Theoretical Description for Diclofenac Electrochemical Determination over an Undoped Conducting Polymer

Volodymyr V. Tkach 1,2,*, Marta V. Kushnir 1, Silvio C. de Oliveira 2, Inna M. Shevchenko 3, Vira M. Odyntsova 3, Volodymyr M. Omelyanchik 3, Ludmila O. Omelyanchik 4, Olga V. Luganska 4, Vira V. Kopylka 4, Zholo V. Kormosh 5,*, Yana G. Ivanushko 6, Viktor V. Kryvetskyi 6, Inna I. Kryvetska 6, Vitalii F. Rusnak 6, Petro I. Yagodynets 1,*, Zoriana Z. Masna 7, Lucinda Vaz dos Reis 8, Oleh M. Grygorenko 9, Galyna T. Piatnytska 9

1 Chernivtsi National University, 58001, Kotsyubynsky Str. 2, Chernivtsi, Ukraine
2 Instituto de Química, Universidade Federal de Mato Grosso do Sul, 79074 – 460, Av. Sen. Felinto Müller, 1555, Vila Ipiranga, Campo Grande, MS, Brazil
3 Zaporizhzhia State Medical University, 69600, Mayakovskiy Ave. 24, Zaporizhzhia, Ukraine
4 Zaporizhzhia National University, 69600, Zhukovsky Str. 66, Zaporizhzhia, Ukraine
5 Volyn National University, 43000, Voli Ave., 13, Lutsk, Ukraine
6 Bukovinian State Medical University, 58001, Teatralna Sq, 9, Chernivtsi, Ukraine
7 Danylo Halytsky Lviv National Medical University, 79010, Pekarska Str. 69, Lviv, Ukraine
8 Universidade de Trás-os-Montes e Alto Douro, Quinta de Prados, 5001-801, Folhadela, Vila Real, Portugal
9 Kyiv National University of Trade and Economics, 02156, Kyiv Str. 21, Kyiv, Ukraine

*Correspondence: nightwatcher2401@gmail.com (V.V.T.); zholt-1971@ukr.net (Z.O.K.); ved1988mid@rambler.ru (P.I.Y.);
Scopus Author ID 557582999100
Received: 24.11.2021; Accepted: 18.12.2021; Published: 2.02.2022

Abstract: The theoretical description for diclofenac electrochemical determination over an undoped conducting polymer in doping conditions. In the basic solution, diclofenac ion enters the polymer matrix as a dopant. The doping is followed by hydrolysis and electrooxidation of the resulting phenolic ion, accompanied by the grafting to the proper polymer backbone. Analyzing the correspondent mathematical model by linear stability theory and bifurcation analysis, we confirm that the electroanalytical process remains efficient despite the high probability of the oscillatory behavior.

Keywords: diclofenac; electrochemical doping; conducting polymer; electrochemical sensors; stable steady-state.

© 2022 by the authors. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Diclofenac (Fig. 1) is one of the anti-inflammatory drugs and pain killers, mostly used worldwide [1–4]. Its mechanism of action is based on the alkaline hydrolysis of chlorine atoms (Fig. 1), yielding a polyphenolic compound, scavenging the ROS, yielding in the inflamed tissue during the inflammation process.

Figure 1. Diclofenac mechanism of action.

X = Na⁺, K⁺, NH₄⁺
New radicals will be more difficult to recombine, thereby detaining the inflammation process and providing pain relief. Diclofenac is applied topically, orally, rectally, intravenously, and intramuscularly.

On the other hand, acidic media provokes gastritis and gastric ulcers due to the acidic hydrolysis, yielding a weak acid (Fig. 2).

![Figure 2. Acidic hydrolysis of diclofenac.](https://biointerfaceresearch.com/)

Also, its excessive concentrations, like long-time use, may lead to the side effects like tiredness, slumber, nausea, and vomiting [5–8]. Therefore, developing an efficient method for diclofenac quantification is actual [9–14].

Diclofenac is one of the most popular objects for electroanalytical processes nowadays [15–20]. Either direct electrooxidation or selective membrane development is admitted. In the first case, chemically modified electrodes are widely used [15–18].

Conducting polymers, combining the metal conductivity with plastics flexibility, corrosion resistance, and modification facility, is why they are widely used in electroanalytical processes [19–25]. Many monomers, including small and large conjugated molecules, may be used. Both doped and undoped conducting polymers may be employed in the electroanalytical detection of diclofenac. Nevertheless, considering the ionic nature of the analyte, the undoped polymer is recommended to provide the immobilization of diclofenac ions towards the polymer matrix.

