Doctoral School of Chemical Engineering and Material Sciences

University of Pannonia

Ph.D. THESIS

"Electrochemical techniques of investigations—a tool for different applications"

Written by:

Juan Santiago Hidalgo Viteri

Supervisors:

dr. Ildikó Galambos & Prof. habil. dr. eng. Graziella Liana Turdean

University of Pannonia

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1. INTRODUCTION

Electrochemical techniques of characterization emerged as a suitable solution for the preparation of different devices with a wide range of applications. Hence, methods such as square wave voltammetry, cyclic voltammetry, linear polarization, or electrochemical impedance spectroscopy have been studied to prepare and investigate electrochemical devices that can be employed in drug delivery systems, in corrosion protection technologies, or in pollution contaminant monitoring. Therefore, in the case of drug delivery techniques, electrochemical methods are a solution to produce the system itself; for example, cyclic voltammetry is a fundamental method to build polymer membranes that can be loaded by active ingredients and release them in the human body by different stimulus. Also, in the case of corrosion protection, electrochemical analyzing techniques such as linear polarization or electrochemical impedances allow monitoring and controlling the appearance of corrosion. Moreover, in the case of pollution control, electrochemical techniques represent as an innovative solution to detect the presence of microcontaminants in different environmental sources such as water or soil. The monitoring is achieved by using the cyclic voltammetry technique to determine the behavior of the analyte, while the square wave voltammetry technique is used to build calibration curves and real sample analysis.

Overall, this thesis is dedicated to the use of the mentioned electrochemical techniques to prepare devices that can be applied in different fields. For example, it deals with the monitoring and construction of the drug release profile by applying electrochemical impedance spectroscopy. Also, it is used in the monitoring and prevention of the corrosion in metallic samples by applying linear polarization and electrochemical impedance. Moreover, it successfully monitors the presence of diclofenac sodium in water samples by applying the square wave voltammetry technique.

2. METHODS

This thesis consisted of three different chapters used to build electrochemical devices applied to different purposes. Thus, the research was divided into: (1) drug delivery system and release profile construction; (2) coating and green extracts as corrosion protection systems; and (3) chemically modified electrodes for the detection of sodium diclofenac salt in wastewater and tablets.

1. A paracetamol - poly(3,4-ethylenedioxythiophene) composite film was built on Ti surface for drug release studies (see figure 1). Therefore, the methodology followed these steps: (a) pretreatment of the metallic surface: Ti plates were cut and introduced in a Teflon tube to obtain a control surface area equal to 0.0765 cm^2 an cleaned; (b) monomeric solution preparation: 10 mL of the monomeric solution was prepared by mixing 10 mM of 3,4-Ethylenedioxythiophene (EDOT), 0.1 M Sodium Dodecyl Sulfate, 0.1 M of lithium perchlorate, and 1 or 2 mM paracetamol; (c) artificial saliva solution preparation: it was prepared 500 mL of solution by mixing appropriate quantities of different salts. The pH of the saliva solution was adjusted to 5, 6 or 7; (d) polymeric film and paracetamol immobilization: the immobilization of both compounds was carried out simultaneously by electropolymerization. For this, Ti plates were immersed in 10 mL of the monomeric solution and by cycling the potential from -1 to 1 V vs. $Ag/AgCl/KCl_{sat}$ for ten cycles at scan rate equal to 5 or 10 mV/s. Finally, the Ti with the PEDOT – Paracetamol membrane was stored in room conditions for further characterization.

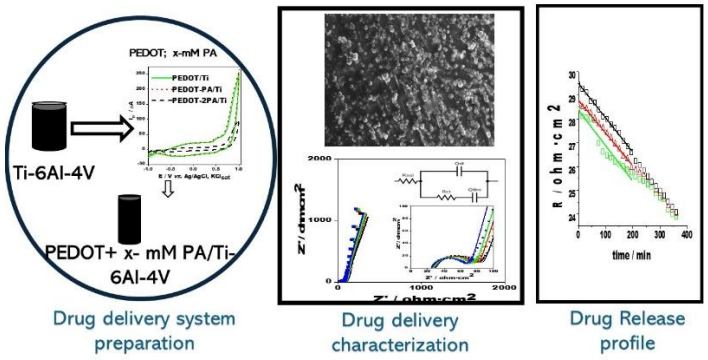


Figure 1. Schematic representation of the PEDOT + x-PA / Ti-6Al-4V delivery system for drug release studies

