Craiova University Doctoral School of Sciences
Chemistry domain

Doctoral thesis summary

Scientific adviser
Univ. prof. dr. Alexandru Popescu
Univ. prof. dr. ing. Adriana Samide (tutelle)

PhD student
Chim. Cristian-Ovidiu Neamțu

2019
Craiova University
Doctoral School of Sciences
Chemistry domain

Electrochemical transformation of organic contaminants in the presence of specific anions for experimentation of some wastewater analysis/depollution models

Scientific adviser
Prof. univ. dr. Alexandru Popescu
Prof. univ. dr. ing. Adriana Samide

PhD student
Chim. Cristian Ovidiu Neamtu
TABLE OF CONTENTS

Chapter I

The current state of knowledge in the field of electrochemical degradation of organic pollutants

1.1. Electrode processes encountered in electrochemical degradation
1.2. Studies on the electrochemical degradation of medicines present in polluted waters
1.3. Studies on electrochemical depollution of polluted water with food additives
1.4. Studies on the use of electrochemical methods in the treatment of polluted waters with organic pesticides
1.5. Kinetic studies on the electrochemical degradation of organic compounds
   1.5.1. Introduction to chemical kinetics
   1.5.2. Kinetics of zero-order reactions
   1.5.3. Kinetics of first order reactions
   1.5.4. Cinetic reacțiilor de ordin II
1.6. Kinetic studies on the electrochemical degradation of compounds with pharmaceutical action in polluted waters
1.7. The study of the kinetics of electrochemical degradation of food additives from aqueous solutions
1.8. Kinetic studies on the use of electrochemical methods in the treatment of polluted waters with organic pesticides

Conclusions

Original contributions

The objectives of the doctoral thesis

Chapter II

Research methodology

2.1. Methods and equipment used in research
   2.1.1. Electrochemical methods
   2.1.2. UV-Vis spectrophotometric analysis
   2.1.3. Thermal analysis
2.2. Materials and methods of operation
   2.2.1. Study of the processes of degradation of retinyl palmitate (RP)
   2.2.2. Study of the processes of electrochemical degradation of 5-fluorouracil (5FU)
   2.2.3. The study of the processes of electrochemical degradation of the food additive Chocolate Brown HT (BHT)
   2.2.4. Study of the processes of electrochemical degradation of the food additive tartrazine (TRZ)
   2.2.5. Study of the electrochemical degradation processes of pesticides acetamiprid, emamectin, imidacloprid and propineb

Chapter III

Study of electrochemical degradation of biologically active compounds
from the class of medicines

3.1. Study of the electrochemical behavior of Vitamin A in hydroalcoholic solution
   3.1.1. Spectrophotometric study of the interactions between retinyl palmitate and colloidal silver nanoparticles in the presence of chloride and nitrogen anions

   3.1.2. Study of the electrochemical behavior of retinyl palmitate in the presence of nitrogen anions
   3.1.3. Study of the mechanism of electrochemical degradation of vitamin A
   3.1.4. Study of the electrochemical stability of vitamin A in the presence of chloride anions

3.2. Study of the electrochemical and thermal behavior of the anti-tumor 5-fluorouracil drug (5FU)
   3.2.1. Study of the electrochemical degradation of 5FU on titanium electrodes
   3.2.2. Study of the mechanism of electrochemical degradation of 5FU
   3.2.3. Study of the thermal degradation of 5FU in an inert atmosphere

Conclusions

Chapter IV

Electrochemical, kinetic and thermal studies on degradation of food additives

4.1. Study of the processes of electrochemical and thermal decomposition of the food additive Chocolate Brown HT (E155)
   4.1.1. The study of the thermal degradation of the food additive Chocolate Brown HT
   4.1.2. Study of the electrochemical stability of the food additive Chocolate Brown HT by cyclic voltammetry
   4.1.3. Study of the electrochemical stability of the food additive Chocolate Brown HT by spectrophotometric assisted electrolysis
   4.1.4. Kinetic studies of electrochemical degradation of the food additive Chocolate Brown HT in the presence of halide anions

4.2. Study of the electrochemical degradation of tartrazine in aqueous solution
   4.2.1. Direct electrochemical degradation of tartrazine
   4.2.2. Indirect electrochemical degradation of tartrazine

Conclusions

Chapter V

Reducing the ecotoxicity of pesticide-contaminated waters by electrochemical methods

5.1. Electrochemical and thermal degradation of acetamiprid
5.2. Study of the electrochemical and thermal decomposition of emamectin
5.3. Electrochemical and thermal degradation of imidacloprid
5.4. Study of the electrochemical and thermal behavior of propineb

Conclusions

General conclusions

Bibliography

Introduction

The industrial activities, in the vast majority, generate, as a result of the technological processes, waste water with a very high content of organic compounds, in particular, those of the food, pharmaceutical, cosmetic and textile industry. This fact requires the necessity of implementing methods of treatment of industrial and domestic effluents with the purpose of reintroducing these waters into the natural circuit without having a negative impact on the
underwater or terrestrial flora and fauna. The current strategies regarding environmental protection involve the use of waste treatment processes but also the development of more efficient processes that do not have harmful effects on the environment.

