The study of the A, C and E vitamin effect on the electrooxidation processes of E155 food additive

Research article

Bogdan Tutunaru *, Amelia Bogatu

University of Craiova, Faculty of Sciences, Department of Chemistry, Calea Bucureşti 107i, Craiova, Romania
*E-mail: tutunaruchim@yahoo.com

Abstract

Electrochemical processes such as electrooxidation represent one of the modern methods of degrading organic pollutants, including food additives. This study examines the electrochemical behavior of the food additive E155 (Brown HT) using platinum electrodes in sodium chloride saline solution by two electrochemical methods, cyclic voltammetry and electrolysis at constant current density, to predict the electrochemical behavior and the possibility of its removal from polluted waters. These electrochemical methods are associated with UV-Vis spectrophotometric analysis. Coloring food additives are frequently used in the presence of vitamins, which also act as antioxidant food additives. The study highlights the influence of vitamins A-palmitate, vitamin C and vitamin E-acetate on the electrochemical stability of the additive E155. The presence of vitamin C in the electrolyte solution has the effect of delaying the processes of electrochemical degradation of E155 and at the same time the degree of degradation has the minimum value for the same electrolysis time.

1. INTRODUCTION

Brown HT, also called Chocolate Brown HT, Food Brown 3, C.I. 20285 or E155 is an azo food coloring used to give brown color to various foods. Brown HT is used to replace cocoa or caramel as a colorant mainly in flour, chocolate cakes, but can also be found in sugar confectionery, fruit products, fish, canned meat, ice cream and sauces and other products, including pills [1-6]. The dietary level as well as the toxic effects of this food additive are controversial and at the same time contradictory topics [1-6]. The 13-week short-term toxicity study showed that no changes in urine composition, weight changes, or histopathological changes were evident after administration of E155 to pigs [1]. The long-term toxicity study of 90 weeks or even 2 years on mice and rats, although they revealed changes in certain tissues [2-4], brown staining of internal organs, infiltration of leukocytes in the liver [2], a reduced concentration of hemoglobin [3], high incidence of adenosis and fibroadenosis [3] concluded that no long-term toxicity or carcinogenic potential was detected with dietary levels of E155 up to 10,000 ppm. Absorption, metabolism and excretion of the additive E155 are dose-dependent and for doses between 50 and 250 mg/kg bw it was observed to be almost completely eliminated within 72 hours [6,7].

The use of the E155 additive in industries important to human health (pharmaceutical, food, cosmetic) has imposed strict regulations on its rational use. Thus, methods for its determination or degradation have been developed such as spectrophotometric, chromatographic and electrochemical methods [8-11].

The electrochemical technologies used in the removal of organic pollutants from polluted waters follow aspects such as the influence of the type of electrode used [12-17], the type of electrochemical method [15,16,18,19], the electrochemical generation of reactive species [12,15,16,18], optimization of operational parameters [14,16,17] including pH, current density, type and concentration of supporting electrolyte, distance between electrodes, temperature, pollutant concentration.

This article presents the experimental results on the electrochemical degradation of the food coloring additive E155 in a

simulated aqueous environment in the presence of chloride ions using platinum electrodes. Knowing the antioxidant activity of vitamins and also the fact that food, cosmetic and pharmaceutical products contain both colorants and antioxidant additives (such as vitamins), the influence of vitamins A, C and E on the electrochemical behavior of E155 was also studied.

2. MATERIALS AND METHODS

2.1. Materials

Sodium chloride used as the supporting electrolyte and vitamins A, C, and E were purchased from Merck and were of analytical and pharmaceutical grade, respectively. The food additive Brown HT (E155) was procured from a local confectionery. Inert platinum electrodes with a purity of 99.99% were in the form of plates with a surface of 1 cm^2.

2.2. Analysis methods

The study of the electrochemical behaviour of E155 was carried out using two electrochemical methods, namely cyclic voltammetry and electrolysis at constant current density.

Electrochemical analysis was performed using a VoltaLab 40 electrochemical potentiostat/galvanostat, VoltaMaster 4 software. In the cyclic voltammetry method, a potential sweep rate of 100 mV·s^{-1} was used between potentials of -2.0 V (E_{start} / E_{stop}) and 2.0 V (E_{switch}). In constant current density electrolysis, a constant current density of 50 mA·cm^{-2} was imposed for different time periods.