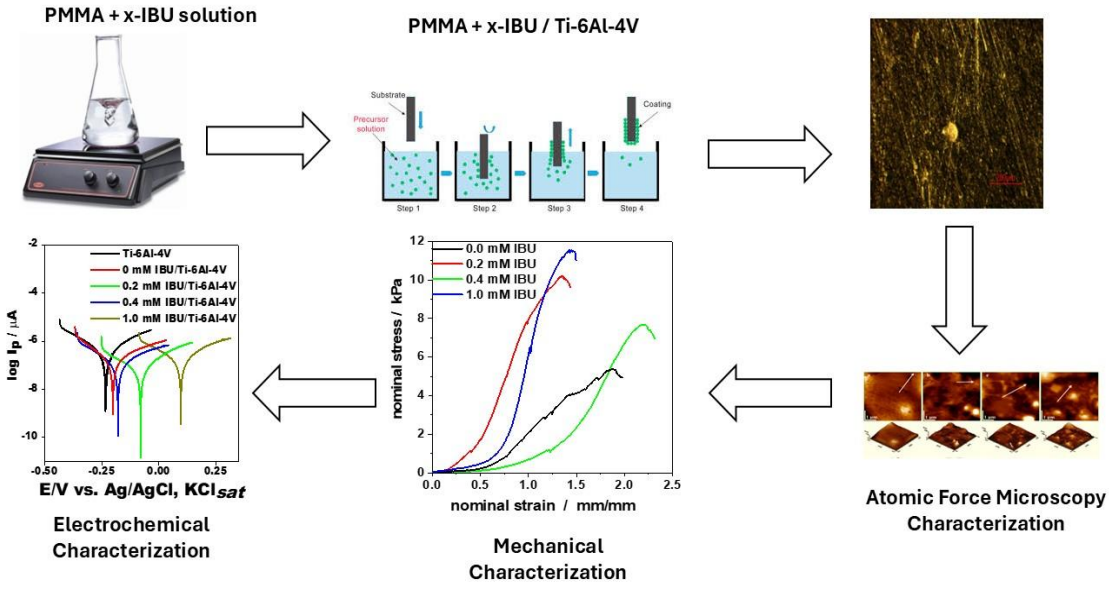
2. Different methods were proposed to produce anticorrosive protection systems via polymeric coating (2.1) to protect Ti-6A-4V alloys samples and green inhibitors (2.2) to protect mild steel samples. Thus, they were produced as follows:

2.1. Polymeric film coating production: This method was developed according to the following steps (see Figure 2A): (a) Ti-6A-4V were polished by using alumina and rinsed with distilled water for further uses; (b) polymeric solution preparation: 50 mL of this solution were prepared by mixing 1 M of poly(methyl methacrylate) (PMMA)–0.3 M of tetrahydrofuran (THF) and xM of ibuprofen (where x = 0.2, 0.4,

1 mM); (c) 3.50% saline corrosive solution was prepared, (d) The pretreated Ti metallic plates were immersed into the polymeric solution and taken off after 3 minutes. This procedure was repeated until a homogeneous polymeric coating appeared above the metallic plates.

2.2. Green inhibitor preparation: Caesalpinia Spinosa (Tara) plant extract, used as a green inhibitor of corrosion, was prepared with two different extraction methods. Therefore, a hot solid-liquid extraction method (Soxhlet Extraction) and a cold solid-liquid extraction method (Maceration). Thus, prior to the extraction method, Tara powder was prepared as follows (see Figure 2B): (a) Tara pod selection; (b) Tara powder preparation. Afterwards, the Soxhlet extraction process was carried out in Soxhlet equipment. Thus, 100 g of Tara powder plus 500 mL of ethanol (diluted to 60%) were charged onto which maintains the temperature at 60 ºC for 24 hours. Then, the product was purified in a rotary evaporator for 1 h (at 100 °C and a vacuum pressure of 20 kPa). On the other hand, solid-cold extract (Maceration) was prepared by the following procedure: 1 kg of Tara powder was introduced in a 3 L bottle which contained 2 L of ethanol-water mixture (60:40 w/w concentration). Then, the bottle was closed and stored in a dark place for 3 days. After this period, the obtained product was filtered, and the filtrate was introduced in a rotary evaporator at same conditions for the obtention of the Soxhlet extract. Finally, the extract was labeled and stored for further use.

(A)



(B)