Protecting the quality of Europe's water resources is one of the priorities of the European Union. European Parliament has developed certain wastewater treatment directives (UWWTs) that require EU Member States to invest in urban waste collection and treatment infrastructure, nitrate directives, which require farmers to control the quantities of nitrogen fertilizers used and Directives on Pollution Prevention and Control (IPPC) with a view to minimizing pollutants discharged from industrial activities. (https://eur-lex.europa.eu/legal-content/RO/TXT/PDF/?uri=CELEX:32000L0060&from=RO)

The application of biological methods in the treatment of polluted waters with organic contaminants is not always possible due to their action on environmental crops. The use of physico-chemical methods such as oxidation with ozone or chlorine dioxide, besides a low efficiency, raises major problems regarding the transport and storage of the reactants.

The disadvantages of the classical depollution methods have been minimized by introducing new electrochemical methods that allow the efficient degradation of organic pollutants up to the values of the concentrations that fall within the values imposed by the environmental legislation in force, concentrations at which the aquatic or terrestrial ecosystems where discharged are not affected. The application of electrochemical technologies to the degradation of organic pollutants from wastewater benefits from advantages such as low costs, ease of implementation and use, compatibility with the environment.

The new technologies for waste water treatment take into account both direct electrochemical oxidation and indirect or mediated electrochemical oxidation, as evidenced by the publication of numerous specialized studies. Some of these electrochemical technologies are comparable to the conventional ones in terms of cost and efficiency.

The main electrochemical technologies developed in this regard are electrooxidation, electrocoagulation, electrofloculation and electrodeposition. Electrooxidation is achieved by the action of species with a highly oxidizing character, similar to chemical oxidation, with the exception that these species are generated electrochemically in situ and lead to a high efficiency of mineralization of organic pollutants.

In order to develop new methods, which are more efficient, but which also have low costs, the use of new experimental conditions and the optimization of methods by the complete and complex study of the factors that influence the electrochemical processes of degradation of organic pollutants have been used. Of these factors, the most important are: the nature and composition of the electrodes (stable dimensional oxide electrodes, Pt, C and graphite, boron doped diamond, SnO / SnO2, PbO / PbO2, Sb2O5), the nature and composition of the electrolyte solution, pH, value of current density, temperature, nature and concentration of the supporting electrolyte, presence of catalysts or photocatalysts, development of electro-Fenton and photoelectro-Fenton methods or advanced electro-oxidation processes. In general, an ideal electrode material in the degradation of organic pollutants must have a high oxygen evolution potential for the secondary oxygen formation reaction to be excluded. For this reason, different types of oxide electrode materials based on iridium, ruthenium, tin or lead have been tested. In each particular case, these electrode materials must be tested, in order to determine the electrocatalytic activity, oxidation stability and durability with the purpose to determine the efficiency of use for a certain process of electrochemical degradation of an organic pollutant.

The doctoral thesis highlights the results of the research activities carried out during the doctoral period and is based on a considerable number of experimental determinations on the electrochemical degradation of some organic pollutants in the class of medicines, food additives and pesticides.
The experimental results obtained, published in ISI / BDI specialized journals or communicated at national and international conferences can be used in the design of electrochemical systems in order to improve the parameters of degradation of organic pollutants.

The research activity pursued a broad characterization of the electrode processes that occur at the electrochemical degradation of the studied organic pollutants. Thus, comparative experiments were performed under different conditions on electrodes made of different materials.

The work is structured in two parts: the literature part and the original contributions part.

I. The current state of knowledge in the field
Pollution has features that affect both the environment and man. Pollutants are substances, organic or inorganic, that once reached the environment (water, air, soil) have at least one harmful effect on the ecosystem.

The literature section includes a chapter. Chapter I refers to studies on electrode processes that occur during electrochemical degradation of organic pollutants. The electrode processes leading to the in situ electrochemical generation of the highly oxidizing active species responsible for the electrooxidation of the pollutant molecules are presented and the results of the research on the electrochemical degradation of some organic pollutants in the class of drugs, food additives and pesticides. Also, both kinetic notions and certain kinetic approaches on decomposition reactions are presented, as well as the ways to optimize pollutant degradation methods.

II. Original contributions
The first general objective of the thesis is to address efficient electrochemical methods for investigating the stability of residual organic compounds from medicinal / industrial / wastewater. Therefore, the results of the study on the interactions between Vitamin A and colloidal silver in the presence of Cl- and NO3- i anions on the electrochemical stability of cytostatic 5-fluorouracil using cyclic voltammetry, constant current electrolysis and UV-Vis spectrophotometry are presented. Within the second general objective of the thesis, the mechanisms of electrochemical transformation / decomposition of both vitamin A on platinum electrodes and the cytostatic 5-fluorouracil on titanium electrodes have been elaborated.

Chapter IV systematizes the results obtained for the thermal and electrochemical degradation processes of two dyes used as food additives, namely chocolate brown HT (E155) and tartrazine (E102). An extensive study on the thermal and electrochemical degradation of the additive E155 was performed; the degrees of electrochemical degradation were determined in the presence of different halide anions using platinum electrodes; methods such as cyclic voltammetry and electrolysis at constant current density, in dynamic regime, coupled with UV-Vis spectrophotometry were used. The thermal stability of the E155 dye was studied by thermogravimetric and calorimetric methods; the thermodegradation mechanism was proposed; the optimal parameters for the decontamination of the waste water were determined (the composition of the environment, the ratio between concentrations - selective anion / dye, the pH of the environment, the temperature). The study is completed by calculating the kinetic parameters of E155 electrochemical degradation, by modeling the experimental data corresponding to the zero, first and second order kinetic models. Also in this chapter are presented the results of the study of the electrochemical behavior of tartrazine in aqueous solution.

