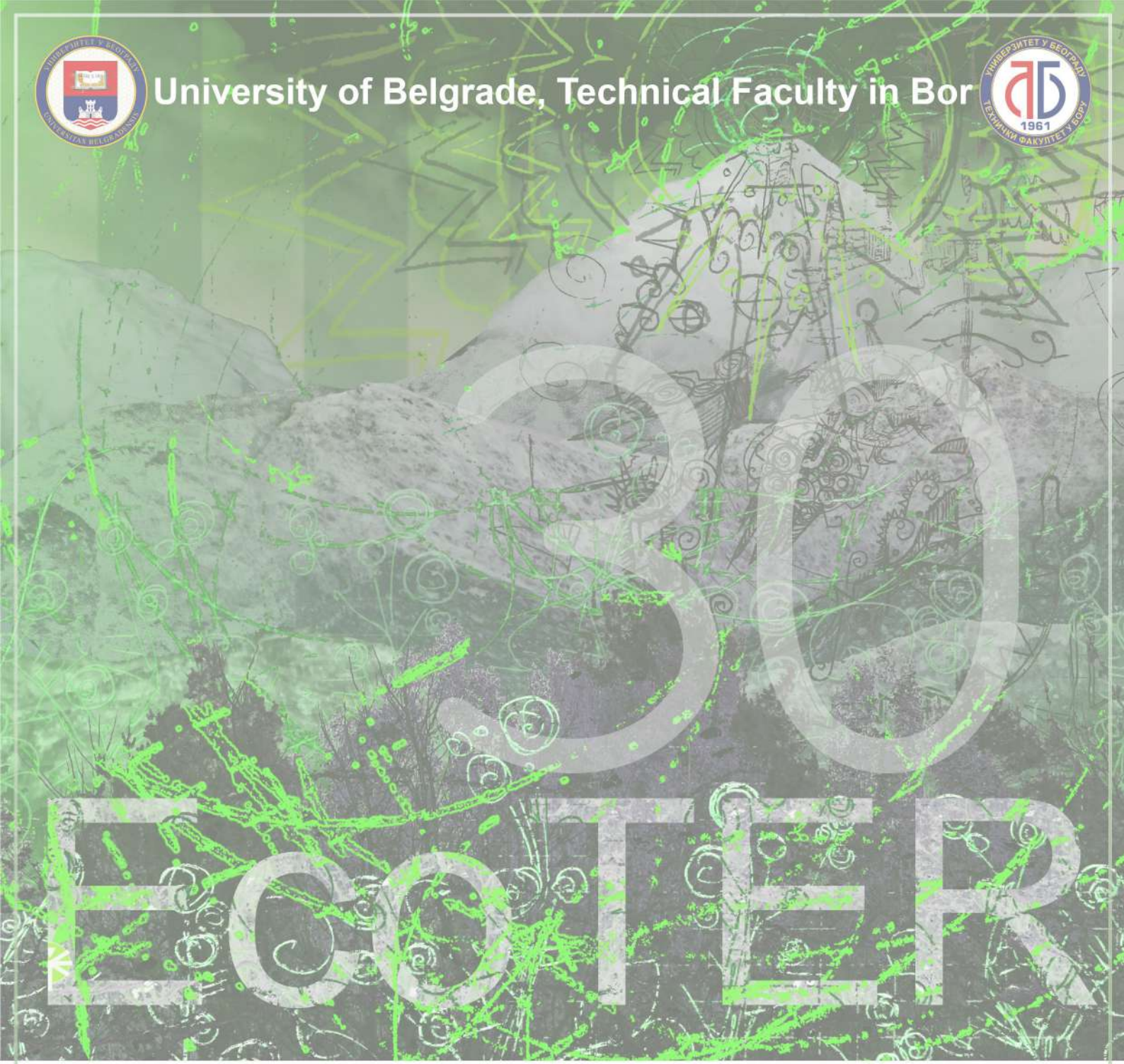
30th International Conference Ecological Truth & Environmental Research 2023