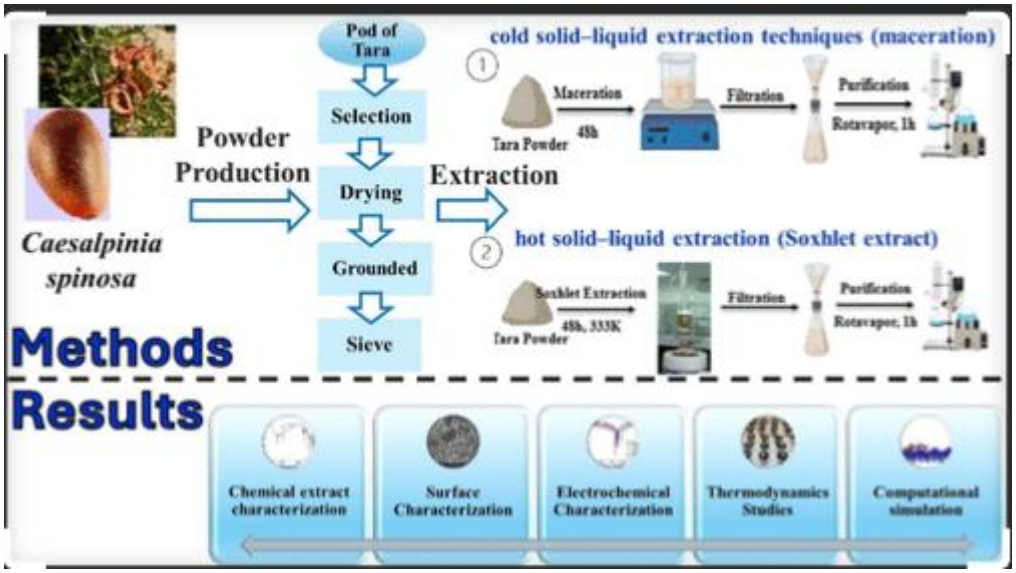


Figure 2. Schematic representation of the production of a polymeric coating composed by PMMA – x-IBU/Ti-6Al-4V (A), and schematic representation of the synthesis of plant extract for corrosion inhibition (B).

3. A glassy carbon electrode was chemically modified by different nanoparticles such as bioengineering flagellin filaments (bioF), commercial titanium dioxide anatase (TiO_2), TiO_2 aerogel (TiO_2A.G), and functionalized multiwalled carbon nanotubes (f-MWCNTs) to detect sodium diclofenac in tablets and wastewater. The modification process involved the following steps (see Figure 3): (a) chitosan solution preparation; (b) modifier solution preparation; (c) glassy carbon electrode (GCE) pretreatment; (d) electrode modification; (e) phosphate buffer (PB) solution preparation; and (f) matrix solution preparation.

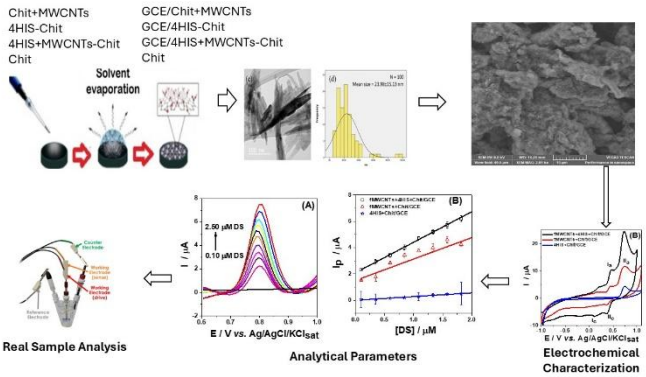


Figure 3. Schematic representation of the production of chemically modified glassy carbon electrodes for the detection of sodium diclofenac.

4. Characterization methods

1. Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray Spectroscopy (EDS): SEM was used in the three chapters of the thesis to investigate the surface morphology of the prepared electrochemical devices, while EDS was used to provide elementary mapping of the components at accelerated voltage varying from 3 to 5 kV.
2. Fourier Transform Infrared Spectroscopy (FTIR): FTIR was used in all the chapters of the thesis to investigate the functional groups of the obtained electrochemical devices. Thus, in the case of PEDOT-Paracetamol film construction, it was used to confirm the in-situ electropolymerization. In the case of the PMMA-Ibuprofen film production, it was used to determine the cross-linking of both components. In the case of the extract production, it was used to determine the principal functional groups which act as corrosion inhibition agents. Finally, in the case of the chemical electrode modification production, it was used to study the interaction between the bioF and the nanoparticles. All the FTIR measurements were carried out in a range spectra equal to 400–4000 cm^{-1}.
3. Electrochemical Impedances spectroscopy (EIS): EIS was used in all the chapters of the present research. In the case of PEDOT-Paracetamol film construction, it was used to study the electrode-electrolyte interface and to build the Paracetamol release profile. In the case of the PMMA-Ibuprofen and the inhibitor extract production, it was used to obtain information about the corrosion protection offered by both techniques. In the case of the production of the modified electrodes, it was used to study the efficiency of the modification by studying the electrolyte-electrode interface. The experiments were carried out in a frequency interval between 0.1– 10000 Hz.
4. Cyclic Voltammetry (CV): CV was used in the first and third chapters of the thesis. In the case of PEDOT-Paracetamol film construction, it was used to electropolymerize the 3,4-ethylenedioxythiophene and to load the Paracetamol. In the case of the preparation of chemically modified electrodes, it was used to study the redox behavior of the sodium diclofenac and to estimate the electrochemical parameters of the modified electrode, such as electrochemical active surface area, controlled process, and pH influences.
5. Linear polarization (LP): LP was used only in the second chapter of the thesis. It was used to study the accelerated corrosion parameters and to evaluate the efficiency in the corrosion protection given by both the polymeric coating, and the green inhibitor

extract. It was carried at a scan rate equal to ± 200 mV vs. open circuit potential (OCP) with a scan rate of 0.5 $mV \cdot s^{-1}$.