The results of studies on reducing the toxicity of pesticide-contaminated waters by electrochemical methods are presented in Chapter V. They predict the behavior of pollutant molecules in the presence of strong oxidants such as electrochemically generated hypochlorite anions during electrode processes. The investigation was performed by cyclic voltammetry and electrolysis at constant current, in association with UV-Vis spectrophotometry. The
The objectives of the doctoral thesis

\textbf{General objectives}

\textbf{O.1.} Addressing efficient electrochemical methods, such as electrolysis at constant current density and cyclic voltammetry, for studying the stability of residual organic compounds from medicinal/industrial/wastewater: organic nutritional compounds, dyes and pesticides.

\textbf{O.2} Proposing mechanisms for electrochemical transformation/decomposition of organic compounds detected in small concentrations in wastewater.

\textbf{Specific objectives}

\textbf{O.S.1.} Coupled systems like Vitamin A-silver nanoparticles analyzed by UV-Vis spectrophotometry and cyclic voltammetry.

\textbf{O.S.2.} Electrochemical stability of drugs, e.g. 5-fluorouracil.

\textbf{O.S.3.} Study of the stability of some dyes, such as Brun HT using electrochemical methods associated with UV-Vis spectrophotometry and thermal analysis.

\textbf{O.S.4.} Reducing the toxicity of pesticide-contaminated waters by electrochemical methods.

\textbf{Motivation of the research topic}

\textit{a.} Control of the purity of wastewater contaminated with different organic compounds.

\textit{b.} Controlling the stability of certain vitamins in order to detect decomposition products with toxic potential on the human body; designing a warning model for the storage of contaminated water.

\textit{c.} Discoloration of waste water polluted with certain chemical dyes; approaching a model of dye removal.

\textit{d.} Decontamination of wastewater containing pesticides in residual quantities; approaching a model for reducing the toxicity of wastewater.

\textit{e.} The beneficial effects of Vitamin A versus the potentially toxic effects of decomposition compounds require the restriction of the discharge of contaminated water prior to purification.

\textit{f.} Large-scale use of colorants in the food industry.

\textit{g.} Use of pesticides in agriculture, generally in the form of solutions.

\textbf{Study of electrochemical degradation of biologically active compounds in the drug class}

\textit{Study of the electrochemical behavior of Vitamin A in hydroalcoholic solution}

\textit{Spectrophotometric study of the interactions between retinyl palmitate and colloidal silver nanoparticles in the presence of chloride and nitrogen anions}
Figure 1 shows UV-Vis spectra of retinyl palmitate hydroalcoholic solution and retinyl palmitate hydroalcoholic solutions containing Cl- or NO3- ions, in the absence and presence of silver nanoparticles (nAg).

**Retinyl palmitate (RP)** has two absorption maxima:
- a well defined maximum at the wavelength of about 325 nm;
- a maximum split at 250 nm, which corresponds to a high absorbance value.

**Colloidal silver nanoparticles (nAg)** have a maximum absorption at 400 nm
  - The chloride anion causes a large increase in the absorption maxima of the RP and a significant decrease in their intensity.
  - Between nAg, RP and Cl-, multiple strong interactions are established, evidenced by the disappearance of the two absorption maxima of the RP, the cleavage and the displacement of the maximum absorption of nAg at wavelengths greater than 400 nm.
  - The gradual increase of the absorbance at wavelength values less than 300 nm can be due to the formation of intermediate species between RP and nAg and / or Ag +.

The superposition of the multiple interferences detected at 400 nm highlights the spontaneity of the interaction between retinyl palmitate and colloidal silver nanoparticles, with the formation of RP_nAg complexes, in the solution containing chloride anions.

Nitrogen anions produce a shift of the absorption peaks of the RP to smaller wavelengths:
- 325 nm → 300 nm
- 250 nm → 230 nm
Figure 1. UV-Vis spectra of the alcoholic solution of RP $5 \times 10^6$ mol $\cdot$ L$^{-1}$; a - in the absence and presence of chloride and nAg anions; b - in the absence and presence of nitrogen anions and nAg; c - in the absence and presence of nAg in a concentration of 500 mg $\cdot$ L$^{-1}$.

In the presence of colloidal silver nanoparticles, the electrolyte solution absorbs strongly at 400 nm, which denotes reduced interactions between RP and nAg. The formation of complexes between retinyl palmitate molecules and colloidal silver nanoparticles explains the disappearance of the maximum at 250 nm and the occurrence of the two absorption maxima at 400 nm and 325 nm.
Scheme 1. Mechanism of electrochemical degradation of retinyl palmitate

The nonatetraene intermediate has a high reactivity due to the four double bonds in its molecular structure. At the same time, the existence of the delocalized π electron system can lead to different electrochemical degradation mechanisms. A possible path of electrochemical degradation is described by the mechanism attached.

UV-Vis spectrophotometry indicated a strong interaction between retinyl palmitate molecules and silver nanoparticles, in the presence of chloride anions and lower interactions in the presence of nitrogen ions.