Proceedings

Editor
Prof. Dr Snežana Šerbula



30th International Conference Ecological Truth & Environmental Research 2023

Proceedings

Editor
Prof. Dr Snežana Šerbula

PROCEEDINGS

30th INTERNATIONAL CONFERENCE

ECOLOGICAL TRUTH AND ENVIRONMENTAL RESEARCH – EcoTER'23

Editor:

Prof. Dr Snežana Šerbula

University of Belgrade, Technical Faculty in Bor

Editor of Student section:

Prof. Dr Maja Nujkić

University of Belgrade, Technical Faculty in Bor

Technical editors:

Jelena Milosavljević, PhD, University of Belgrade, Technical Faculty in Bor

Asst. prof. Dr Ana Radojević, University of Belgrade, Technical Faculty in Bor

Sonja Stanković, **MSc**, University of Belgrade, Technical Faculty in Bor

Cover design:

Aleksandar Cvetković, **BSc**, University of Belgrade, Technical Faculty in Bor

Publisher: University of Belgrade, Technical Faculty in Bor

For the publisher: Prof. Dr Dejan Tanikić, Dean

Printed: University of Belgrade, Technical Faculty in Bor, 100 copies, electronic edition

Year of publication: 2023

ISBN 978-86-6305-137-9

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

502/504(082)(0.034.2)
574(082)(0.034.2)

INTERNATIONAL Conference Ecological Truth & Environmental Research (30 ; 2023)
Proceedings [Elektronski izvor] / 30th International Conference Ecological Truth & Environmental Research - EcoTER'23, 20-23 June 2023, Serbia ; organized by University of Belgrade, Technical faculty in Bor (Serbia) ; co-organizers University of Banja Luka, Faculty of Technology – Banja Luka (B&H) ... [et al.] ; [editor Snežana Šerbula]. - Bor : University of Belgrade, Technical faculty, 2023 (Bor : University of Belgrade, Technical faculty). - 1 elektronski optički disk (CD-ROM) ; 12 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Preface / Snežana Šerbula. - Tiraž 100. - Bibliografija uz svaki rad.

ISBN 978-86-6305-137-9

а) Животна средина -- Зборници б) Екологија – Зборници

COBISS.SR-ID 118723849

30th International Conference
Ecological Truth and Environmental Research – EcoTER'23

is organized by:

UNIVERSITY OF BELGRADE
TECHNICAL FACULTY IN BOR (SERBIA)

Co-organizers of the Conference:

**University of Banja Luka, Faculty of Technology,
Banja Luka (B&H)**

**University of Montenegro, Faculty of Metallurgy and Technology,
Podgorica (Montenegro)**

University of Zagreb, Faculty of Metallurgy, Sisak (Croatia)

**University of Pristina, Faculty of Technical Sciences,
Kosovska Mitrovica**

Association of Young Researchers Bor (Serbia)

Gold Donor of the Conference

HONORARY COMMITTEE

Dr. Petar Paunović
(Zaječar, Serbia)
Prof. Dr Zvonimir Stanković
(Bor, Serbia)
Prof. Dr Velizar Stanković
(Bor, Serbia)
Prof. Dr Milan Antonijević
(Bor, Serbia)
Dragan Ranđelović, Association of Young Researchers Bor
(Bor, Serbia)
Toplica Marjanović, Association of Young Researchers Bor
(Bor, Serbia)
Mihajlo Stanković, Special Nature Reserve Zasavica
(Sremska Mitrovica, Serbia)