6. Square Wave voltammetry (SWV): SWV was used in the third chapter of the thesis. This technique was used to build the calibration curves of the different modified electrodes in the presence of the sodium diclofenac. Also, SWV was used to determine the concentration of the diclofenac sodium in the real samples (tablets and wastewater).

Other experiments

The work also included the study of the mechanical characteristics of the polymeric coating and the metal after the accelerated corrosion process. Also, the adsorption, the adsorption isotherm models, and the kinetics parameter of the interaction between the mild steel samples and the green inhibitor of corrosion were investigated. Furthermore, the surface morphology of the prepared polymeric coatings was evaluated by using atomic force microscopy (AFM). Moreover, X-ray Diffraction (XRD) and N_2 adsorption/desorption were investigated to characterize the TiO_2AG nanoparticles. Finally, liquid chromatography coupled with mass spectrometry (LC – MS/MS) was used to determine the diclofenac sodium concentration in the wastewater samples.

3. THESIS

The new research findings reported in the development of the present PhD dissertation consisted of:

(i) drug delivery filed. The production of a PEDOT-Paracetamol drug delivery system and the evaluation of the drug release profile by EIS technique.

(ii) corrosion field. It was studied the viability to use expired ibuprofen in combination with polymethyl methacrylate, or Tara Soxhlet and maceration extracts to prevent the corrosion of Ti-6Al-4V, and mild steel samples exposed to different saline or acid environments respectively.

(iii) electroanalytical application of chemically modified electrodes. The effectiveness of the chemical modification of GCE electrodes was assessed by analyzing wastewater samples and comparing the obtained results with a standardized method, namely Ultra-Performance Liquid Chromatography-Tandem Mass Spectrometry (UPLC-MS/MS).

Therefore, the new scientifical findings of the present thesis can be summarized in the following points:

1. **A drug delivery system (DDS) based on poly(3,4-ethylenedioxythiophene) and Paracetamol was successfully developed to investigate drug release behavior using electrochemical impedance spectroscopy (EIS).** I produced the DDS system by electropolymerization, and I loaded the Paracetamol (PA) into the polymeric matrix by in-situ doping of the of poly (3,4-ethylenedioxythiophene) (PEDOT) structure with the Paracetamol. The electropolymerization was carried out by cycling the potential of the cell from -1 to 1 V *vs.* Ag/AgCl/KClsat within 10 cycles. I found that the polymerization of the EDOT is divided into four stages, which are (i) formation of an EDOT cation radical, (ii) formation of the dimer by coupling two EDOT cation radicals, (iii) stabilization of the dimer by deprotonation, and (iv) oxidation of the dimer to form cation radicals, which become conjugated PEDOT. This was proved by the apparition of an irreversible oxidation peak at position +0.6 V vs. Ag/AgCl, KClsat and by the increase in the charge storage transfer capacity after each consecutive cycle. **Additionally, I studied the Paracetamol released in an artificial saliva solution adjusted at pH equal to 5, 6, and 7 by means of EIS.** For this purpose, I recorded EIS spectra for 6 h with a predetermined interval of time of 1 min between each measurement. From the EIS spectra, Nyquist plots were obtained, which were fitted by an equivalent circuit fit. The shape of the Nyquist plot was adjusted by the following equivalent circuit (Rs(Qdl (RctQfilm)). The circuit is composed of a solution resistance (Rsol), a double-layer constant phase element (Qdl), a charge transfer resistance (Rct), and a film double-layer constant phase element (Qfilm). Thus, the release of the Paracetamol was associated with the changement in the solution resistance, and the release kinetics were studied by zero-order, Higuchi, and Korsmeyer-Peppas mathematical fitting models. The analysis of the change in the Rsol reported that the release process of the Paracetamol occurred in two steps, with a change of the slope at 200 min, and comparing the adj-R^2 values obtained by applying different fitting models, it can be concluded that for both steps corresponding to a contact time lower or higher than 200 min, the data are well-fitted by the zero-order model ($Q_t = Q_0 + K_0 \cdot t$, where Q_t is the amount of drug dissolved at time t, Q_0 is the initial amount of drug in the solution (most times, $Q_0 = 0$), and K_0 is the zero-order model constant (expressed in units of concentration/time)). In conclusion, the release of Paracetamol is controlled by the diffusion in the saliva solution.