Also, the mechanism of the electrochemical and chemical reactions providing the analytical signal may be unclear. This leads to the necessity of investigating the most probable mechanism of the electroanalytical process, including detecting the parameter region corresponding to the most efficient sensing. Also, the electrochemical instabilities described for the analogous systems [31–33] may impact the electroanalytical behavior.

The resolution of mentioned problems requires the mechanistic theoretical investigation of the electroanalytical process, also capable of comparing the behavior of this system with that of the similar ones without any experimental essay. Therefore, this work gives the theoretical analysis of the system with diclofenac determination over an undoped conducting polymer, including stability and instability analysis and the behavior comparison with similar systems [34 – 35].

2. Materials and Methods

With the anodic potential applied on the first electrochemical stage, diclofenac ion enters the polymer matrix, which becomes doped. After this, diclofenac in the matrix will be hydrolyzed, yielding the hydroquinonic form, which is oxidized to its quinonic form, mimicking the alkaline hydrolysis exposed above in Fig. 1.

The parallel oxidation mechanism involves the polymer backbone, which becomes covalently bound to the dopant, reason why, to describe the system’s behavior, we introduce three variables:
f – diclofenac concentration in the pre-surface layer;
p – diclofenac-doped polymer surface coverage degree;
p* - diclofenac hydrolyse-doped polymer surface coverage degree.

Assuming some suppositions, described in [34 – 35], we may describe this process by the BDES (1):
\[
\begin{align*}
d_f &= \frac{2}{\delta} \left( \frac{\Delta}{\delta} (f_0 - f) - r_d \right) \\
d_p &= \frac{1}{p} \left( r_d - r_h - r_{g1} \right) \\
d_{p^*} &= \frac{1}{p^*} \left( r_h - r_q - r_{g2} \right)
\end{align*}
\]

Herein, \(f_0\) is diclofenac bulk concentration, \(\Delta\) is the diffusion coefficient, \(p\) and \(p^*\) are two doped polymer forms maximal surface concentrations, and the parameters \(r\) are the correspondent reaction rates, calculated as:
\[
\begin{align*}
r_d &= k_d f (1 - p - p^*) \exp \left( \frac{nF\varphi_0}{RT} \right) \\
r_h &= k_h p \exp(-ap) \\
r_{g1} &= k_{g1} p \exp \left( \frac{mF\varphi_0}{RT} \right) \\
r_q &= k_q p^* \exp \left( \frac{pF\varphi_0}{RT} \right) \\
r_{g2} &= k_{g2} p^* \exp \left( \frac{qF\varphi_0}{RT} \right)
\end{align*}
\]

Herein, the parameters \(k\) are the correspondent reaction rate constants, and \(a\) is the parameter related to DEL changes during the dopant hydrolysis, \(n, m, p, \) and \(q\) are the numbers of the transferred electrons, \(F\) is the Faraday number, \(\varphi_0\) is the zero-charge potential, \(R\) is the universal gas constant and \(T\) is the absolute temperature.

Considering the presence of multiple electrochemical processes, the oscillatory behavior in this system will be more frequent. Nevertheless, the electroanalytical process is expected to be efficient, as shown below.

3. Results and Discussion

To describe the system with the electroanalytical determination of diclofenac in basic media over an undoped conducting polymer, we analyze the equation-set (1) using linear stability theory. The steady-state Jacobian matrix members will be described as (7):
\[
\begin{pmatrix}
a_{11} & a_{12} & a_{13} \\
a_{21} & a_{22} & a_{23} \\
a_{31} & a_{32} & a_{33}
\end{pmatrix}
\]