Electrochemical methods were coupled with UV-Vis spectrophotometric analysis using a Varian Cary 50 spectrophotometer, CaryWin UV software (quartz spectrophotometric cuvette with 10 mm optical path length).

All experiments were performed at room temperature under a dynamic stirring regime at 300 rpm.

Five stock solutions were prepared namely:

1) 10^{-2} mol·L^{-1} E155

2) 10^{-2} mol·L^{-1} vitamin A

3) 10^{-2} mol·L^{-1} vitamin C

4) 10^{-2} mol·L^{-1} vitamin E

5) 1.0 mol·L^{-1} NaCl

All stock solutions were prepared on the same working day and were kept in a dark environment throughout the experiments.

The stock solutions were used to prepare the working solutions by appropriate dilutions:

1) 10^{-1} mol·L^{-1} NaCl, (**NaCl**)

2) 10^{-4} mol·L^{-1} E155, 10^{-1} mol·L^{-1} NaCl, (**E155_NaCl**)

3) 10^{-4} mol·L^{-1} E155, 10^{-1} mol·L^{-1} NaCl, 10^{-5} mol·L^{-1} vitamin A (**E155_NaCl_vitA**)

4) 10^{-4} mol·L^{-1} E155, 10^{-1} mol·L^{-1} NaCl, $2\cdot10^{-4}$ mol·L^{-1} vitamin C (**E155_NaCl_vitC**)

5) 10^{-4} mol·L^{-1} E155, 10^{-1} mol·L^{-1} NaCl, 10^{-4} mol·L^{-1} vitamin E (**E155_NaCl_vitE**)

3. RESULTS AND DISCUSSION

3.1. Electrochemical behaviour of E155 in saline solution

Figure 1 shows the cyclic voltammograms corresponding to the platinum electrode in the 10^{-1} mol·L^{-1} NaCl solution both in the absence and in the presence of 10^{-4} mol·L^{-1} E155 and the UV-Vis spectrophotograms of E155_NaCl solution during electrolysis at constant current density.

Through the comparative representation of the two cyclic voltammograms (Figure 1a), it can be seen that they differ at high values of the potentials of the working electrode, respectively high values of the current densities.

At high cathodic overvoltages corresponding to the starting potential of -2 V, high current densities corresponding to hydrogen

depolarization reactions are recorded. As the potential of the working electrode moves to more and more positive values, it is observed that in the potential range between -1 and +1 V, the current densities are small, with values close to 0. When the potential of the platinum electrode reaches value of 1.03 V, a significant increase in current densities occurs due to the cumulative concurrent processes of both oxygen depolarization and electrochemical generation of chlorine species such as hypochlorite, chlorite, chlorate, and perchlorate. The anodic current densities reach a maximum value of 67 mA·cm⁻² and when the polarization is reversed, there are several maxima of the cathodic current density corresponding to the reduction of some species formed during direct sweeping, these species being represented both by species in the liquid phase and platinum surface. The chemical and electrochemical degradation processes of the E155 additive depend on certain experimental parameters, such as pH, the presence of catalysts, the nature and composition of the electrolyte solution [20].
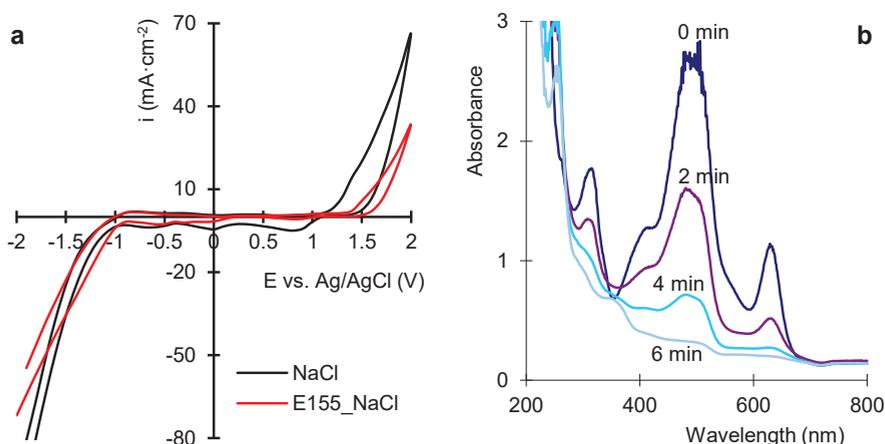
Figure 1. Cyclic voltammograms corresponding to the Pt electrode in NaCl and E155_NaCl solutions (a); UV-Vis spectrophotograms of E155_NaCl solution during electrolysis at constant current density (b).