The results of this work were published in**: Juan Hidalgo Viteri**, Nicoleta Cotolan, Lucian Barbu-Tudoran, Graziella Liana Turdean. "A paracetamol - poly(3,4-ethylenedioxythiophene) composite film for drug release studies". Materials Today Communications 34 (2023) 105084. doi: https://doi.org/10.1016/j.mtcomm.2022.105084 **(Q1, IF: 4.5)**

2. **Anticorrosive strategies were successfully developed either through polymeric coatings incorporating PMMA and expired Ibuprofen, or by applying green corrosion inhibitors derived from Tara extracts obtained via Soxhlet extraction or maceration.** I produced a polymeric coating over Ti-6Al-4V alloys by applying a dip coating methodology. For that, I produced a polymeric solution which was obtained by mixing 1 M of PMMA, 0.4 M and xM of Ibuprofen as it is mentioned in above section. The principal findings of the proposed methodology were as follow: (a) the copolymerization of the PMMA with the Ibuprofen was probed by FTIR technique. Thus, the PMMA-Ibuprofen copolymer reported the typical vibration peaks of both the PMMA and the Ibuprofen. Also, the vibration peak intensity increased when more Ibuprofen was added to the polymeric mixture; (b) The thicknesses of the Ibuprofen–PMMA samples ranged from 11.15 ± 0.62 to 12.86 ± 1.14 μm, with a slight increase with increasing IBU concentration. Also, the Youngs modulus increases when the Ibuprofen concentration increases. Thus, the maximum value was equal to 9.303 ± 0.122 kPa when it was 1 mM of Ibuprofen; (c) the Tafel curves were analyzed and it was determined that indifferent of the concentration of the Ibuprofen, the coating acted as cathodic type inhibitor which mainly restrict the propagation of cathodic reactions; (d) potentiodynamic polarization (PDP) and EIS measurements were used as accelerated corrosion test. Hence, the highest inhibition of corrosion protection in the Ti-6Al-4V titanium plates exposed to saline aggressive environment (3.50% NaCl) was reported by when the 0.4 mM of Ibuprofen was added to the polymeric film with values equal to 69.02 ± 0.76% calculated by PDP and 89.53% calculated by EIS method. Overall, I demonstrated the viability of producing a polymeric coating by using expired Ibuprofen to prevent the corrosion of the titanium alloys. **Also, I have successfully prepared a green inhibitor of corrosion by using the Tara plant, an Ecuadorian native plant, by Soxhlet or maceration extraction, and I used the extract to protect mild steel samples exposed to an aggressive acid (0.1 M nitric acid) corrosion medium.** Therefore,

the principal findings reported during the research were: (a) the FTIR spectrum confirmed the presence of polyphenol indifferent to the extraction process. In these senses, the Soxhlet extract (SE) reported the highest content of these components with a mean percentage equal to 0.36±0.03 (g/kg of extract). Also, both SE and the ME were soluble in distilled water/ethanol/HNO_3/acetic acid; (b) the SEM images reported a destruction of the mild steel surface when they were exposed to acid conditions. Contrary, the microstructure of the metals remained almost constant when 1000 ppm of SE or ME was added to the acid medium; (c) weight loss measurements reported the lowest corrosion rate when 1000 ppm of SE was added to the medium with a value equal to 0.07±0.002 $mm \cdot year^{-1}$; (d) the highest Young's modulus and the highest fracture strain were reported when 1000 SE was added 1000 SE to the medium, with results equal to 181.38±16.57 GPa and 190.43±0.96 GPa, respectively. These values were comparable with those reported by the mild steel samples that were not exposed to the acid environment; (e) the inhibition mechanism of corrosion was a mixed type indifferent to the concentration of extract added to the corrosive environment. This was concluded by Tafel graph analysis: (f) the highest efficiency in the corrosion protection was achieved when 1000 SE was added, with values equal to 97.38±2.04% or 90.73±0.03% obtained by PDP or EIS respectively; (g) the highest energy of activation, enthalpy, and entropy change was achieved when 1000 SE was added, with values equal to 30.52 ± 1.14 $kJ \cdot mol^{-1}$, 22.17 ± 0.22 $kJ \cdot mol^{-1}$, and −43.17 ± 0.17 $kJ \cdot mol^{-1} \cdot K^{-1}$, respectively. These values, together with the other results, probed the viability of using Tara extract as a green inhibitor of corrosion; (h) the isotherm models named Langmuir, Freundlich, Temkin, Flory−Huggins, and El-Awady were studied by weight loss measurement in acid medium. The best model was chosen by comparing the correlation coefficient (R) and the reduced-Chi^2 parameters. Thus, the data that was nearest to 1 in the case of the R and higher than 10^{-3} was selected. Hence, for all other considered models, the Freundlich, Temkin, and El-Awady models described better the adsorption process. With this in mind, I calculated the equilibrium constant of the adsorption process (K_{ads}) and the adsorption's Gibb's free energy (ΔG_{ads} = -2.303 log (55.5 K_{ads})). Therefore. All the ΔG_{ads} values were higher than −40 kJ·mol, so the adsorption process is attributed to an electrostatic interaction between the Tara green inhibitor molecules, irrespective of the method of extraction, and the metal surface (i.e., the coulostatic physisorption process). Overall, the results demonstrated the inhibitor's