SCIENTIFIC COMMITTEE

Prof. Dr Snežana Šerbula, *President*

Prof. Dr Alok Mittal (India)
Prof. Dr Jan Bogaert (Belgium)
Prof. Dr Aleksandra Nadgórska-Socha (Poland)
Prof. Dr Luis A. Cisternas (Chile)
Prof. Dr Wenhong Fan (China)
Prof. Dr Martin Brtnický (Czech Republic)
Prof. Dr Isabel M. De Oliveira Abrantes (Portugal)
Prof. Dr Shengguo Xue (China)
Prof. Dr Tomáš Lošák (Czech Republic)
Prof. Dr Maurice Millet (France)
Prof. Dr Murray T. Brown (New Zealand)
Prof. Dr Xiaosan Luo (China)
Prof. Dr Daniel J. Bain (United States of America)
Prof. Dr Che Fauziah Binti Ishak (Malaysia)
Prof. Dr Richard Thornton Baker (United Kingdom)
Prof. Dr Mohamed Damak (Tunisia)
Prof. Dr Jyoti Mittal (India)
Prof. Dr Miriam Balaban (United States of America)
Prof. Dr Yeomin Yoon (United States of America)
Prof. Dr Chang-min Park (South Korea)
Prof. Dr Faramarz Doulati Ardejani (Iran)
Prof. Dr Ladislav Lazić (Croatia)
Prof. Dr Natalija Dolić (Croatia)
Prof. Dr Milutin Milosavljević (Kosovska Mitrovica)
Prof. Dr Nenad Stavretović (Serbia)
Prof. Dr Ivan Mihajlović (Serbia)
Prof. Dr Milovan Vuković (Serbia)
Prof. Dr Nada Blagojević (Montenegro)
Prof. Dr Darko Vuksanović (Montenegro)
Prof. Dr Irena Nikolić (Montenegro)
Prof. Dr Šefket Goletić (B&H)
Prof. Dr Džafer Dautbegović (B&H)
Prof. Dr Borislav Malinović (B&H)
Prof. Dr Slavica Sladojević (B&H)
Prof. Dr Nada Šumatić (B&H)
Prof. Dr Snežana Milić (Serbia)

ORGANIZING COMMITTEE

Prof. Dr Snežana Šerbula, *President*

Prof. Dr Snežana Milić, *Vice President*

Prof. Dr Đorđe Nikolić, *Vice President*

Prof. Dr Marija Petrović Mihajlović

Prof. Dr Milan Radovanović

Prof. Dr Milica Veličković

Prof. Dr Danijela Voza

Prof. Dr Maja Nujkić

Prof. Dr Žaklina Tasić

Dr Ana Simonović

Dr Tanja Kalinović

Dr Ana Radojević

Dr Jelena Kalinović

Dr Jelena Milosavljević

Sonja Stanković, MSc

Miljan Marković, MSc

Vladan Nedelkovski, MSc

Aleksandar Cvetković, BSc

PREFACE

The 30th international conference Ecological Truth & Environmental Research – EcoTER'23 kept three areas in focus: ecology, environmental protection and sustainable development. The conference will be held on Mt Stara Planina in hotel Stara Planina, Serbia, 20–23 June 2023. The monograph is published on the occasion of the 30th anniversary of the conference. On behalf of the scientific and organizing committee, it is a great honor and pleasure to wish all the participants a warm welcome to the conference.

The monograph is published on the occasion of the 30th anniversary of the conference.

We hope to convey the message of the conference, which is that a transformation of attitudes and behavior would bring the necessary changes. This is also an opportunity for the participants who are experts in this field to exchange their experiences, expertise and ideas, and also to consider the possibilities for their collaborative research.

The 30th international conference Ecological Truth & Environmental Research – EcoTER'23 is organized by the University of Belgrade, Technical Faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology, the University of Montenegro, Faculty of Metallurgy and Technology – Podgorica, the University of Zagreb, Faculty of Metallurgy – Sisak, the University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Association of Young Researchers, Bor.

These Proceedings 103 papers from the authors coming from the universities, research institutes and industries in 11 countries: Australia, USA, Brazil, Spain, Portugal, Libya, Italy, Bulgaria, Bosnia and Herzegovina, North Macedonia, and Serbia.

As a part of this year's conference, the 5th Student Session – EcoTERS'23 is being held. We appreciate the contribution of the students and their mentors who have also participated in the conference.