It can be observed that in the presence of organic molecules of the additive E155, the values of the current densities are lower at the same value of the potential of the working electrode. Figure 1a shows a decrease in current densities associated with a decrease in hysteresis loop. This is due to the adsorption of dye molecules on the electrode

surface and also indicates a decrease in the rate of electrode processes at the metal/electrolyte solution interface. In the presence of the E155 additive, maximum values of the anodic current density of 33.4 mA·cm^{-2} are recorded and, at the same time, the passivity range shows a slight expansion from 1.03 V to 1.29 V. After the polarization reversal, the cathodic current densities show much lower values corresponding to the reduction of the charge transfer rate at the electrode surface.

The UV-Vis spectra of the electrolyte solution (Figure 1b), recorded during electrolysis at constant current density, indicate a significant decrease in the absorbance values corresponding to the food dye E155. From the first moments of the electrolysis, the degradation of BHT is indicated by a decrease of the absorbance values corresponding to the three absorption maxima characteristic of the organic molecule (Figure 1b). At the end of the electrolysis, after 6 minutes, the degree of degradation of the chromophore reaches a maximum value of 97%.

3.2. Influence of vitamin A-palmitate on the electrochemical behaviour of E155

Due to the antioxidant action of vitamins, the influence of vitamin A-palmitate (vitA) on the electrochemical degradation of the food additive E155 was studied.

Figure 2a shows the cyclic voltammograms corresponding to the platinum electrode in the solution of 10^{-1} mol·L^{-1} NaCl, 10^{-4} mol·L^{-1} E155 both in the absence (E155_NaCl) and presence (E155_NaCl_vitA) of 10^{-5} mol·L^{-1} vitA.

Unlike the previous case, in which sodium chloride was used as a supporting electrolyte, it was observed that in the presence of vitamin A-palmitate there is no big difference between the current densities corresponding to the two electrochemical systems studied.

Electrochemical generation of active chlorine species (hypochlorite, chlorite, chlorate, and perchlorate anions) occurs at values greater than 1.0 V of the working electrode potential. The difference in the presence of vitamin A is given by the decrease in current density values from 33.4 mA·cm^{-2} to 18.2 mA·cm^{-2}.
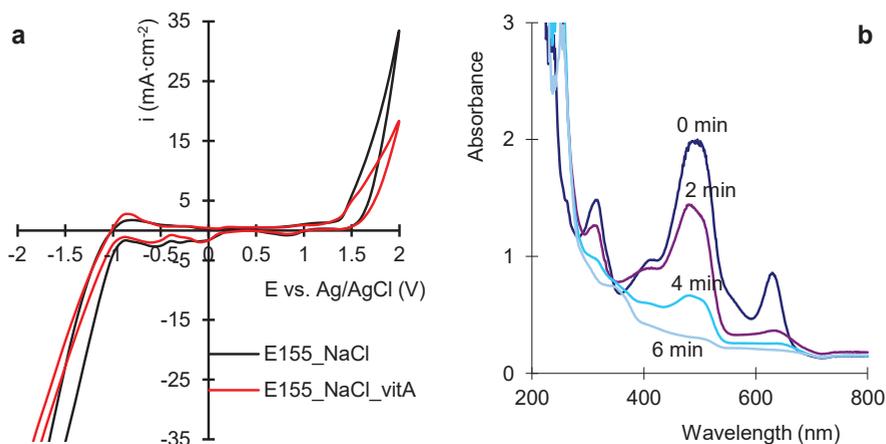
Figure 2. Cyclic voltammograms corresponding to the Pt electrode in E155_NaCl and E155_NaCl_vitA solutions (a); UV-Vis spectrophotograms of E155_NaCl_vitA solution during electrolysis at constant current density (b).

The electrochemical degradation of BHT is achieved both directly through the participation of dye molecules in the charge transfer processes at the electrode surface, and indirectly through the oxygenated species of chlorine inside the electrolyte solution. Recent literature studies show that the electrochemical degradation of the E155 food additive depends on the nature of the counterion, thus different degrees of degradation were obtained when the supporting electrolyte was represented by different halogenated saline solutions [21]. Studies on the reactivity and intermediates generated in the electrochemical processes of vitamin A-palmitate and silver nanoparticles indicated a strong interaction between vitamin A-palmitate molecules and silver nanoparticles in sodium chloride saline solution [22].