effectiveness in preventing the deterioration of mechanical characteristics of the mild steel exposed to an acid medium.

The results of this work were published as follows:

Juan Hidalgo Viteri, Nicoleta Cotolan, Alexandru Lupan, Adrian M. V. Brânzanic, Graziella Liana Turdean. "Poly(methyl methacrylate)–ibuprofen composite film as anticorrosive coating of Ti–6Al–4 V surface". J Solid State Electrochem 28 479–494 (2024). doi: https://doi.org/10.1007/s10008-023-05681-w **(Q2, IF: 2.60).**

Juan Hidalgo Viteri, Luis Hidalgo, Carlos Diego Serrano Aguiar, Daniela Belén García Madronero, Ildiko Galambos, Javier Ernesto Vilasó-Cadre, Ivan Alejandro Reyes-Domínguez, Adrian M.V. Branzanic, Nicoleta Ignat, Graziella Liana Turdean "Study of Caesalpinia spinosa Extracts as Green Corrosion Inhibitor for Mild Steel". Langmuir 2025 41 9406−9421. doi: https://doi.org/10.1021/acs.langmuir.5c00224 **(Q1, IF: 3.90)**

Juan Hidalgo Viteri, Luis Hidalgo, Carlos Serrano, Diego Punina, Erick Rea, Manuel Ilbay, Javier Ernesto Vilasó-Cadre, Ivan Alejandro Reyes-Domínguez "A Study of the Inhibition Capacity of a Novel *Ilex guayusa* Green Extract for Preventing Corrosion in Mild Steel Exposed to Different Conditions". Analytica 2025 6 1. https://doi.org/10.3390/analytica6010001 **(Q2, IF: 3.60)**

Glassy carbon electrodes (GCEs) were successfully modified via a simple drop-casting method and applied for the detection of sodium diclofenac in pharmaceutical tablet formulations and real wastewater samples. Therefore, I modified different GCEs by using the optimal amount of Chit, Chit+bioF, Chit+bioF+TiO_2, Chit+bioF+TiO_2A.G, and Chit+bioF+f-MWCNTs solutions to study the redox behavior of sodium diclofenac (DS), and I demonstrated the application of the modified electrodes in real samples (wastewater or pharmaceutical tablets) by comparing the found DS concentration against the results found by a standard LC-MS/MS method. Therefore, the principal findings were: (a) the optimal concentration values of the bioF, TiO_2, TiO_2A.G., and f-MWCNTs were obtained via the CV technique performed in 25 mM PB (pH 4.6) plus 10 µM DS at a scan rate equal to 50 mV/s. Thus, the response variable was

the anodic peak intensity (Ip_a). Therefore, the optimal value of bioF was equal to 1 g/L, while the optimal value was equal to 2 g/L for the other added nanoparticles; (b) cyclic voltammograms reported a cathodic irreversible anodic peak at positions ranging from +0.70 V to 0.74 vs. Ag/AgCl, KClsat at Chit+bioF/GCE, or Chit+bioF+TiO_2/GCE, or Chit+bioF+TiO_2A.G/GCE. From these electrodes, the highest intensity peak was reported at Chit+bioF+TiO_2A.G/GCE with an Ip value equal to 20.05 μA. On the other hand, the Chit+bioF+f-MWCNTs/GCE reported a redox quasi-reversible peak at positions +0.46 and +0.74 V *vs.* Ag/AgCl/KClsat in the anodic branch and at +0.11 and +0.38 V *vs.* Ag/AgCl/KClsat in the cathodic branch. Thus, the redox reaction mechanism of DS is highly dependent on the type of modifier. In the case of the Chit+bioF/GCE, or Chit+bioF+TiO_2/GCE, or Chit+bioF+TiO_2A.G/GCE electrodes, the voltammograms reported a two-step reaction mechanism, while in the case of the Chit+bioF+f-MWCNTs/GCE, the voltammograms reported a multistep reaction mechanism; (b) the Nyquist plot, obtained by the EIS technique in 5 mM of potassium hexacyanoferrate(III) / potassium ferrocyanide (IV) solution, was fitted with an equivalent electric circuit composed of an uncompensated solution resistance (Rs), a charge transfer resistance (Rct), which appears during electrolyte passage through the membrane, an interface non-ideal capacitor composed of a constant phase element of film (CPE film) and the double layer constant phase element (CPEdl), and Warburg impedance (W) that estimates the mass transport. From the data, the lowest Rct was obtained at the Chit+bioF+TiO_2A.G/GCE with a value equal to 67.81 ± 0.78 ohm·cm², while the highest Rct value was obtained at the Chit/GCE with a value equal to 128.2 ± 0.67 ohm·cm². From the data, it can be affirmed that the addition of highly porous and crystalline nanoparticles facilitates the electron transfer at the electrode/electrolyte interface, which is desirable to improve the characteristics of the electrodes; (c) the optimal pH was studied by comparing the Ipa studied at the different modified electrodes. In all cases the highest signal peak was obtained at pH equal to 4.60 which was expected because in acidic conditions the DS is deprotonated (the pKa value of the DS is 4.20); (d) calibration curves were prepared by using SWV at different concentrations of DS in 0.025 M of PB at pH equal to 4.5 for all the studied electrodes. Thus, from the calibration curve, the limit of detection (LOD, 3sb/m) and the limit of quantification (LOQ, 10sb/m)