Where:
\[
\begin{align*}
a_{11} &= \frac{2}{\delta} \left( \frac{\Delta}{\delta} - k_d (1 - p - p^*) \exp \left( \frac{nF\varphi_0}{RT} \right) \right) \\
a_{12} &= \frac{2}{\delta} \left( k_d f \exp \left( \frac{nF\varphi_0}{RT} \right) - j k_d f (1 - p - p^*) \exp \left( \frac{nF\varphi_0}{RT} \right) \right) \\
a_{13} &= \frac{2}{\delta} \left( k_d f \exp \left( \frac{nF\varphi_0}{RT} \right) - l k_d f (1 - p - p^*) \exp \left( \frac{nF\varphi_0}{RT} \right) \right) \\
a_{21} &= \frac{1}{p} \left( k_d (1 - p - p^*) \exp \left( \frac{nF\varphi_0}{RT} \right) \right) \\
a_{22} &= \frac{1}{p} \left( -k_d f \exp \left( \frac{nF\varphi_0}{RT} \right) + j k_d f (1 - p - p^*) \exp \left( \frac{nF\varphi_0}{RT} \right) - k_h \exp(-ap) + a k_h p \exp(-ap) - k_{g1} \exp \left( \frac{mF\varphi_0}{RT} \right) - j k_{g1} p \exp \left( \frac{mF\varphi_0}{RT} \right) \right) \\
a_{23} &= \frac{1}{p} \left( -k_d f \exp \left( \frac{nF\varphi_0}{RT} \right) + l k_d f (1 - p - p^*) \exp \left( \frac{nF\varphi_0}{RT} \right) - l k_{g1} p \exp \left( \frac{mF\varphi_0}{RT} \right) \right)
\end{align*}
\]
\[ a_{31} = 0 \]  
\[ a_{32} = \frac{1}{p_0} (k_h \exp(-ap) - a k_m p \exp(-ap)) \]  
\[ a_{33} = \frac{1}{p_0} (-k_q \exp\left(\frac{pF\phi_0}{RT}\right) + l k_q p \ast \exp\left(\frac{pF\phi_0}{RT}\right) - k_{g2} \exp\left(\frac{qF\phi_0}{RT}\right) + l k_{g2} p \ast \exp\left(\frac{qF\phi_0}{RT}\right)) \]  
(16)

To simplify the determinant analysis necessary for the stability evaluation, we introduce three variables, rewriting the Jacobian determinant as (17):

\[ \frac{2}{\delta p p_0} \begin{vmatrix} -\kappa - \Xi & \Lambda - \Sigma & \Lambda - T \\ \Xi & \Sigma - H - \Gamma_1 & T - N \\ 0 & H & -\Omega - \Gamma_2 \end{vmatrix} \]  
(17)

The Routh-Hurwitz criterion application to this system with the subsequent determinant analysis yields the steady-state stability requirement, exposed as (18):

\[ -\kappa (H\Omega + H\Gamma_2 + H N + \Gamma_1 \Omega + \Gamma_1 \Gamma_2 - \Sigma \Omega - \Sigma \Gamma_2 - HT) - \Xi (H\Omega + H\Gamma_2 + H N + \Gamma_1 \Omega + \Gamma_1 \Gamma_2 - H\Lambda - \lambda \Omega - \Lambda \Gamma_2) < 0 \]  
(18)

This indicates that the parameters of the most efficient sensing [32–35] form a narrower topological zone due to the higher probability of the destabilization factors realization. Nevertheless, it will remain relatively wide. Moreover, as no side processes compromise the analyte and modifier stability, the steady-state stability will always correspond to the linear dependence between the electrochemical parameter and concentration. For those reasons, this system will remain electroanalytical efficient, and the electroanalytical process will be either diffusion or kinetically controlled.

The detection limit is defined by the monotonic instability, describing the margin between the stable and unstable states. Its condition is \( \text{Det} J = 0 \), or (19)

\[ -\kappa (H\Omega + H\Gamma_2 + H N + \Gamma_1 \Omega + \Gamma_1 \Gamma_2 - \Sigma \Omega - \Sigma \Gamma_2 - HT) - \Xi (H\Omega + H\Gamma_2 + H N + \Gamma_1 \Omega + \Gamma_1 \Gamma_2 - H\Lambda - \lambda \Omega - \Lambda \Gamma_2) = 0 \]  
(19)

The oscillatory behavior generally realized beyond the detection limit is also possible in this system. Moreover, it is far more probable than in similar electroanalytical processes [32–35].

The electrochemical and chemical stages influence the double electric layer (DEL) and polymer backbone ionic force, resistance, and conductivity. Those influences are cyclical, providing the oscillations in electrochemical parameters.

The oscillatory behavior via Hopf bifurcation is described by the positive positivity of the addendums in the main diagonal Jacobian elements. These elements are \( j k_d f (1 - p - p \ast) \exp\left(\frac{pF\phi_0}{RT}\right) \), \( l k_q p \ast \exp\left(\frac{pF\phi_0}{RT}\right) \), \( l k_{g2} p \ast \exp\left(\frac{qF\phi_0}{RT}\right) \) describing the cyclic influences of the electrochemical stages and \( a k_q p \exp(-ap) \) describing the DEL ionic force, conductivity, and impedance cyclic changes during the chemical reactions. The oscillations frequency is expected to be high, and the amplitude is expected to be small. The oscillatory scenario becomes even more realistic if the diclofenac and hydrolysate molecules enter horizontal electropolymerization in the doped state. By this, a bilayer conducting polymer may be yielded. This system will be described in our next works.