The experimental results obtained by cyclic voltammetry show that the addition of colloidal silver nanoparticles to the electrolyte solution leads to a considerable decrease of the current density, followed by a significant change in the hysteresis form due to the interaction between the vitamin A molecules and the silver nanoparticles.

Study of the electrochemical and thermal behavior of the anti-tumor drug 5-fluorouracil (5FU)

Objectives proposed

1. Study of electrochemical degradation of 5FU on titanium electrodes.
2. Study of the mechanism of electrochemical degradation of 5FU.
3. Study of thermal degradation of 5FU in inert atmosphere.
Figure 2. Cyclic voltammograms recorded on Ti electrode in 0.9% NaCl solution, in the absence and in the presence of \( 5\text{FU} \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \) scanning speed of 100 mV s\(^{-1}\) potential; UV-Vis spectra of 0.9% NaCl solution, without and with \( 5\text{FU} \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \), before and after cyclic voltammetry.

The presence of the drug in the saline solution at the cyclical polarization of the titanium electrode determines the following effects:

- Changing the shape of cyclic voltamograms.
- Decreased anodic current densities.
- Extend the passivity range by approximately 0.2 V

During the cyclical polarization of the titanium electrode, the 5-fluorouracil molecules participate in the processes from the electrode / electrolyte interface, the electrochemical activity of the drug being revealed by the complete disappearance of the absorbance trace from the value of the 300 nm wavelength and the decrease of the absorbance values. corresponding to wavelengths less than 250 nm.

**Study of mechanism of electrochemical degradation of 5FU**

5FU molecules participate on the titanium electrode surface in the oxidation, tautomerization and opening processes of the pyrimidine ring, with the formation of two intermediate fragments (A and B), as shown in Scheme 2.
Scheme 2. Mechanism of electrochemical degradation of 5FU

The cyclic voltammetry of the titanium electrode demonstrates that the 5-fluorouracil molecules used as an antitumor drug are electrochemically active.

Spectrophotometric analysis of the electrolyte solution performed comparatively, before and after recording the cyclic voltamogram indicates the change of the absorption maxima, demonstrating that the 5 FU molecules are electrochemically degraded.

Electrochemical, kinetic and thermal studies on the degradation of food additives

The study of the electrochemical stability of the food additive Chocolate Brown HT by cyclic voltammetry

The electrochemical processes that occur on the surface of the platinum electrode in aqueous solutions of BHT, containing NaX support electrolytes are correlated with the processes of the X- ions from the electrode / electrolyte interface. The electrochemical degradation of organic BHT molecules can occur through: i) direct electrochemical degradation (heterogeneous) by directly participating in the processes on the surface of the electrode, as in the case of using inert support electrolytes, such as fluoride anions; ii) indirect (homogeneous) electrochemical degradation in solution, due to the electrochemically generated active species, as is the case with the use of active support electrolytes, such as chloride, bromide and iodide anions.

Figure 3 shows the cyclic voltamograms on Pt electrode in studied electrolytes, in the absence and in the presence of BHT.

Figura 3. Cyclic voltammograms recorded on Pt electrode in: a - NaX $10^{-1}$ mol $\cdot$ L$^{-1}$; b - NaX $10^{-1}$ mol $\cdot$ L$^{-1}$ containing BHT $10^{-4}$ mol $\cdot$ L$^{-1}$; (X = F, Cl, Br, I); $v = 100$ mV $\cdot$ s$^{-1}$

In the presence of fluoride anions, peaks of the low intensity anodic current densities are recorded, in the potential range from -0.5 V to 1.0 V, due to the adsorption and electrooxidation of the BHT molecule on the electrode surface. In this area of potential, the fluoride anions are electrochemically inactive and therefore, the formation of the adequate active oxygenated species cannot take place. In the solution, which contains chloride anions, the slight increase in current density in the corresponding cyclic voltamogram is correlated with the oxidation of chloride ions, which generates hypochlorite species in the proximity of the electrode. In contrast, the presence of bromide ions in the electrolyte solution increased the anodic and cathodic current densities in the potential range between -1.0 V and 0.0 V.
The study of the electrochemical stability of the food additive Chocolate Brown HT by spectrophotometrically assisted electrolysis

Electrolysis was carried out at constant current density of aqueous solutions containing Chocolate Brown HT food additive to test the effect of different electrolytes supporting NaX (X = F, Cl, Br, I) on electrochemical color removal. UV-Vis spectrophotometry can be successfully used to observe the absorbance variations of photosensitive species during electrochemical degradation processes.

Figure 4. shows the UV-Vis spectra of the aqueous BHT solutions recorded at different times of the electrolysis process:

![Figure 4.](image)

Figure 5 represents the UV-vis spectra of the aqueous solutes of the food additive recorded at different times of the electrolysis process, in the presence of bromide and iodide ions.

![Figure 5.](image)

We observe in Figure 5 a greater decrease of the absorbent values when the supporting electrolyte was represented by sodium bromide, requiring 30-40 seconds for the total removal of the dye. This attests to the high oxidation capacity of the oxygenated anions of bromine (BrO-).
The waters contaminated with this additive must be treated with specific techniques for its elimination. Figure 6 shows a maximum value for electrochemical color removal, when using bromide and chloride electrolytes. In the presence of bromide ions (Fig. 6a), the time required for total discoloration is less than 50 seconds, while for the electrolyte chloride, the time required for total discoloration is 5 minutes. In the presence of iodine, the process of electrolysis cannot be highlighted for more than 2 minutes due to the formation of iodine, so that a value bigger than 18% is not reached. Due to its electrochemical stability, the fluoride ions lead to a maximum electrochemical elimination value of the additive color of 60%, after one hour of electrolysis (Fig. 6b).