The support of the Gold donor and their willingness and ability to cooperate has been of great importance for the success of the EcoTER'23. The organizing committee would like to extend their appreciation and gratitude to the Gold donor of the conference for their donation and support.

We appreciate the effort of all the authors who have contributed to these Proceedings. We would also like to express our gratitude to the members of the scientific and organizing committees, reviewers, speakers, chairpersons and all the conference participants for their support to the EcoTER'23. Sincere thanks go to all the people who have contributed to the successful organization of the EcoTER'23.

Prof. Snežana Šerbula,

President of the scientific and organizing committee

TABLE OF CONTENTS

Plenary Lecture

Invited Lectures

Conference Papers

Environmental monitoring and impact assessment

Student Section

OPTIMIZATION OF PHENOL ELECTROCHEMICAL OXIDATION USING MODIFIED Ti/SnO_2-TYPE ANODES

Vladan Nedelkovski[1], Sonja Stanković[1], Milan Radovanović[1], Žaklina Tasić[1], Snežana Milić[1]

[1]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA

[*]*vnedelkovski@tfbor.bg.ac.rs*

Abstract

In this paper, optimization of phenol electrochemical oxidation process using modified Ti/SnO_2-type dimensionally stabile anodes (DSA) is further discussed. This type of anodes can be modified by doping with different transition metals, rare earth elements, metal oxides, carbon nanotubes, etc.; in order to achieve specific anode surface morphology, crystal structure, electrocatalytic properties and prolonged service life. In order to increase the service life of Ti/SnO_2-Sb anodes, the formation of interlayers and modifications in the synthesis methods represent suitable options, alongside the elements through which oxide layers can be reached. These electrodes are applied in the removal of biocides, phenolic compounds, dyes, pharmaceutical products, surfactants, petrochemical compounds, etc. The following factors have the greatest influence when using these electrodes: pH, temperature, current density, and electrolyte selection.

Keywords*:* phenol, electrooxidation, modifications, optimization.

INTRODUCTION

Technological procedures based on the oxidation of organic compounds in the presence of hydroxyl radicals are collectively known as Advanced Oxidation Processes (AOPs) and are increasingly attracting the attention of researchers due to their efficiency, cost-effectiveness, and numerous other advantages such as ease of implementation and process control, automation possibilities, and combination with other purification methods, etc. [3]. The overpotential of the oxygen evolution reaction is actually a decisive factor when considering the catalytic performance of anodes in electrochemical oxidation processes, as it directly depends on the type of anodic material. When decomposing polluting organic substances in these processes, it is necessary for the overpotential of the oxygen evolution reaction to be higher (more positive) than the overpotential of the decomposition reaction of the specific organic compound. This avoids a situation where the reaction of water molecule decomposition becomes the dominant process in the system [4].

Ti/SnO_2-Sb TYPE ANODES IN ELECTROOXIDATION OF POLLUTANTS

DSA electrodes based on RuO_2 and IrO_2, despite numerous positive characteristics, are characterized by a weaker stability of the oxide layer on the substrate and high charge transfer resistance. They also possess lower overpotentials for the oxygen evolution reaction. On the other hand, PbO_2-based anodes can lead to secondary lead pollution due to the degradation of the oxide layer. For these reasons, and due to their high electrocatalytic activity, DSA

electrodes based on SnO_2 are considered more suitable [5]. In contrast to BDD (boron-doped diamond) anodes, which have an overpotential of 2.7 V for the oxygen evolution reaction compared to the standard hydrogen electrode, Ti/SnO_2 anodes have an approximate value of 1.8 V. This results in relatively lower efficiency in removing certain compounds and high electrical energy consumption [6]. However, despite the chemical stability and high catalytic ability (the ability to form hydroxyl radicals necessary for electrochemical oxidation), the high cost and the difficulty in selecting suitable materials for obtaining BDD anodes limit their broader industrial application [7]. Ti/SnO_2-Sb type DSA electrodes can be obtained using various synthesis methods such as thermochemical decomposition, electrodeposition, hydrothermal synthesis, ultrasonic spray pyrolysis, sol-gel process, self-assembly process, etc. [6].