were calculated, where sb is the standard deviation blank analyte signal and m is the slope of the calibration equation. Thus, the lowest LOD and LOQ were obtained at Chit+bioF+TiO_2AG/GCE, with values equal to 17 nM and 55 nM, respectively; (e) the selectivity of the modified electrodes was evaluated by the SWV method in a 0.025 M PB solution containing 1×10^{-5} M DS and 1×10^{-3} M of different interferents (e.g., citric acid, glucose, etc.), and the degree of interference was calculated by comparing the peak intensity with and without interferent ($\%Deviation = \frac{Ip_{DS+interferences}-Ip_{DS}}{Ip_{DS}} \times 100$). Hence, all the electrodes reported a degree of interference lower than 5%; (f) the reproducibility, repeatability, and stability was studied by using SWV in a 25 mM PB solution containing 0.1 mM DS. All the calibrated sensors demonstrated acceptable repeatability. The stability of the modified electrodes was evaluated by keeping them at room temperature for two weeks and evaluating them using the SWV method. After two weeks, the peak current diminished by only 5% of its starting value, indicating the electrodes' remarkable stability at ambient temperature throughout this period; (g) the applicability of the prepared electrodes to detect DS were evaluated in pharmaceutical tablets and wastewater samples obtained at the inlet part of the water treatment plant of Cluj-Napoca. Thus, the determination of the concentration of both real samples was executed by a standard addition method, in which 25 uL of the real sample was introduced in 25 mM PB and the peak intensity signal was recorded. The apparent percentage of recovery was calculated from the calculated data. Therefore, in the case of pharmaceutical tablets, all the prepared electrodes reported a percentage of apparent recovery bigger than 95%; thus, the modified electrodes is suitable for the analysis of DS in commercial tablets. On the other hand, for the wastewater samples, the Chit+bioF/GCE electrode reported a percentage of recovery equal to 80.17%, which is not suitable for precise determination; thus, this electrode cannot be used in water samples. The other three modified electrodes reported a recovery percentage of ≤95%. Overall, the data showed the excellent modification of GCE by using for the first time a modified solution which combined TiO_2, TiO_2AG mesoporous structure, f-MWCNTs and bioF, in order to detect DS. The electrodes exhibit outstanding performance enabled their use on the monitoring of DS in environmental samples such as wastewater.

The results of this work were published as follows:

Juan Hidalgo Viteri, Éva Tóth, Hajnalka Jankovics, Carmen Ioana Fort, Graziella Liana Turdean, Etelka Tombacz, Ildiko Galambos "Bioengineered Flagellin–TiO_2 Nanoparticle-Based Modified Glassy Carbon Electrodes as a Highly Selective Platform for the Determination of Diclofenac Sodium" Chemosensors 2023 11 576. https://doi.org/10.3390/chemosensors11120576 **(Q1, IF: 3.80)**

Juan Hidalgo Viteri, Carmen Ioana Fort, Ildiko Galambos, Hajnalka Jankovics, Luis Hidalgo, Graziella Liana Turdean. "TiO2 aerogel − A sensing electrode matrix for the sensitive detection of diclofenac sodium". Microchemical Journal 207 2024 111855. doi: https://doi.org/10.1016/j.microc.2024.111855 **(Q1, IF: 5.10)**

Juan Hidalgo Viteri, Graziella Liana Turdean, Luigi Falciola, Valentina Pifferi, Ildiko Galambos, Hajnalka Jankovics, Eva Toth, Luis Hidalgo "A functionalized multiwalled carbon nanotubes decorated with an engineered flagellin protein as a modified electrode for the detection of diclofenac sodium". Microchemical Journal In Press. **(Q1, IF: 5.10)**

PUBLICATION LIST

Published articles related to thesis research.