**The study of the kinetics of electrochemical degradation of the food additive Chocolate Brown HT in the presence of halide anions**

In order to determine the mode of electrochemical degradation of the food additive Chocolate Brown HT, kinetic models of zero order, first order and second order were obtained from the experimental data obtained by the spectrophotometric method.

The values of the velocity constants obtained for the electrochemical degradation of the additive Chocolate Brown HT in the presence of the different anions are compared in Table 1.

### Table 1. The values of the velocity constants obtained for the electrochemical degradation of the additive Cholocate Brown HT in the presence of different anions

<table>
<thead>
<tr>
<th>anion</th>
<th>Zero order</th>
<th>First order</th>
<th>Second order</th>
</tr>
</thead>
<tbody>
<tr>
<td>F^-</td>
<td>exponential variation</td>
<td>linear variation</td>
<td>exponential variation</td>
</tr>
<tr>
<td>Cl^-</td>
<td>linear variation</td>
<td>exponential variation</td>
<td>polynomial variation</td>
</tr>
<tr>
<td></td>
<td>k = 0,468 u.A·min^{-1}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br^-</td>
<td>polynomial variation</td>
<td>linear variation</td>
<td>exponential variation</td>
</tr>
<tr>
<td></td>
<td>k = 6,7476 min^{-1}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I^-</td>
<td>linear variation</td>
<td>polynomial variation</td>
<td>polynomial variation</td>
</tr>
<tr>
<td></td>
<td>k = 0,4263 u.A·min^{-1}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The values in Table 1 indicate a maximum electrochemical degradation rate when in the electrolyte solution the bromide anion is found and a minimum, in case of the use of the fluoride anion. At the same time, the degradation processes arise from simple kinetic models of zero or first order, without there being a similarity in terms of the electrochemical behavior between any two anions.
The study of the electrochemical degradation of tartrazine (TRZ) in aqueous solution

Direct electrochemical degradation of tartrazine

Direct electrochemical degradation of food additive E102 (tartrazine; TRZ) was studied by cyclic voltammetry associated with UV-Vis spectrophotometry, using sodium sulfate and sodium chloride as the supporting electrolyte.

Figure 7 shows the cyclic voltamograms of the platinum electrode in sodium sulphate solution $10^{-1}$ mol L$^{-1}$ in the absence and in the presence of tartrazine $5 \times 10^{-5}$ L$^{-1}$. Figure 7b shows the details of cyclic voltamograms at low values of current densities.

Figure 7a shows that the two voltammograms are very similar and differ only at very high values of anodic (> 1.5 V) and cathodic (< -1.0 V) overvoltages. At values of the working electrode potential greater than 1.5 V, the values of the recorded current densities are much higher when the electrolyte solution also contains the TRZ food additive; which shows an intensification of the charge transfer processes at the electrode / electrolyte interface.

The UV-Vis spectra of the working solution containing tartrazine in concentrations of $5 \times 10^{-5}$ mol L$^{-1}$ and Na$_2$SO$_4$ $10^{-1}$ mol L$^{-1}$ before and after the cyclic voltamogram recording are shown in Figure 8.

The oxidation stability of tartrazine was also studied by coupling the electrolysis method to constant current density with the spectrophotometric analysis of the electrolyte solution at different time points from the beginning of the electrolysis process. The value of the current density used in the electrolysis process was $i = 50$ mA cm$^{-2}$, and the electrolysis time of one hour. The UV-Vis spectra of the electrolysis solution, recorded from 10 to 10 min, are shown in figure 8.

Figure 8. UV-Vis spectra of TRZ 5 solution $\times 10^{-5}$ mol L$^{-1}$ and Na$_2$SO$_4$ $10^{-1}$ mol L$^{-1}$, recorded before and after cyclic voltammetry. UV-Vis spectra of TRZ 5 solution $\times 10^{-5}$ mol L$^{-1}$ and Na$_2$SO$_4$ $10^{-1}$ mol L$^{-1}$, at different electrolysis times (10 to 10 minutes).
**Indirect electrochemical degradation of tartrazine**

Indirect electrochemical degradation of tartrazine was studied by cyclic voltammetry associated with UV-Vis spectrophotometry using sodium chloride as the supporting electrolyte. Figure 9 shows the cyclic voltammograms of the platinum electrode in the solution of sodium chloride $10^{-1}$ mol $\cdot$ L$^{-1}$, in the absence and presence of tartrazine $5 \cdot 10^{-5}$ mol $\cdot$ L$^{-1}$. The cyclic voltammograms of the Pt electrode show a decrease of the current densities in the presence of the tartrazine molecules. The cyclic voltammogram recorded in the presence of tartrazine indicates the emergence of a new maximum (1.4 V vs. Ag / AgCl, KCl) of the current density, this being attributed to the electro-oxidation of the organic dye molecules.