4. Conclusions

From the theoretical description of diclofenac electrochemical determination over an undoped conducting polymer, it has been possible to conclude the polymer may serve as an
excellent modifier for sucralose quantification. The stable steady-state is maintained easily. And the process may be diffusion-controlled or kinetically controlled. The oscillatory behavior in this system may be caused only by DEL influences of both electrochemical and chemical stages.

**Funding**

This research received no external funding.

**Acknowledgments**

This research has no acknowledgment.

**Conflicts of Interest**

The authors declare no conflict of interest.

**References**

1. Alves de Lima e Silva, A.; Viana, A.S.; Silva, P.M.; de Matos Nogueira, E.; Salgado, L.T.; Tomazetto de Carvalho, R.; Geraldo da Silva Filho, R. Diclofenac May Induce PIA-Independent Biofilm Formation in *Staphylococcus aureus* strains. *Int. J. Microbiol.* 2021, 2021.
2. Thomas, E.T.; Richards, G.C. Diclofenac in adolescents: diagnosing and treating gastrointestinal adverse drug reactions can prevent future deaths. *BMJ Evidence-Based Medicine* 2021, 26, https://doi.org/10.1136/bmjebm-2020-111640.
3. Banihani, S.A. Effect of diclofenac on semen quality: A review. *Andrologia* 2021, 53, https://doi.org/10.1111/and.14021.
4. Sills, J.; Margalida, A.; Green Rhys, E.; Hiraldo, F.; Blanco, G.; Sánchez-Zapata José, A.; Santangeli, A.; Duriez, O.; Donázár José, A. Ban veterinary use of diclofenac in Europe. *Science* 2021, 372, 694-695, https://doi.org/10.1126/science.abj0131.
5. Ailincai, D.; Agop, M.; Marinas, I.C.; Zala, A.; Irimiciuc, S.A.; Dobreci, L.; Petrescu, T.-C.; Volovat, C. Theoretical model for the diclofenac release from PEGylated chitosan hydrogels. *Drug Delivery* 2021, 28, 261-271, https://doi.org/10.1080/10717544.2021.1876181.
6. Yang, L.; Li, J.; Li, Y.; Zhou, Y.; Wang, Z.; Zhang, D.; Liu, J.; Zhang, X. Diclofenac impairs the proliferation and glucose metabolism of triple-negative breast cancer cells by targeting the e-Myc pathway. *Exp Ther Med* 2021, 21, https://doi.org/10.3892/etm.2021.10016.
7. Panda, P.C.; Mishra, N.R.; Patra, C.S.; Nayak, B.K.; Panda, S.K. Intravenous Acetaminophen vs Intravenous Diclofenac Sodium in Management of Skeletal Vaso-occlusive Crisis Among Children with Homozygous Sickle Cell Disease: A Randomized Controlled Trial. *Indian Pediatrics* 2021, 58, 229-232, https://doi.org/10.1007/s13312-021-2160-3.
8. Bano, F.; Malik, A.; Ahammad, S.Z. Removal of Estradiol, Diclofenac, and Triclosan by Naturally Occurring Microalgal Consortium Obtained from Wastewater. *Sustainability* 2021, 13, https://doi.org/10.3390/su13147690.
9. Ferreira, M.; Güney, S.; Kuźniarska-Bieracka, I.; Soares, O.S.G.P.; Figueiredo, J.L.; Pereira, M.F.R.; Neves, I.C.; Fonseca, A.M.; Parpot, P. Electrochemical oxidation of diclofenac on CNT and M/CNT modified electrodes. *New Journal of Chemistry* 2021, 45, 12622-12633, https://doi.org/10.1039/d1nj01117k.
10. Kumari, P.; Pal, B.; Das, R.K. Superior adsorptive removal of eco-toxic drug diclofenac sodium by Zn–Al LDH-xBi2O3 layer double hydroxide composites. *Applied Clay Science* 2021, 208, https://doi.org/10.1016/j.clay.106119.
11. Siozou, E.; Sakkas, V.; Kourkoumelis, N. Quantification and Classification of Diclofenac Sodium Content in Dispersed Commercially Available Tablets by Attenuated Total Reflection Infrared Spectroscopy and Multivariate Data Analysis. *Pharmaceuticals* 2021, 14, https://doi.org/10.3390/ph14050440.
12. Kovačs, E.D.; Silaghi-Dumitrescu, L.; Kovács, M.H.; Roman, C. Determination of the Uptake of Ibuprofen, Ketoprofen, and Diclofenac by Tomatoes, Radishes, and Lettuce by Gas Chromatography–Mass Spectrometry (GC–MS), *Analytical Letters* 2021, 54, 314-330, https://doi.org/10.1080/00032719.2020.1779278.
13. Magdy, G.; Belal, F.; Abdel-Megied, A.M.; Abdel Hakiem, A.F. Two different synchronous spectrofluorimetric approaches for simultaneous determination of febuxostat and ibuprofen. *Royal Society open science* 2021, 8, https://doi.org/10.1098/rsos210354.
14. Bahadori, Y.; Razmi, H. Design of an electrochemical platform for the determination of diclofenac sodium utilizing a graphenized pencil graphite electrode modified with a Cu–Al layered double hydroxide/chicken feet yellow membrane. *New Journal of Chemistry* **2021**, *45*, 14616-14625, https://doi.org/10.1039/d1nj02582j.