1. Juan Hidalgo Viteri, Nicoleta Cotolan, Lucian Barbu-Tudoran, Graziella Liana Turdean. "A paracetamol - poly(3,4-ethylenedioxythiophene) composite film for drug release studies". Materials Today Communications 34 (2023) 105084. doi: https://doi.org/10.1016/j.mtcomm.2022.105084 **(Q1, IF: 4.5)**

2. Juan Hidalgo Viteri, Nicoleta Cotolan, Alexandru Lupan, Adrian M. V. Brânzanic, Graziella Liana Turdean. "Poly(methyl methacrylate)–ibuprofen composite film as anticorrosive coating of Ti–6Al–4 V surface". J Solid State Electrochem 28 479–494 (2024). doi: https://doi.org/10.1007/s10008-023-05681-w **(Q2, IF: 2.60).**

3. Juan Hidalgo Viteri, Luis Hidalgo, Carlos Diego Serrano Aguiar, Daniela Belén García Madronero, Ildiko Galambos, Javier Ernesto Vilasó-Cadre, Ivan Alejandro Reyes-Domínguez, Adrian M.V. Branzanic, Nicoleta Ignat, Graziella Liana Turdean "Study of Caesalpinia spinosa Extracts as Green Corrosion Inhibitor for Mild Steel". Langmuir 2025 41 9406−9421. doi: https://doi.org/10.1021/acs.langmuir.5c00224 **(Q1, IF: 3.90)**

4. Juan Hidalgo Viteri, Luis Hidalgo, Carlos Serrano, Diego Punina, Erick Rea, Manuel Ilbay, Javier Ernesto Vilasó-Cadre, Ivan Alejandro Reyes-Domínguez "A Study of the Inhibition Capacity of a Novel *Ilex guayusa* Green Extract for Preventing Corrosion in Mild Steel Exposed to Different Conditions". Analytica 2025 6 1. https://doi.org/10.3390/analytica6010001 **(Q2, IF: 3.60)**

5. Juan Hidalgo Viteri, Éva Tóth, Hajnalka Jankovics, Carmen Ioana Fort, Graziella Liana Turdean, Etelka Tombacz, Ildiko Galambos "Bioengineered Flagellin–TiO_2 Nanoparticle-Based Modified Glassy Carbon Electrodes as a Highly Selective Platform for the Determination of Diclofenac Sodium" Chemosensors 2023 11 576. https://doi.org/10.3390/chemosensors11120576 **(Q1, IF: 3.80)**

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7. Javier E. Vilasó-Cadre, **Juan Hidalgo Viteri**, Lázaro A. González-Fernández, Juan J. Piña, Osney Leiva-Peláez, Luis Hidalgo, Iván A. Reyes-Domínguez, Roel Cruz, Israel Rodríguez-Torres, Nahum Andrés Medellín-Castillo, Jorge Arce-Castro, Ildiko Galambos, Graziella Liana Turdean. "Recent advances in electrochemical sensors applied to samples of industrial interest". Microchemical Journal 210 (2025) 105084. doi: https://doi.org/10.1016/j.microc.2025.112931 **(Q1, IF: 5.10)**

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Conference oral presentation related to thesis research

1. **Juan Hidalgo**, Multiwalled carbon nanotubes modified glassy carbon electrodes as a platform for sensing diclofenac sodium, XXI Conference of the George Olah Doctoral School, Budapest-Hungary, 12 September 2023, **BEST PRESENTER AWARDED**
2. **Juan Hidalgo Viteri**, Electrochemical Sensors for the determination of Diclofenac Sodium in wastewater. Soós Ernő Nemzetközi Tudományos Konferencia WATER AND WASTEWATER TREATMENT IN THE INDUSTRY, Zalakaros-Hungary, 19 October 2023.

3. **Juan Hidalgo Viteri**, Graziella Turdean, Ildikó Galambos, Modification of glassy carbon nanoparticles using titanium nanoparticles as a platform for determining diclofenac sodium, 29th International Symposium on Analytical and Environmental Problems Szeged – Hungary, November 13-14, 2023.
4. **Juan Hidalgo Viteri**, Turdean Graziella, Galambos Ildiko, Jankovics Hjanalka, Hidalgo Luis, Falciola Luigi, A Multiwalled Carbon Nanotubes-Nanoengineering Filaments composite biosensor for Diclofenac Sodium determination, 36th Topical Meeting of the International Society of Electrochemistry, Šibenik – Croatia, 26 - 29 May 2024

SCIENTOMETRIC DATA

Number of publications which are based on the PhD thesis: 8
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