In order to improve the performance and stability of DSA anodes, researchers are focusing on synthesizing nanostructured DSA anodes, which involve forming nanostructures of different shapes and compositions (TiO_2 nanotubes, carbon nanotubes, IrO_2, Au, Pt, etc.) with the aim of enhancing electrocatalytic activity. Antimony is the most common accompanying element in tin-based DSA anodes, and its incorporation into the tin oxide layer achieves improved charge transfer capability and facilitates the generation of hydroxyl radicals to a greater extent [8].

Montilla *et al*. [1] determined that platinum doping of Ti/SnO_2-Sb anodes leads to the formation of a more compact layer. By doping with platinum in relatively small amounts (3 at.%), an increase in the anode's lifespan is also achieved. Sun *et al*. [9] synthesized a Ti/SnO_2-Sb anode doped with palladium using the method of thermochemical decomposition. The doped anode had a lifespan of 150 hours, while the undoped anode (synthesized using the same method) had a lifespan of 2.8 hours, confirming the positive effect of doping. Liang *et al*. [8] found that molybdenum-doped Ti/SnO_2-Sb anode possesses a more compact oxide layer, contributing to a 36.6% longer lifespan compared to the undoped anode. Chen *et al*. [10] synthesized a Ti/SnO_2-Cu anode with an overpotential value for the oxygen evolution reaction of 2.7 V (determined relative to the standard hydrogen electrode), significantly higher than that of undoped DSA anodes based on tin and antimony.

PROCESS PARAMETERS IN ELECTROCHEMICAL OXIDATION

The factors used to assess the cost-effectiveness of a process are energy consumption (EC) and specific energy consumption (EEO) - the electrical energy required to achieve a reduction in the concentration of the compound being removed in 1 m^3 of water/solution. The electrical energy consumption (EC) can be determined using the following expressions [11,12]:

$$EC\ (kWh(g\ TOC)^{-1}) = \frac{E_{cell} It}{(\Delta TOC)_t V_s} \tag{1}$$

$$E_{EO}\ (kWhm^{-3}order^{-1}) = \frac{E_{cell} It}{V_s \log(C_0/C_f)} \tag{2}$$

In expressions (1) and (2), the following are defined: E_{cell} – the average cell voltage, I – current intensity (A), t – process duration (h), $(\Delta COD)_t$ and $(\Delta TOC)_t$ – reductions in COD (mg O_2/l) and TOC (mg C/l) after a certain time t, Vs – electrolyte volume (dm^3), C_0 – initial concentration of phenol, and C_f – final concentration of phenol [11].

To select the optimal current density, it is necessary to consider not only the oxidation/decomposition time but also the degree of current utilization. In addition, the parameter MCE (Mineralization Current Efficiency) is also present in the investigations as a direct indicator of the efficiency of the current invested in complete mineralization of a specific compound in the corresponding solution in the mineralization reaction, and it is expressed as [11]:

$$MCE = \frac{nFV_s \Delta(TOC)_t}{4,32 \cdot 10^7 mIt} 100 \ (\%) \tag{3}$$

In the expression (3), the following variables are defined: n – (theoretical) number of electrons exchanged in the decomposition, F – Faraday's constant (96485 C/mol), V_s – volume of the solution (dm^3), $\Delta(TOC)_t$ – reduction in total organic carbon content during electrochemical oxidation (mg/l), $4.32 \cdot 10^7$ – conversion factor (= 3600 s/h · 12000 mgC/mol); m – number of carbon atoms in the given compound; I – current intensity (A) and t – time (h) [11].