The UV-Vis spectra of electrolyte solutions subjected to electrolysis at constant current density (Figure 2b) show a delay in the electrochemical degradation of E155 food additive. And in this case the electrochemical degradation is also total (97%) in just a few minutes.

3.3. Influence of vitamin C on the electrochemical behaviour of E155

Vitamin C or ascorbic acid is one of the vitamins with the strongest antioxidant action, and the results of voltammetric analyses associated with spectrophotometric ones prove this.

In figure 3a, the cyclic voltammograms corresponding to the Pt electrode, in 10^{-1} mol·L^{-1} NaCl solution, 10^{-4} mol·L^{-1} E155, in the absence and presence of $2·10^{-4}$ mol·L^{-1} vitC are shown.

When vitamin C is present in the electrolyte solution, higher current densities are recorded compared to the solution that contain vitamin A. The increase in current densities indicates an intensification of the electrode processes in the presence of vitamin C.

The presence of vitamin C in the electrolyte solution modifies both anodic and cathodic processes; it is observed that only the cathodic peaks recorded at the potential values of -0.1 V and 0.8 V present higher current densities, instead the cathodic peak recorded at the potential of the working electrode of -0.6 V is reduced in intensity. This is also correlated with the processes taking place in the electrolyte solution.
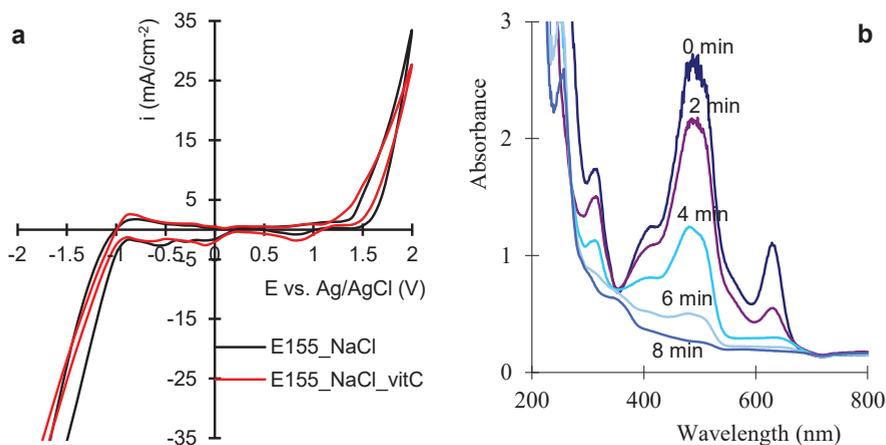
Figure 3. Cyclic voltammograms corresponding to the Pt electrode in NaCl and E155_NaCl_vitC solutions (a); UV-Vis spectrophotograms of E155_NaCl_vitC solution during electrolysis at constant current density (b).

At the same time, electrode processes involving both the supporting electrolyte and E155 additive molecules must also consider the processes in which vitamin C molecules participate. The presence in the electrolytic solution of colloidal species such as silver nanoparticles (nAg) leads to a faster electrodegradation of vitamin C (VitC) in NaCl solution according to zero-order reaction kinetics. The value of the rate constant in the presence of nanoparticles was 0.78 u.A. min^{-1}, while in the absence of nanoparticles a value of 0.39 u.A. min^{-1} was obtained [23].

The UV-Vis spectra of the electrolyte solution subjected to electrolysis at constant current density (Figure 3b) show a delay in the electrochemical degradation of food dye E155; practically after 1 minute the UV-Vis spectra are almost identical. In this case the electrochemical degradation is almost total (92%) in just a few minutes (8 minutes).

3.4. Influence of vitamin E-acetate on the electrochemical behaviour of E155

To observe how the electrochemical degradation of the food additive Brown HT is influenced by the presence of vitamin E-acetate, the corresponding cyclic voltammograms of the electrolyte solutions, both in the absence and in the presence of vitamin E, were experimentally performed. The working solutions containing the supporting electrolyte, E155 and vitamin E were subjected to electrolysis, and at different times from the start of the electrolysis were analyzed by UV-Vis spectrophotometry.

