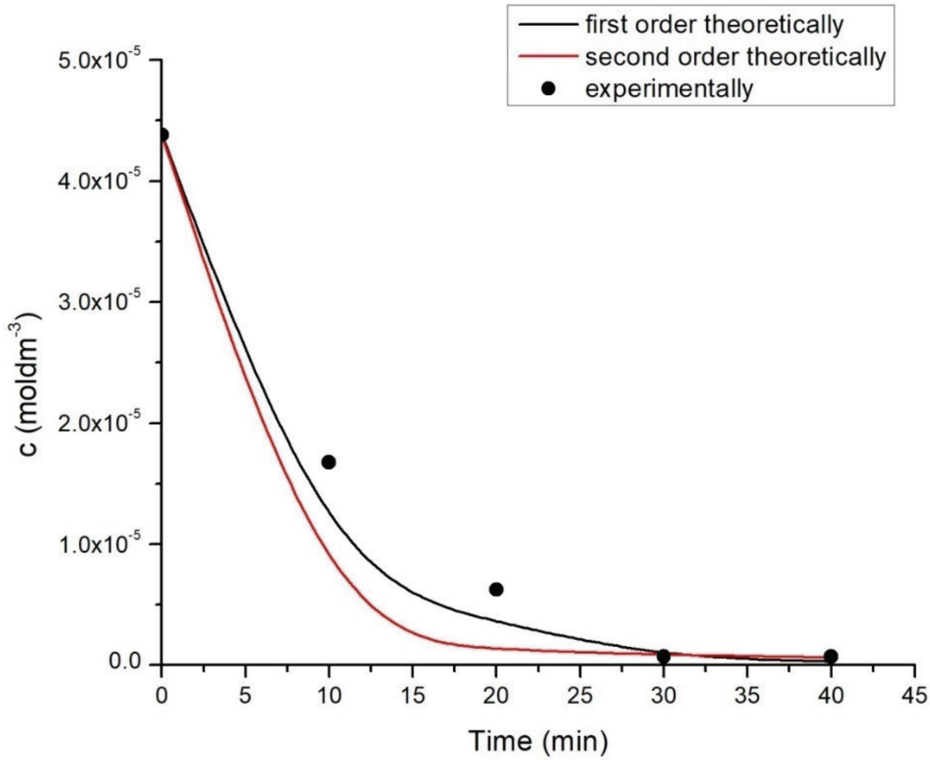

Figure 3. *The theoretically calculated electrolytic degradation profile (line) and experimental data (scatter) of benzophenone-3 degraded in 0.05M NaCl aqueous electrolytes*

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 0.05M 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.

4. 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.

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ИСПИТИВАЊЕ ЕЛЕКТРОХЕМИЈСКЕ ДЕГРАДАЦИЈЕ БЕНЗОФЕНОНА-3 НА ЕЛЕКТРОДАМА ОД ТИТАНА

Апстракт: Бензофенон-3 је општепознат молекулски УВ филтер који се користи у комерцијалним козметичким препаратима за сунчање и негу коже. Услед пораста употребе крема за заштиту од сунца, расте и концентрација наведеног једињења у површинским и отпадним водама што утиче на квалитет воде и здравље људи. Досадашња научна истраживања показују да бензофенон-3 делује канцерогено и мутагено и проузрокује поремећај функције ендокрилних жлезда у живим организмима. Као такав, представља ризик по здравље живих бића и треба га уклонити из околине. Електрохемијска технике за пречишћавање отпадних вода од органских загађивача показала су бројне предности у односу на стандардне технике пречишћавања укључујући практичност, сигурност и једноставну примену како на малим тако и на великим системима. Презентовано истраживање има за циљ испитивање могућности примене титанијумских електродних плоча за електрохемијску деградацију бензофенона-3 у 0.05M воденом раствору натријум хлорида. Електролиза је рађена у галваностатском режиму при густини струје од 25 mA cm^{-2}. Током 40 минута електролизе, ефикасност деградације бензофенона-3 износи 98,3%. Додатна испитивања кинетике процеса показују да деградација бензофенона-3 следи кинетику првог реда

Кључне ријечи: бензофенон-3, електрохемијска деградација, титанијумска електрода