Table 1 *Parameters determined during the electrooxidation of phenol under different conditions [12]*

Parameter		Phenol degradation efficiency t_{10min} (%)	k (min^{-1})	Total organic carbon (%)	EC (kWh/ gTOC)	E_{EO} (kWhm^{-3} $order^{-1}$)	MCE (%)
NaCl concentration (mol/dm^3)	0	12.75	0.012	20.9	2.09	47.76	14.34
	0.01	84	0.208	22.5	2.32	3.29	18.20
	0.03	100	0.592	52.9	0.8	0.81	58.35
	0.05	100	0.555	45.8	0.75	0.76	24.7
	0.07	99.7	0.422	39.4	0.55	0.67	13.04
pH	2	99.7	0.627	50	2.01	1.6	61.2
	10	99.6	0.563	38	1.52	1.77	34.18
E (V)	6	35.6	0.041	4	1.02	1.31	1
	10	95.8	0.316	34	0.51	0.72	13.2
Initial phenol concentration (mg/l)	10	99.4	0.509	55	0.71	0.21	7.9
	100	52.9	0.086	20	0.93	5.67	13.2

By analysing the data in Table 1, it was concluded that the addition of NaCl reduces energy consumption to minimum values of 0.55 kWh/gTOC and 0.67 kWh/m^3 for a NaCl

concentration of 0.07 mol/dm^3. This can be explained by the increased conductivity of the electrolyte. However, at a NaCl concentration of 0.03 mol/dm^3, the fastest removal of phenol, i.e., total organic carbon, is achieved, which is consistent with the MCE value of 58.35%. The obtained MCE values reflect the influence of pH on the process efficiency, confirming that in acidic conditions, hypochlorous acid is the primary chemical species with higher oxidation capacity than hypochlorite ions, which are the primary species in alkaline conditions [12]. Increasing the potential to 8 V eventually results with maximum removal of total organic carbon, while further increase up to 10 V leads to a reduction in the polluting substance removal percentage due to the competitiveness of oxygen evolution and chlorine evolution reactions [13]. Table 2 shows the removal efficiency – EU (%) of certain pollutants using modified electrodes under different process parameters: Time τ (min), pH values, temperature (°C), initial phenol concentration (g/l), current density j (A/cm^2), i.e., cell voltage U (V) or current intensity I (A).

Table 2 *Phenol removal efficiency using Ti/SnO_2-type electrodes under different process parameters*

Electrode	τ (min)	j (A/cm^2) *U (V)	t (°C)	Electrolyte	C_0 (g/l)	pH	EU (%)	Reference
Ti/SnO_2-Sb	<20	*8	25	0.03 M NaCl	0.05	6	100	[12]
Ti/Sb-SnO_2-La	120	1	30	0.25 M Na_2SO_4	0.1	/	86.7	[13]
Ti/Mn/Sb-SnO_2-La							81.9	
Ti/Fe-Mn/Sb-SnO_2-La							67.3	
Ti/Ce-Mn/Sb-SnO_2-La							88.8	
Ti/SnO_2-Sb-RuO_2/α-PbO_2/β-PbO_2	360	20	30	0.014 M Na_2SO_4	0.5	/	86	[14]
Ti/SnO_2-Sb-RuO_2/α-PbO_2/β-PbO_2		40					73	
Ti/SnO_2-Sb-RuO_2/α-PbO_2/β-PbO_2		100		0.5 M H_2SO_4	1		77	
Ti/SnO_2-Sb	60	0.01	25	0.34 M NaCl	0.1	7	90	[15]
Ti/SnO_2–Sb_2O_4	>60	0.04	25	0.25 M NaCl	0.1	10.5	99	[16]
Ti/SnO_2-Sb	300	0.02	25	0.25 M Na_2SO_4	0.49	5.3	100	[17]
Ti/SnO_2–Sb_2O_3–Nb_2O_5/PbO_2	120	0.02	20	0.05 M Na_2SO_4	0.5	7	78.6	[18]
				0.36 M NaCl			97.2	

At higher potential values, a greater removal of phenol is achieved, while the process rate at lower potential values is influenced by mass transfer degrees. When the process is limited by mass transfer, increasing the potential promotes the occurrence of undesired reactions (RSK). Increasing the potential up to 8 V leads to maximum removal of total organic carbon, while further increase up to 10 V results in a decrease in the removal percentage due to the competitiveness of oxygen evolution and chlorine evolution reactions. Therefore, a potential value of 8 V is considered optimal, with the lowest energy consumption and the highest achieved removal of total organic carbon. Higher initial concentrations of phenol have shown a decrease in removal efficiency.