15. Genç, N.; Durna, E.; Erkişi, E. Optimization of the adsorption of diclofenac by activated carbon and the acidic regeneration of spent activated carbon. *Water Science and Technology* **2020**, *83*, 396-408, https://doi.org/10.2166/wst.2020.577.

16. Boumya, W.; Taoufiq, N.; Achak, M.; Bessbousse, H.; Elhalil, A.; Barka, N. Electrochemical sensors and biosensors for the determination of diclofenac in pharmaceutical, biological and water samples. *Talanta Open* **2021**, *3*, https://doi.org/10.1016/j.talo.2020.100026.

17. Kozak, J.; Tyszczuk-Rotko, K.; Wójciak, M.; Sowa, I. Electrochemically Activated Screen-Printed Carbon Sensor Modified with Anionic Surfactant (aSPCE/SDS) for Simultaneous Determination of Paracetamol, Diclofenac and Tramadol. *Materials* **2021**, *14*, https://doi.org/10.3390/ma14133581.

18. Yaghoubian, H.; Tajik, S.; Beitollahi, H.; Sarhadi, H.; Sheikhshoaie, I. Fe2MoO4 magnetic nanocomposite modified screen printed graphite electrode as a voltammetric sensor for simultaneous determination of nalbuphine and diclofenac. *Journal of Materials Science: Materials in Electronics* **2021**, *32*, 17311-17323, https://doi.org/10.1007/s10854-021-06244-3.

19. de Carvalho, R.C.; Betts, A.J.; Cassidy, J.F. Diclofenac determination using CeO2 nanoparticle modified screen-printed electrodes – A study of background correction. *Microchemical Journal* **2020**, *158*, https://doi.org/10.1016/j.micjoc.2020.105258.

20. Fadhel, S.; Al-kadumi, A.S.H.; Imran, N.A.; Abdulateef, M.H. A Developed Method for the Estimation of Diclofenac Sodium via Coupling with Diazotized 4-Aminocetophenone. *Egyptian Journal of Chemistry* **2021**, *64*, 3703-3709, https://doi.org/10.21608/jechem.2021.68509.3497.

21. Kumar, Y.; Vashistha, V.K.; Das, D.K. Synthesis of Perovskite Type NdFeO3 Nanoparticles and Used as Electrochemical Sensor for Detection of Paracetamol. *Lett. Appl. NanoBioSci.* **2020**, *9*, 866-869, https://doi.org/10.33263/LIANBS91.866869.

22. Sá, A.C.d.; Barbosa, S.C.; Raymundo-Pereira, P.A.; Wilson, D.; Shimizu, F.M.; Raposo, M.; Oliveira, O.N. Flexible Carbon Electrodes for Electrochemical Detection of Bisphenol-A, Hydroquinone and Catechol in Water Samples. *Chemosensors 2020*, *8*, https://doi.org/10.3390/chemosensors8040103.

23. Alberti, G.; Zanoni, C.; Losi, V.; Magnaghi, L.R.; Biesuz, R. Current Trends in Polymer Based Sensors. *Chemosensors 2021*, *9*, https://doi.org/10.3390/chemosensors9050108.