Figure 4a shows the cyclic voltammograms corresponding to the platinum electrode in the solution of 10^{-1} mol·L^{-1} NaCl, 10^{-4} mol·L^{-1} E155 both in the absence and in the presence of 10^{-4} mol·L^{-1} vitE.
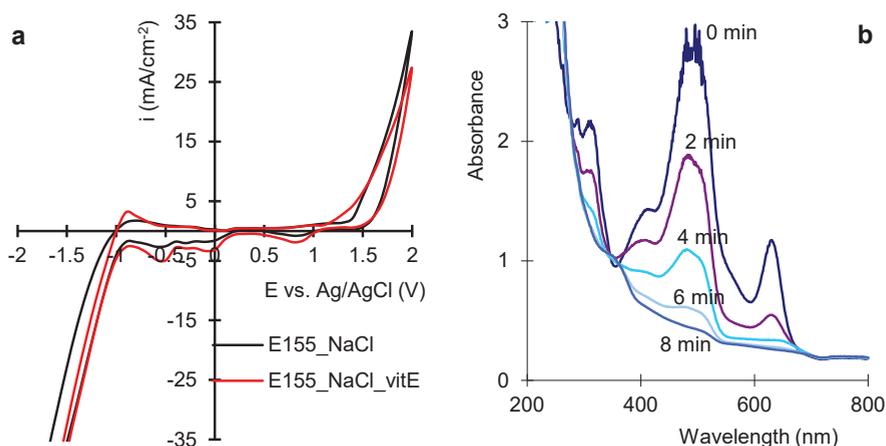
Figure 4. Cyclic voltammograms corresponding to the Pt electrode in NaCl and E155_NaCl_vitE solutions (a); UV-Vis spectrophotograms of E155_NaCl_vitE solution during electrolysis at constant current density (b).

In the experimental conditions used, it was observed that in the presence of vitamin E molecules, the current densities present high

values, this is explained considering the strong hydrophilic nature of vitamin E; vitamin E exhibits a stronger adsorption on the surface of the platinum electrode.

Recent studies comparatively use Electro-Fenton (EF), Photo-Electro-Fenton (PEF), Electro-Oxidation (EO) and EO/Ozone (O_3) methods for the decolorization of E155 additive [23]. This study indicates a decrease in the degradation efficiency of E155 in the order PEF > EF > EO > O_3. Electrochemical or radiolytic degradation of E155 shows the formation of non-toxic degradation intermediates such as oxalic, oxamic and glyoxylic acid, accompanied by a decrease in chemical oxygen demand [24,25].

Under electrolysis conditions at constant current density (i = 50 mA·cm^{-2}), the UV-Vis spectra of the electrolyte solution were recorded from minute to minute and are shown in Figure 4b. It can be seen that the spectrum recorded after 1 min. from the start of electrolysis is almost identical to that at time zero. This indicates a delay in the electrochemical degradation processes of the E155 additive.

In this case the electrochemical degradation is almost total (95%) in less than 10 minutes.

The variation of the degree of electrochemical degradation (ED) of E155 in the absence and in the presence of all the three studied vitamins is summarized in Figure 5. The presence of vitamins in the electrolytic solution results in a decrease in ED values, the obtained results show that vitamin C has the most pronounced effect.
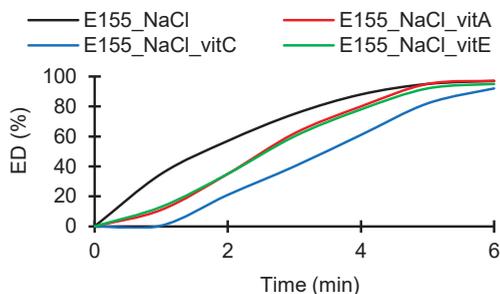
Figure 5. The variation of the degree of electrochemical degradation (ED) of E155 in the absence and in the presence of A, C and E vitamins.

4. CONCLUSION

The study presents the experimental results obtained regarding the electrochemical behaviour of the food additive E155 in sodium chloride saline solutions using platinum electrodes and the influence of vitamins A-palmitate, vitamin C and vitamin E-acetate on the electrochemical stability of this additive. The electrochemical methods cyclic voltammetry and constant current density electrolysis were used in association with UV-Vis spectrophotometric analysis.

Cyclic voltammetry study indicates the formation of electrochemically active chlorine species and the participation in the electrode processes of the supporting electrolyte, E155 additive molecules and vitamin molecules (A-palmitate, C and E-acetate).

Furthermore, the cyclic voltammograms of the Pt electrode indicate the presence on the electrode surface of much more complex processes than a simple metal/electrolyte solution interaction.

The variation of the degree of electrochemical degradation (ED) of E155 (Brown HT) in the presence of antioxidant vitamins shows that vitamin C has the most pronounced effect.