CONCLUSION

In addition to the widespread use of DSA electrodes in laboratory tests and industrial wastewater treatment processes, the use of this type of electrode limits electrochemical oxidation processes due to disadvantages in terms of shorter working life and/or potential leaching of cations of toxic metals in highly acidic solutions. Based on a large number of studies on the decomposition of poorly soluble compounds, it was found that DSA anodes exhibit better performance at higher temperatures and in acidic environments, which is consistent with the fact that the oxidation ability of reactive species is largely determined by the pH value. Electrochemical oxidation as a purification process has numerous advantages in industrial application, such as automation, absence of additional chemicals, the possibility of treating cloudy and colored wastewater, relatively low operating costs, etc. In order to achieve the complete application of DSA anodes for the electrochemical oxidation of poorly soluble organic compounds, researchers are increasingly directed towards examining the mechanisms of decomposition and the role of reactive chemical species in the oxidation itself, more economical but - effective methods of preparation and synthesis (for the purpose of obtaining DSA electrodes with the desired physical and chemical properties), as well as the possibility of coupling with other technological purification procedures - in order to reduce the costs of the electrochemical oxidation process and increase degradation efficiency of many toxic organic compounds.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Science, Technological Development and Innovation of the Republic of Serbia for financial support according to the contract with the registration number 451-03-47/20223-01/200131.

REFERENCES

[1] Montilla F., Morallón E., De Battisti A., *et al*., J. Phys. Chem. B. 108 (2004) 5036–5043.

[2] Wu W., Huang Z., Lim T., Appl. Catal. 480 (2014) 58–78.

[3] Santos D. H. S., Duarte J. L. S., Tavares M. G. R., *et al*., Chem. Eng. Process. 153 (2020) 107940.

[4] Shao C., Zhang F., Li X., *et al*., J. Electroanal. Chem. 832 (2019) 436–443.

[5] Duan Y., Chen Y., Wen Q., *et al*., J. Electroanal. Chem. 768 (2016) 81–88.

[6] Chen A., Xia S., Ji Z., *et al*., Appl. Surf. Sci. 471 (2019) 149–153.

[7] Li X., Yan J., Zhu K., J. Electroanal. Chem. 878 (2020) 30373-30383.

[8] Liang J., Geng C., Li D., *et al*., JMST 31 (2015) 473–478.

[9] Sun, Y., Cheng, S., Yu, Z., *et al*., J. Alloys Compd. 834 (2020), 155184.

[10] Chen, A., Zhu, X., Xi J., *et al*., J. Alloys Compd. 683 (2016), 501–505.

[11] Brillas E., Sirés I., Oturan M. A., Chem. Rev. 109 (2009) 6570–6631.

[12] Santos G. O. S., Dória A. R., Vasconcelos V. M., *et al*., Chemosphere 259 (2020) 127475.

[13] Bi Q., Wang Z., Dang C., *et al*., J. Alloys Compd. (2020) 158033.

[14] Zheng Y., Su W., Chen S., *et al*., J. Chem. Eng. 174 (2011) 304–309.

[15] Santos I. D., Gabriel S. B., Afonso J. C., *et al*., Mater. Res. 14 (2011) 408–416.

[16] Loloi M., Rezaee A., Aliofkhazraei M., *et al*., ESPR 23 (2016) 19735–19743.

[17] Li X. Y., Cui Y. H., Feng Y. J., *et al*., Water Res. 39 (2005) 1972–1981.

[18] Yang X., Zou R., Huo F., *et al*., J. Haz. Mat. 164 (2009) 367–373.

eco.tfbor.bg.ac.rs ISBN 978-86-6305-137-9 tfbor.bg.ac.rs