24. Ramanavicius, S.; Ramanavicius, A. Conducting Polymers in the Design of Biosensors and Biofuel Cells. *Polymers 2021*, *13*, https://doi.org/10.3390/polym13010049.

25. Ramanaviciene, A.; Pikusiene, I. Polymers in Sensor and Biosensor Design. *Polymers 2021*, *13*, https://doi.org/10.3390/polym13060917.

26. Manjunatha, J. Poly(Adenine) Modified Graphene-Based Voltammetric Sensor for the Electrochemical Determination of Catechol, Hydroquinone and Resorcinol. *The Open Chemical Engineering Journal* **2020**, *14*, 52–62, https://doi.org/10.2174/1874123102014010052.

27. Ahmad, K.; Kumar, P.; Mobin, S.M. A highly sensitive and selective hydroquinone sensor based on a newly designed N+GO/SiZrO3 composite. *Nanoscale Advances* **2020**, *2*, 502-511, https://doi.org/10.1039/c9na00573k.

28. Romero-Montero, A.; del Valle, L.J.; Puiggali, J.; Montiel, C.; García-Arrazola, R.; Gimeno, M. Poly(gallic acid)-coated polycaprolactone inhibits oxidative stress in epithelial cells. *Materials Science and Engineering: C* **2020**, *115*, https://doi.org/10.1016/j.msec.2020.111154.

29. Zamudio-Cuevas, Y.; Andoneyi-Elguera, M.A.; Aparicio-Juárez, A.; Aguillón-Solís, E.; Martínez-Flores, K.; Ruvalcaba-Paredes, E.; Velasquillo-Martínez, C.; Ibarra, J.; Martínez-López, V.; Gutiérrez, M.; et al. The enzymatic poly(gallic acid) reduces pro-inflammatory cytokines in vitro, a potential application in inflammatory diseases. *Inflammation* **2021**, *44*, 174-185, https://doi.org/10.1007/s10753-020-01319-5.

30. Yang, P.; Zhang, S.; Chen, X.; Liu, X.; Wang, Z.; Li, Y. Recent developments in polypyrrole fluorescent nanomaterials. *Materials Horizons 2020*, *7*, 746-761, https://doi.org/10.1039/c9mh01197h.

31. Das, I.; Goel, N.; Agrawal, N.R.; Gupta, S.K. Growth Patterns of Dendrimers and Electric Potential Oscillations during Electropolymerization of Pyrrole using Mono- and Mixed Surfactants. *The Journal of Physical Chemistry B* **2010**, *114*, 12888-12896, https://doi.org/10.1021/jp105183q.

32. Das, I.; Goel, N.; Gupta, S.K.; Agrawal, N.R. Electropolymerization of pyrrole: Dendrimers, nano-sized patterns and oscillations in potential in presence of aromatic and aliphatic surfactants. *Journal of Electroanalytical Chemistry* **2012**, *670*, 1-10, https://doi.org/10.1016/j.jelechem.2012.01.023.

33. Tkach, V.; Kushnir, M.; Skrypska, O.; Ivanushko, Y.; de Oliveira, S.; Yagodynets’, P.; Luganska, O.La descripción teórica de la electropolimerización de compuestos hidroquinónicos, obtenidos electroquimicamente. *South Florida J. Dev.* **2021**, *2*, 2552–2561, https://doi.org/10.46932/sfdvd2n2-111.

34. Tkach, V.V.; Kushnir, M.V.; de Oliveira, S.C.; Ivanushko, Y.G.; Tkach, V.O.; Myrofanova, H.Y.; Zadoia, A.O.; Yagodynets, P.I.; Kormosh, Z.O.; Luganska, O.V. Theoretical Description for Copper (II) Electrochemical Determination and Retention on a (2-pyridilazo)-2-naphthole-Modified Anode. *Lett. Appl. NanoBioSci.* **2021**, *10*, 2078 – 2084, https://doi.org/10.33263/LIANBS102.20782084.
35. Tkach, V.; Kushnir, M.; Ahafonova, O.; Mytchenok, M.; Bocharov, A.; Kovalchuk, P.; de Oliveira, S.; Yagodynets, P.; Kormosh, Z.; Reis, L. The theoretical description for the electrochemical determination of 4-4'-dihydroxyazobenzene, assisted by a composite of squarainedye with cobalt (iii) oxyhydroxide in pair with cobalt (iv) oxide. *Appl. J. Env. Eng. Sci.* **2021**, *7*, 55–62, https://doi.org/10.48422/IMIST.PRSMS/ajeess-v7i1.23046.