The cyclic voltammograms of the Pt electrode (Fig. 9) show a decrease of the current densities in the presence of the tartrazine molecules. Chloride anions are reduced to the surface of the platinum electrode to form chlorine molecules, which react with water molecules and form hypochlorite anions. Consequently, tartrazine molecules are indirectly degraded by hypochlorite anions.

The UV-Vis spectra of the TRZ 5 solution $\cdot$ $10^{-5}$ mol $\cdot$ L$^{-1}$, 10-1 mol NaCl $\cdot$ L$^{-1}$, before and after the cyclic voltamgram recording, show that the absorbance value decreases significantly. After recording the cyclic voltamgram, the chromophoric system of tartrazine is electrochemically degraded in about 75%, according to the UV-Vis spectra introduced in Figure 10.

UV-Vis absorption spectra in the wavelength range (430 nm) indicate rapid electrochemical degradation. After 2 minutes from the beginning of the electrolysis process, the maximum absorption initially recorded at the wavelength of 430 nm, completely disappears. UV-Vis absorption spectra in the small wavelength range (258 nm) indicate a more complex process.
This indicates the formation of an intermediate species with increasing concentration over time. In the saline solution the UV-Vis spectra show the disappearance of the initial absorption peaks (258 nm and 430 nm) and the appearance of a new absorption peak (332 nm).

**Reducing the ecotoxicity of pesticide-polluted waters by electrochemical methods**

**Electrochemical degradation of acetamiprid**

Figure 11 shows the cyclic voltamograms of platinum electrode in aqueous solution containing $10^{-1}$ mol • L$^{-1}$ sodium chloride, both in the absence and in the presence of acetamiprid in a concentration of $10^{-4}$ mol • L$^{-1}$.

Through the comparative representation of the voltamograms (Fig. 11), two significant differences are identified:

✓ in the absence of pesticide molecules, three maxima of the cathodic current densities corresponding to the electrochemical reduction of the active chlorine species are observed;

✓ in the presence of pesticide molecules, an anodic peak is recorded at the value of 1.35 V of the potential of the working electrode attributed to the electrooxidation of the pesticide molecules on the platinum electrode surface.

UV-Vis spectrophotometric analysis shows a maximum absorption in the Vis range ($\lambda = 630$ nm) for high pesticide concentrations ($10^{-2}$ mol • L$^{-1}$) (Fig. 12a).

At lower values of the pesticide concentration ($10^{-4}$ mol • L$^{-1}$) a maximum absorption corresponding to the wavelength of 250 nm is recorded (Fig. 12b).

By recording the UV-Vis spectra of the electrolysed solution, a new absorption maximum ($\lambda = 290$ nm) is recorded indicating the presence / formation of a new compound whose concentration increases over time, this compound may represent a final or intermediate product of electrochemical degradation of the pesticide.
at different electrolysis times (10 to 10 minutes)

**Study of the electrochemical decomposition of emamectin**

Figure 13 shows the cyclic voltamograms on the platinum electrode in $10^{-1}$ mol • L$^{-1}$ NaCl solution, both in the absence and in the presence of the emamectin pesticide in the concentration of $10^{-5}$ mol • L$^{-1}$. At potential values greater than 1.0 V, the two voltammograms differ significantly. A new maximum of the anodic current density is recorded (at 1.3 V), so that the charge transfer processes at the metal interface / electrolyte solution intensify when the pesticide molecules are present in the electrolyte solution (Fig. 5.4).

![Figure 13](image_url)

**Figure 13.** Cyclic voltammograms recorded on a platinum electrode in $10^{-1}$ mol NaCl solution • L$^{-1}$, in the absence and presence of $10^{-5}$ mol emamectin • L$^{-1}$, 100 mV • s$^{-1}$

At both negative and small positive values of the potential of the working electrode, it is observed that the current densities of the voltammogram recorded in the presence of pesticide molecules are lower than those corresponding to the supporting electrolyte, due to the strong adsorption of the pesticide molecules on the electrode surface.

The emamectin molecules are photolytic active in the UV domain, exhibiting a maximum absorption at the wavelength of 228 nm (Fig. 14).

![Figure 14](image_url)

**Figure 14.** UV-Vis spectra of emamectin in $10^{-1}$ mol NaCl solution • L$^{-1}$ at different times from the beginning of the electrolysis process (every 2 minutes)

UV-Vis spectra of the electrolyte solution containing $10^{-5}$ mol • L$^{-1}$ and $10^{-1}$ mol NaCl • L$^{-1}$ recorded at different electrolysis times (Fig. 14.) indicate a decrease in the corresponding absorbance values of emamectin, in while a new absorption maximum is recorded at the wavelength value $\lambda = 290$ nm. This maximum absorption, recorded at the wavelength of 290 nm, is attributed to the formation of an intermediate compound of the degradation of the emamectin molecule.
Electrochemical degradation of imidacloprid

Figure 15 shows the cyclic voltammograms obtained on the platinum electrode in $10^{-1}$ mol $\cdot$ L$^{-1}$ NaCl solution, both in the absence and in the presence of the imidacloprid at a concentration of $10^{-4}$ mol $\cdot$ L$^{-1}$. The imidacloprid molecules exhibit an electrochemical behavior similar to the two pesticides studied previously (acetamiprid and emamectin respectively). A new peak of the anodic current densities is recorded (Fig. 15.a) at a potential of the working electrode of approximately 1.5 V. Ag / AgCl, being associated with the electrochemical oxidation of pesticide molecules.