The spectrophotometric method associated with cyclic voltammetry and electrolysis at constant current density confirms the electrochemical degradation of the food additive Brown HT (E155) and its total degradation in a very short time of 5 - 7 minutes.

REFERENCES

[1] R.J. Hendy, K.R. Butterworth, I.F. Gaunt, J. Hooson, P. Grasso, *Toxicology*, 11 **(1978)** 189.
[2] J.J-P. Drake, K.R. Butterworth, I.F. Gaunt, J. Hardy, *Toxicology*, 10 **(1978)** 17.
[3] F.M.B. Carpanini, K.R. Butterworth, I.F. Gaunt, I.S. Kiss, P. Grasso, S.D. Gangolli, *Toxicology*, 11 **(1978)** 303.
[4] B.A. Mangham, S.R. Moorhouse, D. Grant, P.G. Brantom, I.F. Gaunt, *Food Chem. Toxic.*, 25 **(1987)** 999.
[5] D. Grant, I.F. Gaunt, *Food Chem. Toxic.*, 25 **(1987)** 1009.
[6] J.C. Phillips, D. Mendis, I.F. Gaunt, *Food Chem. Toxic.*, 25 **(1987)** 1013.
[7] D.R. Tennant, *Food Chem. Toxic.*, 46 **(2008)** 1985.
[8] F. Karimi, E. Demir, N. Aydogdu, M. Shojaei, M.A. Taher, P.N. Asrami, M. Alizadeh, Y. Ghasemi, S. Cheraghi, *Food Chem. Toxic.*, 165 **(2022)** 113075.
[9] A. Shokrollahi, S. Ahmadi, *J. Taibah Univ. Sci.*, 11 **(2017)** 196.
[10] K. Yamjala, M.S. Nainar, N.R. Ramisetti, *Food Chem.*, 192 **(2016)** 813.

[11] N. Martins, C.L. Roriz, P. Morales, L. Barros, I.C.F.R. Ferreira, *Trends Food Sci. Technol*., 52 **(2016)** 1.

[12] C.A. Martińez-Huitle, M.A. Rodrigo, Ignasi Sires, O. Scialdone, *Appl. Catal. B: Environ*., 328 **(2023)** 122430.

[13] F. Deng, E. Brillas, *Sep. Purif. Technol*., 316 **(2023)** 123764.

[14] F.E. Titchou, H. Zazou, H. Afanga, J. El Gaayda, R.A. Akbour, P.V. Nidheesh, M. Hamdani, *J. Water Process Eng*., 41 **(2021)** 102040.

[15] C.A. Martınez-Huitle, E. Brillas, *Appl. Catal. B: Environ*., 87 **(2009)** 105.

[16] E. Brillas, C.A. Martınez-Huitle, *Appl. Catal. B: Environ*., 166–167 **(2015)** 603.

[17] J. Qiao, Y. Xiong, *J. Water Process Eng*., 44 **(2021)** 102308.

[18] F.Y. AlJaberi, S.A. Ahmed, H.F. Makki, A.S. Naje, H.M. Zwain, A.D. Salman, T. Juzsakova, S. Viktor, B. Van, P.-C. Le, D.D. La, S.W. Chang, M.-J. Umk, H.H. Ngo, D.D. Nguyen, *Sci. Total Environ*., 867 **(2023)** 161361.

[19] K.G. Pavithra, P.S. Kumar, V. Jaikumar, P.S. Rajan, *J. Ind. Eng. Chem*., 75 **(2019)** 1.

[20] A.S.M. Kuba, A.M.J.AL- Shamari, *Mater. Today: Proc*., 49 **(2022)** 2741.

[21] B. Tutunaru, A. Samide, C. Neamţu, I. Prunaru, *Chem. Ind. Chem. Eng. Q*., 25 **(2019)** 89.

[22] B. Tutunaru, A. Samide, C. Neamtu, C. Tigae, Int. J. Electrochem. Sci., 13 **(2018)** 5850.

[23] A. Samide, B. Tutunaru, *Electroanal.*, 29 **(2017)** 2498.

[24] M. Corona-Bautista, A. Picos-Benítez, D. Villasenor-Basulto, E.K Bandala, J.M. Peralta-Hernandez, *Chemosphere*, 267 **(2021)** 129234.

[25] A.V. Ponomarev, E.M. Kholodkova, A.V. Bludenko, *Radiat. Phys. Chem*., 199 **(2022)** 110357.