![Cyclic voltammograms of Pt electrode in 10^-1 mol NaCl solution • L^-1, in the absence and presence of imidacloprid 10^-4 mol • L^-1 (a), detail of the area of small current densities (b) 100 mV • s^-1](image)

The imidacloprid molecules are active in the UV domain and are characterized by a maximum absorption at the wavelength value of 270 nm. Figure 16 shows the UV-Vis spectra recorded at different time periods from the beginning of the electrolysis process of the electrolyte solution containing $10^{-1}$ mol NaCl $\cdot$ L$^{-1}$ and imidacloprid $10^{-4}$ mol $\cdot$ L$^{-1}$ indicating an increase of the corresponding absorbance values wavelength $\lambda = 270$ nm.

![UV-Vis spectra of the solution containing 10^-1 mol NaCl • L^-1 and imidacloprid 10^-4 mol • L^-1, at different periods of electrolysis (from 5 to 5 minutes)](image)

Study of the electrochemical and thermal behavior of propineb

Figure 17 shows the cyclic voltammograms of the platinum electrode in $10^{-1}$ mol NaCl solution $\cdot$ L$^{-1}$ in the absence and presence of propineb $5 \times 10^{-4}$ mol $\cdot$ L$^{-1}$.

Current densities corresponding to voltammograms recorded in the presence of pesticide molecules have lower values than those corresponding to the supporting electrolyte, which shows that the charge transfer processes take place by the initial adsorption of pesticide molecules on the electrode surface. By performing a detail of the cyclic voltammograms at low values of the current densities (b), a new maximum of the anodic current densities
attributed with the electrooxidation of the pesticide molecules is easier to identify. This process is also demonstrated by recording UV-Vis spectrophotograms.

![Cyclic voltammograms recorded on Pt electrode in 10^{-1} mol NaCl solution • L^{-1}, in the absence and presence of propineb 5 • 10^{-4} mol • L^{-1}, 100 mV • s^{-1}](image)

**Figure 17.**

Figure 18 shows the UV-Vis spectrum of the 10^{-1} mol • L^{-1} NaCl solution containing propineb 5 • 10^{-4} mol • L^{-1}, at different times from the beginning of the electrolysis process; 0 minutes and after 20 and 40 minutes respectively after the beginning of the electrolysis process.

![UV-Vis spectra of the solution containing 10^{-1} mol NaCl • L^{-1} and propineb 5 • 10^{-4} mol • L^{-1}, at different periods of electrolysis (0, 20, 40 min.)](image)

**Figure 18.**

According to Figure 18, it can be concluded that after 40 minutes from the beginning of electrolysis, the electrochemical degradation of propineb is complete.

An important feature of the electrochemical degradation of propineb, as opposed to the behavior of the other three pesticides studied, is that propineb does not form other intermediate degradation products.

**General conclusions**

1. Electrochemical processes of oxidative degradation of organic compounds are increasingly used in the removal of organic pollutants from wastewater, pollutants from different branches of industry or pollutants discharged into domestic or municipal wastewater.

2. The identification of the optimum conditions for electrodegradation of an organic pollutant is a subject of much scientific research lately and aims: (1) to obtain the
highest degree of degradation (ideally 100%); (2) the use of a current density as low as possible in order to obtain a low cost; (3) the possibility of implementation at the macro level; (4) the replacement of a conventional method with an alternative electrochemical method due to the ability to transform a certain organic pollutant into non-toxic or inorganic degradation intermediates such as mineral acids, carbon dioxide and water; (5) the elaboration of electro-disinfection systems and their use in continuous flow; (6) the study of the experimental conditions of temperature, pH, composition of the electrolyte solution, in order to generate species with very high reactivity and in sufficient quantity to facilitate the electrochemical degradation of the organic pollutants; (7) identification of electrodes with superior electrocatalytic properties capable of conducting the electrooxidation processes by direct mechanisms to non-toxic products or with very low toxicity.

3. The general objective of the thesis - the study of the stability of polluting organic compounds in the category of medicines, food dyes and pesticides - was accomplished by carrying out activities regarding the identification of the electrochemical behavior of two drugs (vitamin A and 5-fluorouracil), two dyes in the category of food additives (Chocolate Brown HT and tartrazine) and 4 pesticides (acetamiprid, emamectin, imidaclorpid and propineb).

4. The second general objective of the thesis regarding the elaboration of mechanisms of decomposition of pollutants by correlating the results obtained experimentally, was achieved by proposing the mechanism of electrochemical degradation of vitamin A (retinyl palmitate) on platinum electrodes, elaboration of the mechanism for electrodegradation of the 5-fluorouracil cytostatic drug on titanium electrodes and the elaboration of the mechanical degradation of the Chocolate Brown HT food additive.

5. The first specific objective was achieved by studying the electrochemical behavior of vitamin A in the form of retinyl palmitate in aqueous solutions on platinum electrodes. The research studies were conducted in the presence of two different support electrolytes, namely nitrate and sodium chloride, in the absence and respectively in the presence of silver nanoparticles. Investigation of the electrochemical behavior of vitamin A using cyclic voltammetry and UV-Vis spectrophotometry led to the conclusion that in the presence of nitrogen anions the interactions are much weaker as opposed to the case where the electrolyte solution contains chloride anions and silver nanoparticles. Cyclic voltammograms showed different forms in hydroalcoholic solutions containing vitamin A and vitamin A / nAg in the presence of nitrate ions compared to those recorded in the presence of chloride anions due to specific
interactions with the silver nanoparticles depending on the type of the anion. Thus, the presence of the nitrate anion mainly leads to the electrochemical interaction as compared to the presence of the chloride anion which favors the chemical interaction. Based on the results obtained by cyclic voltammetry, in the presence of nitrate ions, the mechanism of electrochemical decomposition of vitamin A. has been proposed.

6. The second specific objective was achieved by studying the electrochemical stability of the anti-tumor drug 5-fluorouracil. The shape of the cyclic voltamograms of the titanium electrode was modified then the electrolyte solution, represented by the 0.9% saline solution, contained the drug molecules, the values of anodic current densities had lower values than those recorded in the electrolyte saline solution support, and the corresponding passivity interval was higher. The electrocatalytic properties of the titanium made possible the participation of 5FU molecules in the electrode processes at the electrode / electrolyte interface.

7. The study of the electrochemical stability of the cytostatic 5-fluorouracil allowed the elaboration of the mechanism of electrochemical degradation of the drug molecules contributing to the fulfillment of the second specific objective of the thesis.

8. Organic pollutants commonly encountered are drugs, dyes and pesticides with complex structures, are obtained by chemical synthesis and water soluble, have high resistance to the action of oxidizing agents, and many of them are not biodegradable.

9. The specific objective represented by the study of the stability of the dyes such as Chocolate Brown HT and tartrazine was achieved through an extensive research on the electrochemical and thermal behavior. Kinetic studies of electrochemical degradation were also performed.

10. The thermal behavior of the food additive Chocolate Brown HT (E155) was studied based on thermogravimetry (TG) and differential scanning calorimetry (DSC) methods using Diamond thermal analyzer, Perkin Elmer.

11. Studies on the melting and pyrolysis behavior of the food additive of color E155 observed by TG / DTG analysis have indicated changes in its composition through several stages of mass reduction. At the end of the experiment, a residue of 33% was observed. The thermal decomposition of E155 examined by DSC analysis in an inert atmosphere was also used to study its stability. This analysis accurately indicates temperatures of use of the dye in the food industry or in domestic use.

12. The electrochemical behavior of Brown HT dye (E155) was studied in the presence of different halogenated anions. The experimental results obtained by cyclic voltammetry were corroborated with the data obtained by electrolysis at constant current density;
thus it was observed that the degree of electrochemical degradation of the BHT molecule has the highest value in the presence of bromide anions and the lowest value in the presence of fluoride ions.

13. From the kinetic point of view, the degradation processes proceed according to simple kinetic models of zero or first order, without there being a similarity in terms of the electrochemical behavior.

14. Within the same specific objective was studied the decontamination of simulated waters polluted with chemical dyes of azo dyes such as tartrazine.

15. This activity was achieved by applying electrochemical methods, such as direct and indirect electrochemical degradation from aqueous solutions, in the presence of the supporting electrolytes represented by sodium sulfate and sodium chloride.

16. The effect of the supporting electrolyte on the degree of electrochemical degradation of tartrazine has been studied by electrolysis at constant current density in association with UV-Vis spectrophotometry. In the presence of sulphate anions, the degree of electrochemical degradation reaches a value of 37% at 60 minutes of electrolysis, while in the presence of chloride anions, the degree of degradation reaches the maximum value of 100% in only 2 minutes.

17. The experimental results indicate a total electrochemical degradation of the tartrazine molecules in the sodium chloride solution, whereas in the sodium sulfate solution only partial electrochemical degradation takes place.

18. Four commonly used pesticides such as acetamiprid, emamectin, imidacloprid and propineb were studied to optimize electrochemical methods for their degradation from contaminated simulated waters. The results obtained by cyclic voltammetry confirm that their molecules are active in the potential range used having anodic oxidation maxima attributed to the electrooxidation of pesticides.

19. Spectrophotometric analysis of electrolysed solutions at constant current density shows that three of the studied pesticides (acetamiprid, emamectin and imidacloprid) form new absorption maxima attributed to the appearance of intermediate degradation compounds. In the case of propineb, there is a classic decrease in absorbance, indicating that it is degraded electrochemically without forming intermediate products.

20. TG / DTG / DSC thermal analysis shows that all compounds are degraded in consecutive steps at specific temperature ranges.
Bibliography


62. O. Surucu, G. Bolat, S. Abaci, Electrochemical behavior and voltammetric detection of fenitrothion based on a pencil graphite electrode modified with reduced graphene oxide (RGO/poly(E))-1-(4-(4-(phenylamino)phenyl)diazencyl)(phenyl)ethanone (DPA) composite film, Talanta, 168 (2017) 113-120.


85. I. Baldea, Cinetica Chimică și mecanisme de Reacție, presa universitară Clujana, 2002.
Craiova University
Science College
Doctoral School of Science
Department of Chemistry

LIST OF WORKS
Drd. Cristian-Ovidiu Neamțu

Papers published in ISI journals


**Hirsch index: 3,695**

Papers published in specialized magazines


Studies presented at national/international symposiums/conferences


27.09.2019

Drd. Cristian-Ovidiu Neamțu